

Textile Finishing

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2003

Society of Dyers and Colourists

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Preface

When I was first approached by the Society of Dyers and Colourists to be managing editor of *Textile Finishing*, I realised that this gave me the opportunity to say thank you to an industry that had given me pleasure and friendships during the last years. Also I realised how much had changed in the field of textile finishing during that period of time. Entering into finishing when home-made urea formaldehyde resins where state-of-the-art and Borax was the main flame resistant finish.

The finishers who taught me so much at the start of my career (Jim Lowe, Heaton Mills Printing Company; Ron Bradley, Bollington Printing Company; George Donague, J H Earl) would be amazed at the chemicals and techniques used in the present industry, together with the durability and quality of the final product. Throughout this book we have brought together all the major techniques and auxiliaries used in present day finishing which will be invaluable to finishers and students alike.

I doubt in the years to come if there will be as many major advances as we have seen in the last years of textile finishing. Therefore I would like to thank all the authors and the SDC for the opportunity of producing this book which should provide an excellent building block for the future generations of finishers in all countries where textile finishing is carried out.

DEREK HEYWOOD

CHAPTER 1

Mercerisation and liquid ammonia treatment

Peter F Greenwood

1.1 INTRODUCTION

1.1.1 Early development of mercerisation

'When cloth made from vegetable fibre, cotton, flax and so on, has been subjected to the action of caustic soda or potash as above described, by padding, immersion or any other way, and then freed from the alkali by souring and washing according to my said invention, the cloth will have been found to have undergone certain changes and alterations and have acquired certain new and valuable properties; the most remarkable I here describe. It will have shrunk in its length and breadth, or have become less in its external dimensions, but thicker and closer, so that by the chemical action of caustic soda or potash I produce on cotton and other vegetable fibres effects somewhat analogous to that which is produced on woollen by the process of fulling or milling. It will have acquired greater strength and firmness, each fibre requiring greater force to break it. It will also have become heavier than it was before it was acted on by the alkali, if in both cases it be weighed at the temperature of 60 °F or under. It will have acquired greatly augmented and improved powers of receiving colours in printing and dyeing.' [1]

Although John Mercer's patent application, from which the excerpt above is taken, summarises much of the technology and results of the process which bears his name, the technique of mercerisation did not achieve widespread industrial use for another forty years, until Horace Lowe discovered that if shrinkage could be prevented by applying tension during the swelling period, or if the dimensions could be restored by applying tension after swelling, a highly lustrous product could be obtained. Lowe's patent [2] proved to be the step forward that took the scientific curiosity of mercerisation into full industrial development, and gave us the process as we know it today.

The first commercial developments of Lowe's process were mercerised yarns, produced by Thomas and Prevost, of Krefeld, Germany, who filed patents in Germany in 1895. This led to considerable litigation in the British and German courts, which was resolved in favour of Lowe in 1902. However, in the meantime the process was being exploited on a large scale in

America by the American Mercerizing Company, which was set up in 1899 to take over the sole rights of the Thomas and Prevost patents. Between 1899 and 1904 the American Mercerizing company and its licensees produced about 14 million pounds of mercerised yarn. After the American courts followed the European lead and rejected the German claims in 1906, the process of mercerising for lustre became unrestricted, as Lowe had allowed his patent to lapse.

1.1.2 The modern mercerising process

Most mercerising today is carried out very much along the lines suggested by Mercer and Lowe. Cotton, in the form of yarn or fabric, is impregnated with sodium hydroxide solution (caustic soda) of a concentration in the range 20–27 g per 100 g (45–60 °Tw. – see note below) at or about 20 °C. After squeezing to remove excess liquor, a short time is allowed for the solution to penetrate into the fibre – a wetting agent may be included to facilitate this – and the sodium hydroxide is then removed by hot water while the material is held under tension. The final traces of alkali are usually neutralised with an acid treatment.

Mercerising may be carried out on grey, scoured, bleached or even dyed material. Singeing prior to mercerising is advisable, to remove surface fibres that would shrink freely and mask the desired lustre, and desizing of woven cloth will improve absorbency and give a more uniform result. At entry into the mercerising machine the material is normally in the dry state, but wet-on-wet impregnation is not unknown.

Hot mercerising, in which the sodium hydroxide is applied at about 60 °C, is widely practised. Problems relating to the mercerising of knitted fabrics have largely been overcome, and piece-mercerised knitgoods now present a strong challenge to the traditional, more expensive fabrics knitted from mercerised yarns.

As well as sodium hydroxide, Mercer included in his patent the effect of other swelling agents, such as caustic potash, sulphuric acid and zinc chloride. More recently, treatment with anhydrous liquid ammonia has developed into a commercial process, conferring its own distinctive properties.

Traditional mercerising methods, and some of the newer techniques, are described in this chapter.

Note: Concentrations of sodium hydroxide solutions

In mercerising practice, the concentration of sodium hydroxide solution (caustic soda) is usually monitored with a hydrometer, and several hydrometer scales are today in common use. Mercer used the Twaddell hydrometer scale, which is still employed today in England, the USA and elsewhere, especially in the mercerising of woven fabrics. The mercerisation of circular knits developed in continental Europe, where the Baumé scale has been traditionally used, and most knitgoods mercerisers are familiar with that system. To avoid misunderstanding, and often adding to the confusion, concentrations may be described in the literature in terms of specific gravity (SG), normality, g per 100 g, or g per 100 ml. Some conversion formulae are given on the next page.

At 15 °C:

$$\text{degrees Twaddell } (^{\circ}\text{Tw.}) = (\text{SG} - 1) \times 200$$

$$\text{degrees Baumé } (^{\circ}\text{Bé.}) = 144.38 \times (\text{SG} - 1)/(\text{SG})$$

It should be noted that a mercerising liquor often contains significant amounts of impurities – carbonate, size residues, hydrolysis products and auxiliaries – which will affect the hydrometer readings. The method can thus be regarded as only approximately accurate.

1.2 YARN MERCERISING

The main reason for mercerising cotton yarn is to develop lustre; therefore, the process is carried out under tension, usually sufficient to maintain the original yarn length. In general, this means that the technique is limited to doubled yarns, as lustre is not satisfactorily produced on singles yarns. Maximum lustre occurs when the surface fibres are parallel to the axis of the yarn. Adderley and Oxley [3] reported that maximum lustre is obtained when the doubling twist is seven-tenths of the original twist of the component singles. The yarn should be singed ('gassed') before mercerising, or the protruding surface hairs would shrink in processing and the overall lustre would be reduced.

A second reason for yarn mercerising is to increase the strength of the yarn. Sometimes singles yarns have been mercerised for this purpose – to improve weaving efficiency, for example – but mercerising will not turn a bad yarn into a good one, and yarn breakage in the mercerising machine can give additional problems.

Mercerised yarns are used:

- (1) for sewing and embroidery thread, where lustre, strength and smoothness are required;
- (2) for top quality knitted fabrics;
- (3) for weaving, especially high quality, expensive shirtings [4].

There are three main types of yarn mercerising methods:

- (1) hank mercerising;
- (2) warp mercerising;
- (3) cone-to-cone mercerising.

Most European processors employ the batchwise hank mercerising process (Figure 1.1), while warp mercerising used to be known as the 'American process' not only because of its widespread use in the United States, but also because it is a continuous, high production technique.

The main disadvantage of hank mercerising is the necessity for reeling the yarn into hanks for treatment, and then rewinding afterwards for subsequent use.

With the advent of automatic controls [5] and robotic systems for loading and unloading, hank mercerising has become a high production operation, rivalling the output of warp mercerising. Both methods can give between 100 and 200 kg h⁻¹ per machine.

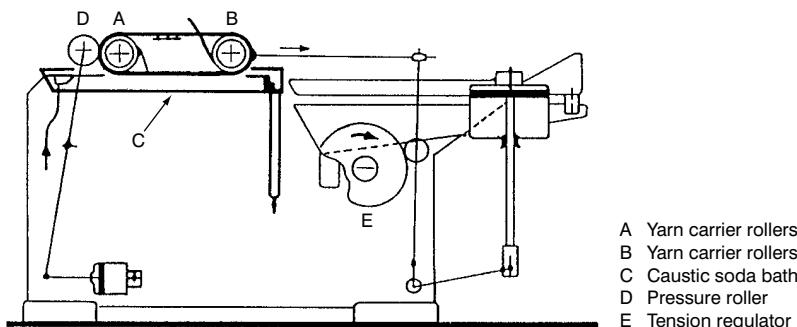


Figure 1.1 Yarn mercerising machine

Cone-to-cone mercerising, on the other hand, is suitable for small lots. The MM-CO machine from Kleinewefers-Jaeggli, for example, produces about 1 kg h^{-1} per machine unit, although it is claimed that up to 96 machines can be installed with a single liquor distribution system.

1.3 PIECE MERCERISING

Mercerisation of fabric can be carried out by either batchwise or continuous means. A modern batch merceriser is shown in Figure 1.2. Batch mercerising machines are useful for processing small lots, but it must be remembered that they have no means for controlling fabric width. In consequence, the use of a batch merceriser should be reserved for a process properly known as ‘causticisation’, in which the concentration of sodium hydroxide used is below mercerising strength. This takes advantage of the fact that, with concentrations in the range 25 to 30 °Tw., dye affinity is markedly improved while the resulting cloth shrinkage is small.

As the dye affinity of immature cotton is raised more than that of mature fibres, causticisation can be used to improve the dyeability of fabric containing a high proportion of

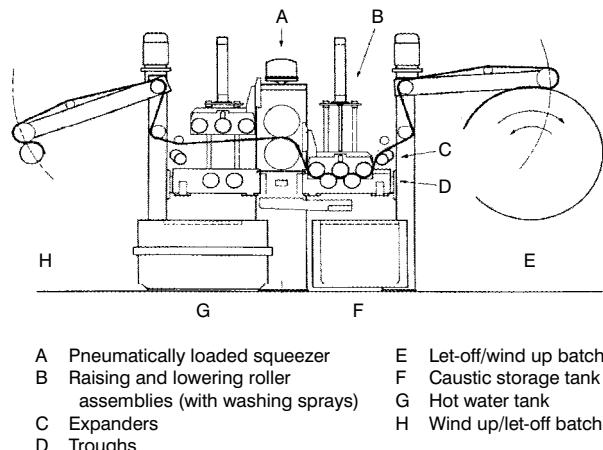


Figure 1.2 Batch mercerising machine (Sir James Farmer Norton)

'dead', or unripe cotton, which is often present in the form of 'neps' – entanglements of thin, immature fibres that would normally take up dyestuff to a lesser degree than the bulk, and appear after dyeing as lightly coloured spots.

Most woven fabric is mercerised by continuous methods.

Continuous process machines are of two main types: chain and chainless (Figures 1.3 and 1.4). Chainless machines have predominated in the development of the process in Continental Europe, while British and American manufacturers have favoured the chain machines.

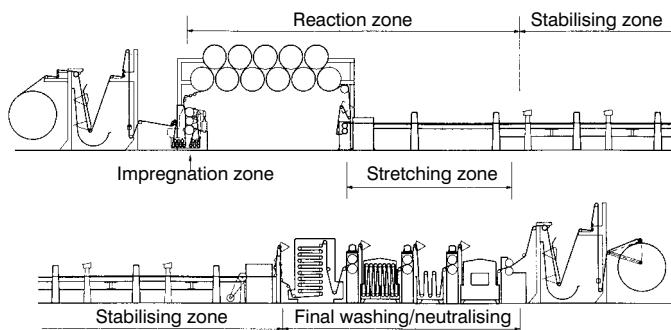


Figure 1.3 Chain mercerising machine (Sir James Farmer Norton)

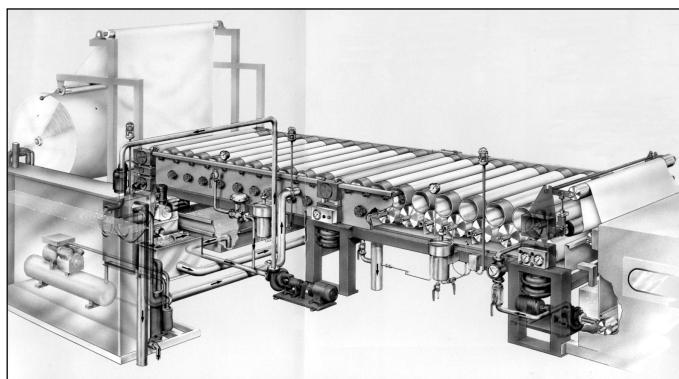


Figure 1.4 Chainless mercerising machine (Brugman Machinefabriek)

In chain mercerising machines, the fabric is allowed to shrink to some extent in the mercerising liquor, but then is re-stretched in both directions by means of a clip stenter. Washing-off begins while the cloth is on the stenter, and continues in a washing range, with final neutralisation with acid. For the process to be carried out successfully:

- (1) sufficient time must be allowed for complete absorption of the liquor into the fabric and for fibre swelling to be completed. This is done by passing the fabric over a series of rollers, known as 'timing drums', for the required length of time. At least 30 seconds is generally accepted, but there is considerable evidence to show that, at room temperature at least, the process is by no means complete after that time;

- (2) the fabric must be held at the desired dimensions until most of the sodium hydroxide has been removed. It is generally accepted that the caustic concentration of the liquor in the cloth should be below 10 °Tw. at the exit from the stenter.

In chainless machines, the cloth is held at the required dimensions throughout impregnation and washing. Specially constructed adjustable bowed rollers, called Mycock expanders, are incorporated into the stabilising zone (during swelling) to maintain the fabric width.

Some manufacturers produce both types of machine. Goller, for example [6], offer the 'Optima' chainless machine and the 'Perfecta' chain merceriser, and have listed the advantages of each.

Advantages of the 'Optima' mercerising concept:

- (1) extremely high flexibility for light to heavy fabrics;
- (2) two fabric runs next to and above each other can be processed at the same time, thus increasing the machine performance without additional capital outlay for a bigger installation;
- (3) hot and cold mercerisation possible;
- (4) investment costs are lower than for chain mercerising machines;
- (5) low maintenance costs;
- (6) economical, can also be used for low fabric speeds.

Advantages of the 'Perfecta' mercerising concept:

- (1) suitable for fabric speeds from 40–100 m min⁻¹;
- (2) no compacting of the selvedges thanks to free shrinkage in the mercerising and impregnating section;
- (3) the mercerising or causticising effect with respect to the degree of lustre or dye uptake is adjustable;
- (4) particularly suitable for striped or checked fabrics, which demand an absolutely accurate repeat over the entire width of the textile fabric.

It has been shown that less force is required to hold the dimensions during mercerisation than to restore dimensions after the fabric has been permitted to shrink.

1.4 KNITGOODS MERCERISING

Piece mercerisation of knitted fabrics is a relatively modern development, as machinery designed for the purpose did not appear until the 1970s. Before this, it had been widely held to be impractical. Certainly, the tensions applied by normal cloth mercerising machines produce so much distortion on knitgoods that the aesthetic advantages of drape, bulk and softness are lost forever.

Circular knitted fabrics can be processed in two ways: tubular or open-width. If the fabric has to be delivered for making-up in the tubular state, the finisher has no choice, but if it is

to be delivered at open-width the finisher must decide at what point in the processing sequence slitting should take place.

Early attempts at mercerising knitted fabrics were carried out on chainless machines originally designed for woven fabric processing, modified to reduce length tension. Only open-width fabric could be usefully treated in this way, as the mercerising of tubular fabric resulted in the formation of edge creases which could not be removed.

Another serious problem with this technique appeared when the fabric was subsequently dyed. The edges often appeared to be darker in shade than the centre. This was found to be due to variations in stitch density, caused by a difference in tension across the fabric width during mercerising [7].

The demand for machinery for the mercerisation of tubular fabric having been clearly established, it was the Japanese [8], closely followed by the Italians [9], who made the early developments. The German machine builder, Dornier, then entered the market with a design that has proved to be very successful. In later versions, the manufacturers offer the possibility for combining singeing and bleaching units to enable a full knitgoods preparation treatment to be carried out [10] (see Figure 1.5).

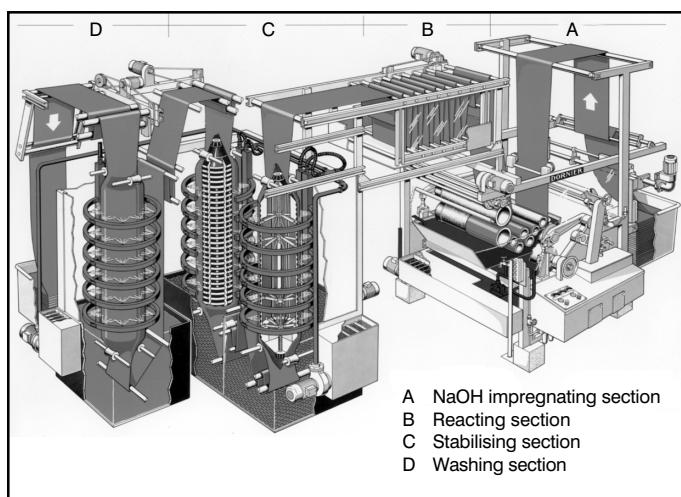


Figure 1.5 Knitgoods mercerising machine (Dornier)

The Dornier machine consists of three main sections:

- (1) impregnation;
- (2) reaction;
- (3) stabilising and washing.

The functions of these sections are the same as the corresponding units in a woven fabric mercerising range, but the design of the stabilising and washing section is fundamentally different. It consists of a series of vertical circular spraying units, through which the fabric

passes while being stretched over a tubular frame known from its shape as a 'cigar'. Up to four cigar units have been included in commercial installations. The diameter of each cigar is adjustable by means of external controls. Claims for this machine include complete absence of edge-marking.

A list of machines for tubular mercerising, indicating particular design features, has been published [11].

The dimensions of a knitted fabric are markedly altered as a result of mercerisation. This must be taken into account both in designing the fabric, to ensure that the desired weight, width and stability of the final product can be obtained, and in processing after mercerising, to adjust the dimensions to give the desired result. Many finishers have had to embark on expensive, time-consuming trials to establish the right conditions for the production of marketable fabrics.

A short-cut to this result is afforded by computer-based predictive systems that can model the behaviour of knitted cotton fabrics in various finishing processes including mercerising. One of the best-known of these is the 'Starfish' system developed by the International Institute for Cotton [12].

The basis of the 'Starfish' predictive system is the 'Reference State' of the fabric, on which all the calculations are based. This is determined in a standard laundering test [13].

Full-scale trials on a wide range of cotton fabrics were used to prepare the database for the Starfish models, including open-width mercerising on a Kleineuwefers machine and several runs on a Dornier continuous tubular processing range. Test results from one such trial are given in Table 1.1, and show not only the effect of the mercerising process on fabric structure, but also the influence of tension variations caused by changing the diameter of the cigar.

Table 1.1 Results from Dornier knitgoods merceriser trial

	Reference States:				
	Courses (per 3 cm)	Wales (per 3 cm)	Width (cm)	Stitch length (cm)	Yarn tex
Unmercerised after dyeing	58.4	44.7	76.5	0.284	19.14
Circumference of 'cigar' (cm)					
116	57.4	51.3	66.7	0.268	19.99
124	56.4	51.5	66.4	0.269	20.17
132	55.6	51.5	66.4	0.271	20.07
140	55.8	51.7	66.2	0.272	19.96
148	54.9	51.8	66.0	0.272	19.73

Nominal knitted structure: 28G single jersey, Ne30/1 yarn
stitch length, 0.280 cm
2280 needles in machine circumference

The tubular width of the fabric is markedly decreased by mercerising, and the effect of increasing width stretching has, in fact, only served to produce an even narrower fabric. This is probably due to increased frictional 'drag' on the cigar, which would have the effect of transferring the stretch to the length direction. Fabric length is thereby increased, as evidenced by the reduction in course density.

1.5 IMPROVING UNIFORMITY OF MERCERISING

Penetration of mercerising liquor into yarns and fabrics is slow and incomplete at normal mercerising temperature (20 °C or below). Swelling of the outermost fibres forms a barrier, preventing the absorption of liquor into the yarn centre. In the case of fabrics, swelling is further restricted by the yarn crossing points.

Before the development of 'crease-resistant' resin finishing, the main purpose of mercerisation had been to improve lustre and colour yield in dyeing. These aims, as has been pointed out [14] are satisfied adequately by a superficial treatment.

However, it has long been known that mercerisation decreases the loss of strength caused by subsequent resin finishing [15]. Many research workers believe [14,16] that if the mercerising effect could be made more uniform, considerable benefits could be obtained, particularly in the response to crosslinking, or resin finishing – the so-called 'balance of properties' between crease recovery and durability.

Studies on fabrics made from mercerised yarns [17,18] indicated that strength losses arising from crosslinking were lower than those produced on mercerised fabrics. Fabric woven from slack mercerised, partially re-stretched yarns showed almost no strength loss after crosslinking with 7% DMEU [19]. However, the commercial interest in these results was limited, because of the relatively high cost of yarn mercerising and the need to use expensive plied yarns.

Attention turned to the discovery of methods for improving the uniformity of the fabric mercerising process.

Vacuum impregnation – the creation of a vacuum within the fabric prior to immersion in the application bath – was developed by two machine manufacturers: Farmer Norton in England and Kleinewefers in Germany. The units these manufacturers devised clearly increased liquor pick-up into the cloth and improved wettability. Kleinewefers called the technique 'core mercerising' [20]. The main advantages claimed by the manufacturers are:

- (1) improved wettability, eliminating the need for wetting agents, which could cause problems in caustic recovery plants;
- (2) smaller liquor tanks, and therefore cost savings, due to faster impregnation.

Although an improved response in subsequent crosslinking has not been reported, it would seem that vacuum impregnation should produce an improvement in uniformity of mercerisation. However, the mainstream of research turned to another technique for improving penetration – hot mercerisation.

1.5.1 Hot mercerising

De Boer and Borsten [21] showed that penetration is dependent both on liquor viscosity and fibre swelling, both of which decrease as the temperature is increased.

Bechter, Fiebig and Heap [14] reported that mercerising at elevated temperatures gives a more uniform treatment, but less swelling, and inferred that a second treatment at low temperature would complete the swelling effect.

In order to improve uniformity of the mercerising effect, an interest has developed in treatments at elevated temperatures. Several patents have been published, the first probably being that of Rusznak and coworkers [22], who claimed a process for combining scouring and mercerising in 1965. This was followed by claims on behalf of Heberlein [23], and Duckworth and Mather and Platt [24,25]. The interest of the last-named was clearly aroused by the possibility for extending the versatility of the Vaporloc pressure scouring unit, and several publications followed describing co-operation between the British and Hungarian interests. In one of these [25] Duckworth and Wrennall describe the basic principles of the process as follows.

- (1) Saturate with sodium hydroxide solution (caustic soda) of mercerising strength, preferably under relaxed conditions, at an elevated temperature approaching the boiling point of the sodium hydroxide solution.
- (2) Controlled hot-stretching following saturation.
- (3) Controlled cooling of the hot-stretched fabric.
- (4) Traditional, tension-controlled washing (chain or chainless).
- (5) Traditional final washing (in multiple-box washers).

The authors claim that when the process is carried out in this way the penetration of sodium hydroxide solution into the textile structure is extremely rapid, thorough and uniform.

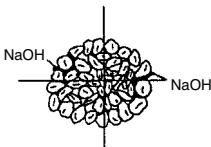
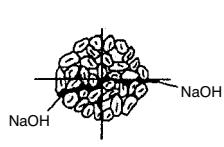
Care must be taken to avoid oxidation of the alkali-cellulose by exposure to air. Measurements of oxygen uptake of soda-cellulose over a range of temperatures have shown that the same volume of oxygen is adsorbed in 1.2 hours at 60 °C, as in 48 hours at 20 °C [26].

Fundamental studies on the influence of temperature on the mercerising of cotton have been reported in a series of articles by Bechter and other workers at the Institute for Textile and Fibre Research, Stuttgart [27–32]. In one of these [28], Bechter summarises the practical results of these experiments with regard to hot mercerising of yarns and woven fabrics, noting that mercerising at elevated temperatures can lead to improvements in lustre and shrinkage, has no adverse effect on strength and, under certain recommended conditions, can result in a softer handle. A comparison between cold and hot mercerisation was later tabulated (Table 1.2) [32].

1.5.2 Mercerising using a pin stenter

In 1980, the German machinery builder Artos announced a development that surprised those finishers experienced in conventional mercerising [33]. In the process – called the Mercevic

Table 1.2 Advantages of hot mercerising [32]

Conventional mercerisation (10–20 °C)	Hot mercerisation (60 °C)
<ul style="list-style-type: none"> • Higher fibre swelling  <ul style="list-style-type: none"> • Slow swelling: slow relaxation incomplete relaxation higher residual shrinkage • Surface swelling: irregularity  <ul style="list-style-type: none"> • Tight fibre packing: harsher handle NaOH diffusion into yarn obstructed • Lustre: a few, strongly swollen (round) fibres in the surface of the yarns – interior less lustrous 	<ul style="list-style-type: none"> • Less fibre swelling  <ul style="list-style-type: none"> • Fast swelling: fast relaxation good relaxation less residual shrinkage • Uniform swelling: regularity  <ul style="list-style-type: none"> • Loose fibre packing: softer handle NaOH diffusion into yarn unhindered • Optimal lustre: significantly less strongly swollen fibres throughout the yarn cross-section – interior equally lustrous

technique after its inventor, José Vico – the fabric is first padded with sodium hydroxide solution of mercerising strength, and after a delay period, is dried on a pin stenter. It is claimed that the fabric suffers no adverse effects even if stored in this condition for several months. The process was developed initially for knitgoods, to improve dye uptake, but it was said to be suitable also for woven goods.

Details of a similar technique, called the SM ‘Stenter Mercerising’ process, were revealed soon afterwards by the chemical manufacturer Sandoz (now Clariant) [34, 35].

Both processes are claimed to produce true mercerising effects: lustre, improved dye uptake, coverage of dead and immature fibres, and improved fabric stability. For knitgoods processing, a further advantage is the absence of stitch density variation across the width, in contrast to the results of processing on a chainless machine. Sandoz claim also that the treatment reduces ‘spirality’ in single jersey fabric.

Trials with the SM process at the International Institute for Cotton [36] showed that colour yield and lustre compared well with other methods. However, certain precautions were necessary in operating the process. The machinery must be completely resistant to strong alkali, and must be thoroughly cleaned after each run. The dry fabric can emit an unpleasant and hazardous dust, from which operatives must be protected.

In addition, it is clear that, especially if the fabric is stored for a period before washing, much of the sodium hydroxide will be converted to carbonate, and recovery will be impractical, adding to costs and perhaps creating effluent problems. However, these techniques may be of interest to a finisher with spare stenter capacity.

The use of a perforated beam for washing-off after the SM treatment has been described [37]. Fabric rinsing begins during winding-on, so that the yellow colour is removed in a uniform manner; subsequent bleaching can be effected by circulating peroxide liquor through the batch on the beam.

1.5.3 The Benninger 'Dimensa'

The Dimensa mercerising range developed by Benninger [38] is a combination of ideas from both chain and chainless designs. Conceding that the basic weakness of chainless machines is the lack of width control during the early stages of caustic removal, Benninger have introduced a short pin stenter at this point in the treatment to set the fabric width. Hot water jets over the stenter begin the wash-off process, which is then completed in a roller unit similar to a conventional chainless machine (Figure 1.6).

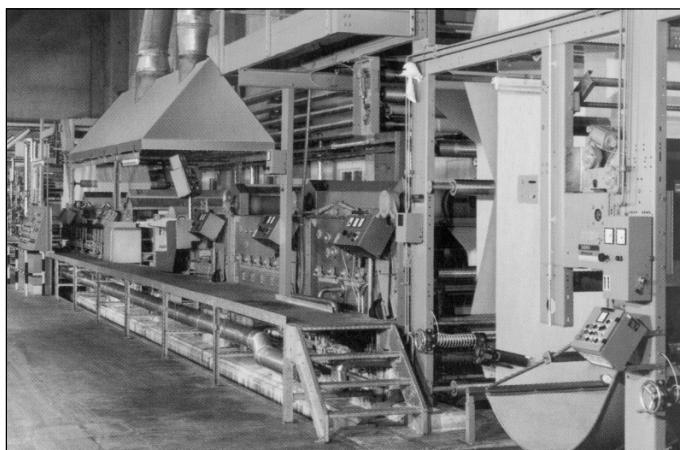


Figure 1.6 'Dimensa' machine (Benninger)

The use of a pin stenter is unusual in conventional chain mercerising. Clips are normally used, for robustness and resistance to strong alkali. The development of the Mercevic and SM systems may have encouraged Benninger in this development. However, the developers of these processes seem to be content to promote them only for knitgoods treatment, whereas the Dimensa is marketed as a machine for processing either wovens or knitgoods at open-width. It is important in the processing of heavyweight woven fabrics that the pins must be strong enough to withstand the considerable contraction force generated.

By the use of the pin frame, the Dimensa avoids the problems of distortion produced by conventional chainless machines. However, the unit is quite short, and the facility for width stretching, especially in knitgoods processing, may be limited.

1.5.4 Wet-on-wet mercerising

If mercerising is carried out after scouring or bleaching, some finishers prefer to impregnate the cloth in the wet state, to save the cost of an intermediate drying process. In the past this has been regarded as inferior practice; Marsh [26] points out that the procedure not only dilutes the sodium hydroxide solution, it also entails risk of uneven treatment. The goods must be evenly expressed before mercerising and all danger of local drying must be avoided.

With the introduction of sophisticated control devices into the system, the risk of problems arising from wet-on-wet impregnation is reduced. High performance squeezing mangles, or vacuum extractors, after the preceding washing range can ensure that the moisture content of the entering cloth is as low as possible. Most machinery manufacturers offer means for controlling caustic concentration by means of density measurement. The incoming liquor concentration should be more concentrated, of course, than for wet-on-dry application [39].

Greif [40] has described a technique that combines wet-on-wet application with hot mercerising. The process utilises the 'Flexnip' applicator developed by Küsters, which has a very small capacity so that, it is claimed, no dilution of the bath takes place, hence the name 'addition mercerising' (Figure 1.7).

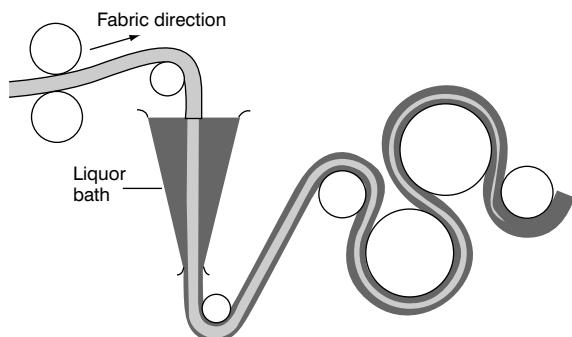


Figure 1.7 'Ecommerce' addition mercerising using the Flexnip (Küsters)

Greif gives an example, as follows: after the preceding washing process, the goods leave the high-performance squeeze system with an expression of 65%. In the Flexnip, 440 g NaOH per litre is added to give a further pick-up of 90%. The total liquor pick-up is then 155%. With this pick-up, the goods pass through the diffusion zone, at the end of which the lye concentration within the cloth is 226 g NaOH per litre. The lye to be added to the Flexnip can be prepared from the mercerising liquor coming from the NaOH evaporating system, or from fresh strong lye together with an addition of the rinsing lye coming from the stabilising or washing systems.

The goods leave the high-performance squeeze system at a temperature of 60–90 °C. By the time they enter the Flexnip, they have cooled to 60–70 °C, which is also the temperature of the lye in the Flexnip. Owing to the heat of reaction created during diffusion, this temperature is

maintained satisfactorily until the beginning of the stabilisation (washing) process in front of the high-performance squeezing system at the end of the diffusion zone.

1.5.5 Slack mercerising

Mercerising without tension has been used to produce 'stretch' or bulked effects in cotton yarns and fabrics.

'Stretch' cottons are so-called because of their ability to extend and recover after stretching. The degree of extensibility can be controlled by introducing some tension; for example, in the treatment of fabrics the warp may be held under tension and the fabric allowed to shrink only in the width. Such products have found end-uses in casual wear and sportswear markets, and at one time were used extensively in the manufacture of elastic support bandages [41, 42].

Colbran and Thompson [43] examined the effect of cloth construction on the properties of slack-mercerised cotton fabrics, showing that the cloth must be woven in such a way that weft shrinkage during processing will not be restricted by jamming of the weft threads between those in the warp. They recommended that sufficient warp tension should be applied during the process to effect adequate crimp interchange, and that the weft yarn should be of a finer count than the warp yarn, to assist the development of high weft crimp.

An easy-care finish is often applied to stretch-mercerised fabrics in order to retain the elastic recovery.

1.6 MERCERISATION OF BLENDS

The possibility for mercerisation of blends of cotton with other fibres depends on the effect of concentrated sodium hydroxide on the other fibre concerned. Polyester and polyamide fibres are resistant to normal mercerising conditions, but acrylic fibres may be adversely affected, especially at high temperature.

Blends of cotton with viscose fibres are rarely given a full mercerisation. Viscose fibre is only slightly affected by sodium hydroxide at mercerising strength; however, during removal of the alkali by washing, the concentration has to pass through a critical level at about 9% NaOH, when the viscose fibre swells to a very high degree and loses nearly all its strength.

The problem can be minimised by the inclusion of certain protective agents in the wash water. Common salt has been found to be particularly effective [44].

If potassium hydroxide is used as the swelling agent there are no technical problems. Mecheels [45] suggested a concentration of about 30 °Bé., which confers lustre on the cotton component without damaging the viscose.

Sandoz have developed a process, called Sandoflex, which is claimed to produce many of the desirable effects of mercerising on a wide range of fabrics including blends of cotton and viscose [46]. A special swelling agent is used, together with a multifunctional wetting, washing, dispersing, lubricating and fibre protective agent, and an additive to prevent

shrinkage. The precise nature of these products has not been divulged, but the process is not based on sodium hydroxide.

Because shrinkage is prevented, the process is said to be suitable for pile fabrics such as towelling, velvet and plush.

1.6.1 Modal fibres

Unlike ordinary viscose, modal fibres have been found to be capable of withstanding the mercerising process, so that benefits can be obtained, for example, in the treatment of blends with cotton. Cotton/polynosic blends can be mercerised by normal methods without the necessity for special precautions [47]. HWM (high-wet-modulus) fibres are less resistant. Bechter [48] examined the influence of temperature on the swelling characteristics of polynosic and HWM fibres in 250 g l^{-1} NaOH at 20°C and 60°C . Both types showed a faster rate of swelling compared with cotton, but the difference is less marked at higher temperatures.

1.7 THE MERCERISATION OF LINEN

Because of the natural lustre of the flax fibre, the mercerisation of linen under tension is unnecessary. However, a mercerisation treatment causes strengthening of the fibre nodes resulting in an improvement in abrasion resistance. Some fabric shrinkage is allowed.

Chemical treatments to improve the crease recovery of linen should be carried out on mercerised fabric [49]. The application of crease-resisting resins to linen fabric is accompanied by a large reduction in fabric strength, which is much more than that found in cotton. If urea-formaldehyde (dimethylol urea) is used, fabric strength loss can be minimised by a ‘post-mercerisation’ treatment. This is carried out ‘wet-on-wet’; the fabric, after the resin has been applied, dried and cured, is wet out in a hot solution of sodium carbonate and a wetting agent and squeezed off, and then impregnated with mercerising liquor at a concentration of about 50 to 63°Tw . The fabric is allowed to relax for up to fifteen minutes or so, after which it is re-stretched and washed off.

This process is now carried out to a very limited extent, because of the limitations on formaldehyde in textile products. In cotton finishing, urea-formaldehyde has been supplanted by the use of reactant resins, which contain much less formaldehyde, and may even be formaldehyde-free. Unfortunately, post-mercerisation does not have any beneficial effect on the strength of linen treated by these products, and no alternative has yet been found.

1.8 WETTING AGENTS

Grey goods in particular present difficulties in obtaining uniform wetting and thorough penetration during impregnation with sodium hydroxide, due to the presence of significant quantities of wax. Grey cotton contains not only natural wax (about 1% of the fibre weight) but

also warp sizing mixtures that may contain waxes. Knitted fabric will contain paraffin wax, applied to the yarn to promote good knittability.

Surface-active agents are therefore often added to the sodium hydroxide solution in the mercerising process, in order to ensure uniform wetting and penetration. The properties of such surface-active agents have been listed [50]:

- (1) solubility in alkaline media;
- (2) high wettability, particularly in concentrated alkali;
- (3) no affinity for the fibre;
- (4) efficiency at low concentration;
- (5) low foaming;
- (6) stability in sodium hydroxide recovery systems.

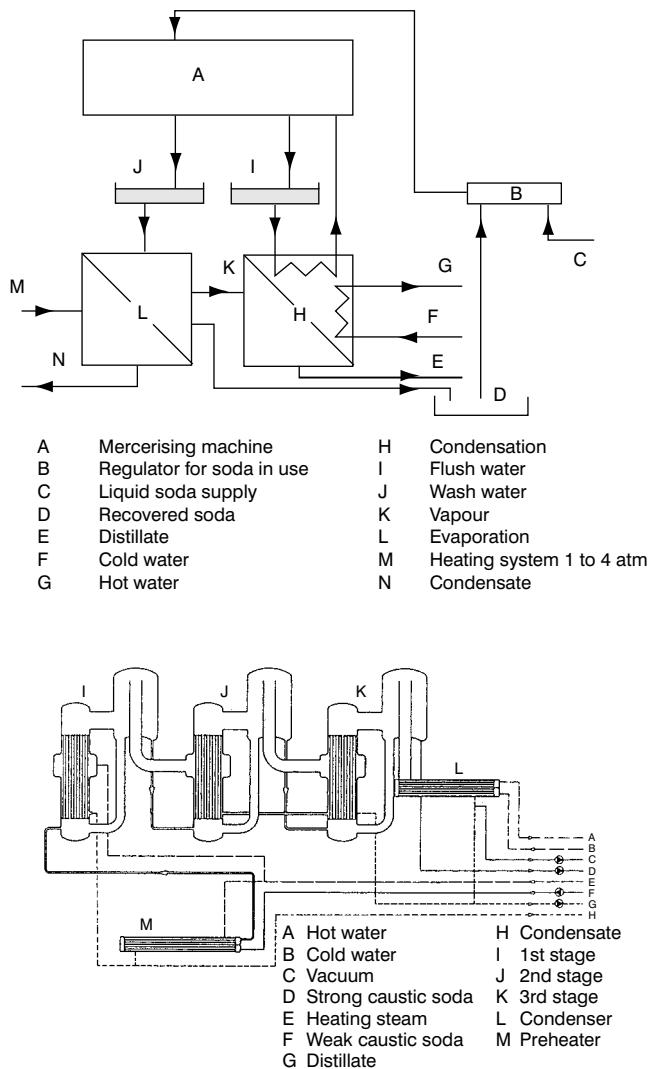
Although phenolic and cresolic products have been found to give these properties, their use has been curtailed in recent years because of their toxicity and non-biodegradability. Low molecular weight alkyl sulphates (4–8 carbon atoms) are effective: 2-ethyl hexyl sulphate has been found to give particularly good wetting in concentrated sodium hydroxide [51].

1.9 CAUSTIC RECOVERY

Park and Shore [52] showed that mercerising has a negligible effect on biological oxygen demand and pollution load when compared with other cotton finishing processes, particularly desizing and scouring. However, this conclusion must be based on the assumption that most of the sodium hydroxide is either recovered or neutralised, as a typical wash liquor concentration from a mercerising range could contain as much as 50 g l^{-1} of NaOH, with a pH of about 14. This would be quite unacceptable for discharge without treatment into public sewers, and neutralisation – for example, by the use of flue gas from the boiler plant – is often carried out to comply with local environmental regulations.

However, economic considerations alone lead to the conclusion that recovery and re-use of sodium hydroxide is almost always a worthwhile proposition. Some of the dilute caustic liquor from the washing range can, of course, be used in other dyehouse operations – in scouring, for example. Sodium hydroxide is delivered from the manufacturers either in solid form or in very concentrated solutions, and can be diluted to mercerising strength with liquor from the wash range. These operations can use only a small fraction, however, of the dilute caustic washings. If waste is to be avoided, the installation of a caustic recovery plant must be considered.

Most recovery plants are based on an evaporative process, often assisted by a partial vacuum. A typical installation is shown in Figure 1.8. Efficient heat recovery is, of course, essential for economical operation. Other methods, such as ultrafiltration and reverse osmosis, are being examined, but present difficulties that have been well reviewed by Bechtold and coworkers [53]. The membranes that are available for these techniques are not sufficiently resistant to strong alkaline liquors, and some mercerising auxiliaries can



cause the membranes to swell. In addition, the increasing viscosity of the lye as it becomes more concentrated means that high pressures and large filter surfaces are required to ensure adequate throughput.

Gassmann [54] has described a two-stage evaporator system that will accept dilute (6°Bé) liquor at a rate of 1180 kg h^{-1} and produce 180 kg h^{-1} at 30°Bé . The savings to be gained by the operation of a caustic recovery system have been well documented. When a French company, producing four tonnes per day of mercerised cotton yarn, installed a two-stage evaporative recovery system, savings were estimated at 750 000 francs in the second half of 1984 [55]. A German finisher was able to recover the cost of a three-stage evaporative system – DM 800 000 – in less than a year [56]. In the latter case, it was

pointed out that mercerisation of grey cloth should be avoided because of difficulties with size and other residues in the recovery process, and as far as possible, the fabric is first desized and then mercerised wet-on-wet.

Methods have been suggested to overcome the problem of contaminants in the waste liquor. The use of lime or alum to remove size mucilage has been proposed. Studies at the University of Innsbruck [57] have indicated methods, such as treatment with peroxide, which can be used to purify contaminated lye.

For maximum efficiency of recovery, the washing process in the mercerising machine should be operated under conditions that will produce liquor of as high a concentration of alkali as possible. This means operating on strict counter-current conditions, the importance of which has been shown in a paper by Athanasopoulos and Karadimitris [58], describing an improvement in recovery of sodium hydroxide from 5–15% to over 85% by re-designing the wash water flow to a counter-current system. Further savings were found in energy and water consumption, and in decreased requirement for neutralising acid.

The counter-current system was well understood in the design of the ‘recuperator’, a machine that seems to have fallen out of favour in modern times. This is a sealed unit from which all air is excluded. The cloth passes over two rows of rollers, the top row being driven. The bottom row is immersed in a counter-current water flow. The alkali is extracted from the cloth by means of jets of steam. Marsh [26] has commented that by using an efficient counter-current system of washing and a recuperator, followed by ‘suitable handling’, it would be possible to recover and use 90–95% of the original sodium hydroxide carried over from the impregnation part of the mercerising process.

1.10 LIQUID AMMONIA TREATMENT

Although often referred to as ‘ammonia-mercerising’, the treatment of cellulosic materials with anhydrous liquid ammonia is not, strictly speaking, mercerisation. Ammonia was not covered in Mercer’s patent, and in any case the two processes give rather different effects.

Treatment of cellulosic fibres with liquid ammonia takes one of two forms, depending on the mode of removal of the ammonia. These have been characterised as the ‘ammonia–water’ process and the ‘ammonia–dry–steam’ process [59].

In the first treatment, the fabric swollen with anhydrous liquid ammonia is run into a bath of water in order to evaporate and wash out the ammonia. In the second treatment, ammonia is removed from the cloth mainly by dry heat (for example, by passing over hot cylinders), and only the last traces are removed by steam.

The ammonia–water process gives results that are very similar to those produced by mercerisation: improvement in colour yield after subsequent dyeing, increased lustre and, in the case of fabric treatment, removal of creases or rope-marks. To some extent, the process can be controlled to produce a degree of fabric stabilisation. The handle is softer and more supple than that obtained by mercerisation with sodium hydroxide.

Ammonia–dry–steam, on the other hand, gives very different results. Colour yield may not

be improved at all, but in some instances may be significantly decreased. Other effects are similar to those obtained by ammonia–water, but in addition woven fabric treated by the ammonia–dry–steam process acquires a much-improved level of crease recovery.

The two processes appeared almost simultaneously as commercial developments in the mid-1960s.

The Prograde process, developed by J and P Coats as a treatment for cotton sewing threads and knitting yarns, was an example of the ammonia–water process. At around the same time, the research company Omnium de Prospective Industrielle (OPI) in France was developing a similar system for the treatment of knitted fabrics [60]. The Prograde process has ceased operation, but the French activity has now been transferred to a Belgian company, Veramtex S A who operate the process under the name ‘Beau-Fixe’. Treatment of knitgoods is still carried out as an alternative to mercerising, but Veramtex has found new markets for the process as a treatment for woven goods, in the cotton shirting, workwear and leisurewear sectors [61]. The installation is shown in Figure 1.9.

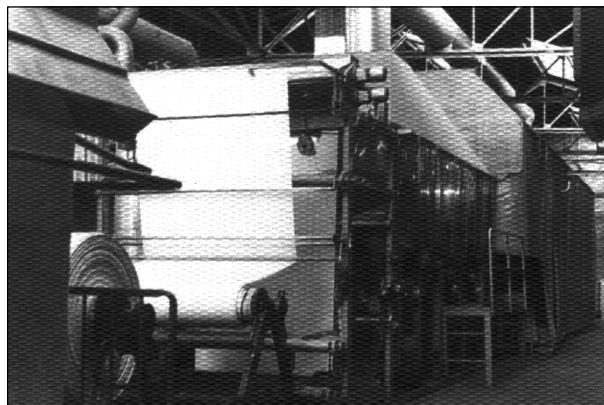


Figure 1.9 Liquid ammonia processing (Veramtex)

The ammonia–dry–steam process, first developed by the Norwegian Textile Research Institute, has been commercialised by the Sanforized Company under the name ‘Sanfor-Set’. A diagram of the process is given as Figure 1.10. The process enjoyed a brief popularity in the United States, particularly for the treatment of denim, but the advantages that it confers – improved stability, colour retention and crease recovery – were not of lasting interest to the mass denim market. Other products – shirts and bedsheets, particularly – were launched but could not compete in the US market with cotton/polyester blends, which exhibit similar easy-care properties.

In Europe and the Far East, however, probably due to a stronger consumer preference for pure cotton products, interest has continued. Hazard [61] has described the commercial developments in Belgium and Germany.

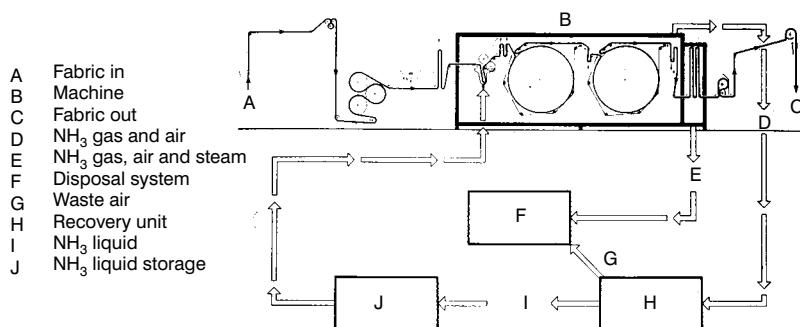


Figure 1.10 'Sanfor-Set' liquid ammonia treatment

The economic viability of both processes depends to a large extent on the efficiency of ammonia recovery. The Veramtex operation was an exception, in that it was set up within a plant manufacturing ammonia-based fertilisers, so that it not only had a ready supply of anhydrous ammonia, but also was able to return aqueous ammonia to the main manufacturing line. This symbiosis came to an end when the fertiliser plant closed down, and a recovery plant then had to be installed. The level of chemical engineering required for containment and recovery of ammonia is very sophisticated compared with most textile processing, adding considerably to the overall cost.

1.10.1 Properties of ammonia-treated textile products

Cotton

In 1987, the International Institute for Cotton published results of a study on the behaviour of ammonia-treated cotton in the manufacturing, use and laundering of workwear and careerwear [62].

It was reported that in laundering trials extending up to 40 industrial wash cycles, ammonia-treated cotton garments showed several advantages over untreated cotton:

- (1) better dimensional stability in repeated laundering;
- (2) improved smooth-drying appearance indicating possibilities for tunnel-drying;
- (3) decreased drying costs due to low moisture retention after centrifuging;
- (4) low soil redeposition from dirty liquors. This was much better than that shown by cotton/polyester blends, and eliminated the need, it was claimed, for expensive soil-suspending chemicals in the wash formula.

The ammonia treatment was carried out on the Sanfor-Set range at Martini GmbH in Germany. Similar claims have been made for workwear products treated by the ammonia-water system at Veramtex [63].

These results confirm work carried out earlier in various research studies, notably by Bredereck and coworkers at the University of Stuttgart [64–67]. Bredereck [65] considered

the improvement in stability to be due to conversion from cellulose III to cellulose I during ammonia removal while the fabric is held under tension.

Many workers [59,65], particularly in studies of the ammonia-dry-steam system, have reported improvements in dry, but not wet, crease recovery after ammonia treatment; for lightweight fabrics, the lack of wet recovery means that a subsequent crosslinking treatment is necessary. Less information is available on the ammonia-water system, although there are indications that this gives lower dry crease recovery, but better wet crease recovery, than the ammonia-dry-steam technique. Both systems provide excellent pretreatments for subsequent crosslinking, as lower chemical add-on levels can be used, with consequent improvements over conventional easy-care finishes in terms of fabric strength and durability.

Care must be taken, however, not to lose these advantages by inappropriate after-treatment. Bredereck has pointed out [66] that the fibre structure produced by liquid ammonia can be impaired by subsequent alkaline treatment. The high pH used in vat dyeing or some reactive dyeing processes, for example, can destroy the effects.

Several examples of the reduction in water retention after centrifuging have been reported by Bredereck [66]. A water retention value of 52% in a cotton twill fabric after bleaching was decreased to 40% after ammonia treatment. In a later study [67] Bredereck obtained similar reductions with cotton fabrics treated by both types of ammonia process.

Flax and ramie

Results of the liquid ammonia treatment of linen fabrics were reported by Lambrinou [68]. Although the average degree of polymerisation was decreased somewhat by the process, it was found that, after washing, tensile strength, resistance to abrasion and dry crease recovery were all significantly improved. Hazard [61] reported significant improvements in the dimensional stability, crease recovery and abrasion resistance of linen fabrics that had been subsequently treated by either dry or moist crosslinking, compared with fabric that had not been ammonia-treated.

Kratz and Funder [69] examined the effect of Sanfor-Set ammonia treatment on a range of flax line and tow fabrics, blends of flax with cotton, viscose rayon and polyester, and some fabrics containing ramie as weft yarn. The ammonia treatment was carried out either before dyeing, after dyeing or after a resin finishing treatment. The dye used was a direct dye, Sirius Light Blue BR-LL; the ammonia-treated linen dyed less deeply than the untreated.

The water retention value of the linen was significantly decreased, from 70–80% to 50–60%, by the ammonia treatment. Confirming Lambrinou's results, it was noted that the degree of polymerisation (DP) was decreased by 10–15%; strength was also significantly decreased. Unfortunately, very few test figures are actually reported in this paper. Shrinkage in laundering was said to be much improved; however, the finished fabric dimensions were in all likelihood not identical. Dry crease recovery was said to be improved to such a degree that in many cases it may be possible to reduce or eliminate the use of resin finishes. From the results on the linen–cotton and linen–viscose blends it was concluded that increasing the flax content led to more pronounced improvements.

Positive improvements were also found on the ramie components, although these were not quite as apparent.

Wool

The action of liquid ammonia on wool fibres produces results that have been exploited commercially. The French research company, Omnim de Prospective Industrielle (OPI), obtained a patent for the bulking of wool fibres by a liquid ammonia treatment in 1972 [70]. The patentees later set up a company, Sitralaine S A at Armentières, to carry out the process commercially on wool sliver [71]. Wool has a bilateral structure, the cells on one side of the fibre being known as orthocortex, and on the other, paracortex. In liquid ammonia, preferential swelling of the orthocortex cells occurs, leading to a crimping and bulking effect. Treatment time must be at least 30 minutes for the bulking to be permanent [72]. It was considered that the treated wool would offer possibilities in the manufacture of carpet yarns. However, the OPI group ceased business in 1977 [73] and the process appears no longer to be carried out.

1.11 PROPERTIES OF MERCERISED AND AMMONIA-TREATED TEXTILE PRODUCTS

In his patent, Mercer claimed a number of improvements in properties resulting from his process, naming increased strength and firmness, increased weight and augmented powers of receiving dyestuffs. To these, Lowe was able, by applying tension during the process, to add increased lustre to the list. Later workers have shown how the conditions of treatment – particularly caustic concentration, time and temperature – can affect the nature and degree of these improvements. The type of cotton and the structure of the yarn or fabric are also important factors that must be taken into account.

1.11.1 Strength

Edelstein [74] carried out a study of the influences of concentration, tension and temperature on the strength of mercerised 2/40s yarn. He found that while the yarn strength was sensitive to temperature when treatment was carried out with 30 °Tw. solution, at a concentration of 50 °Tw. the resulting yarn strength was almost independent of temperature. He concluded that there were no great advantages in cooling the lye when mercerising was being carried out using 50 °Tw. sodium hydroxide.

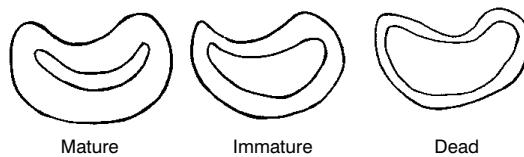
The effect of swelling treatments on fibre bundle strength has been examined by several workers. Warwicker [75] deduced ‘average’ values from a number of published reports, warning that because of the wide scatter, they should be regarded only as indicating general trends (Table 1.3).

There is general agreement that weak places in the cotton fibre are strengthened by mercerisation, so that less uniform cottons gain more in strength than more uniform cottons. Lawson and Ramey [76] believed that three causes of weak places were removed in

Table 1.3 Effect of swelling treatments on fibre bundle strength [75]

Property	Material	Slack mercerised	Tension mercerised
Tenacity	Fibres – zero test length	-20	+5
	Fibres – $\frac{1}{8}$ inch or more	+10	+300
	Yarns	+10	+25
Elongation at break	Fibres	+90	-15
	Yarns	+175	-15
Young's modulus		-10	
Secant modulus	Fibres	-50	+15
	Yarns	-60	+50

mercerising. Places with low cross-sectional area disappear, structural distortions are eliminated or modified, and internal strains are released during swelling. This was shown, for example, by Lawson, Ramey and Jones [77], in looking at the effect of fibre maturity on strength improvement. A mature fibre has two to three times the wall thickness of an immature fibre (see Figure 1.11), so that there is not as much space available for swelling and the release of strains.

**Figure 1.11** Mature versus immature fibre cross-sections

Treatment of plied sewing threads by the ammonia–water process, followed by re-stretching, gives significant strength increases. Bowles [78], reporting data obtained on ‘Prograde’ treated yarn, noted that while the resultant linear density of a three-ply cotton yarn decreased from 50.7 to 48.1 tex after ammonia treatment, tenacity rose from 25.8 to 36.1 g tex⁻¹. Extension at break, however, was decreased from 7.8% to 3.8%. Gailey [79] gave results of laboratory trials on 21 threads, all of which showed large increases in tenacity, from 42 to 100%.

1.11.2 Lustre

Marsh [26] considered that increasing the temperature of mercerising decreased lustre; but this has been contradicted in more recent studies. Bechter, in a series of papers describing experiments on the effect of temperature in mercerising, reported on optimisation of the increase in lustre, by varying tension, temperature and time [27,80]. Cotton yarn (Nm100/2) was mercerised in hank form with 28 °Bé. sodium hydroxide, under sufficient tension to maintain dimensions, at temperatures ranging from 0 to 60 °C. It was found that the lustre increased with temperature. Repeating the treatment a second time resulted in a

further increase, but after a third treatment the lustre was decreased. In each case the time of treatment was one minute.

Treatment of fabrics gave similar results [28]. Up to three treatments gave improvements in lustre, but subsequent mercerising resulted in decreasing lustre. Bechter considered that improvement in lustre was linked to improving the uniformity of mercerising.

1.11.3 Dyeability

The increase in colour yield resulting from mercerisation is well known; indeed, it was one of Mercer's claims in the original patent.

Measurements of colour in dyed fabrics are analysed in various ways, but for the purpose of comparing colour yield changes due to mercerising, most workers have used the Kubelka-Munk function, K/S. The derivation of this is outside the scope of this review, but it is useful to note that K is an absorption coefficient and S is a scattering coefficient [81]. The ratio K/S increases with increasing depth of shade.

Studies at the Technical University of Budapest [82,83] indicated that about half the total dye savings could be attributed to optical effects, and half to increased dyestuff adsorption.

In a study involving 60 dyestuffs, the relative dye savings resulting from the mercerisation of bleached cotton were 30–33%, increasing slightly with concentration. Similar results were obtained at the International Institute for Cotton on mercerised knitgoods [84].

1.11.4 Moisture content and water retention

Mercer claimed in his patent that the cloth would be heavier in weight after treatment. His own measurements indicated the increase to be between 4.5 and 5.5% based on the original weights. This is explained by an increase in moisture content of the material after mercerisation.

Because of a hysteresis effect, the regain of cotton is dependent not only on the ambient conditions, but also on whether the measurement is made under desorption or adsorption conditions. At 65% relative humidity, the adsorption regain of soda-boiled cotton is about 6.8%. For fully mercerised cotton, figures of over 11% have been recorded in laboratory treatments without tension, but Urquhart, Bostock and Eckersall [85] reported a moisture absorption ratio for commercially mercerised cotton of 1.2 (about 8.2% moisture).

There may be a difference in response between cotton varieties. In a study carried out at the University of California [86] five *Gossypium barbadense* cottons were compared with one *Gossypium hirsutum*. After a standard (slack) mercerising treatment, the range of regains of the *barbadense* cottons increased from 6.09–6.37% to 8.97–9.27%, while that of the *hirsutum* increased from 6.13% to 9.67%. The crystallinity of the *hirsutum* variety, as deduced from X-ray diffraction diagrams, was said to have been decreased more than that of the *barbadense* types.

Bredereck and Saafan [67] reported figures of 7.3–7.7% for unmercerised cotton, 8.3–8.8% for mercerised cotton, and 9.2% for ammonia-treated and steamed cotton.

In the same paper, measurements of water retention after a centrifuging treatment were 40–50% for unmercerised, 42–52% for mercerised and 37–46% for ammonia-treated, indicating that while mercerising might increase the water retention value, ammonia treatment by the ammonia–dry–steam method tends to reduce it.

1.11.5 Changes in molecular structure

In the early literature, the form of cellulose found in mercerised cotton was called ‘hydrate cellulose’ in the mistaken belief that water was involved in the lattice of the dried sample. It has now been renamed cellulose II after later work proved that water is not included in the structure.

Structural changes associated with mercerisation do not occur at one particular, well-defined concentration of alkali, but take place over a range of concentrations, referred to as the ‘transition range’. Over this range the cotton becomes gradually more accessible and hydrogen-bond disordered.

With increasing alkali concentration, the crystal lattice gradually changes from cellulose I to cellulose II, and the levelling-off degree of polymerisation (LODP) is gradually decreased. Warwicker and coworkers [75] listed several published results using various methods, and concluded that at 20 °C the transition begins at about 9.5 g NaOH/100 ml and is complete at 15 g NaOH/100 ml.

The unit cell now accepted for cellulose II is that given by Andress [87]. This monoclinic unit cell has the dimensions:

$$a = 8.14 \quad b = 10.3 \text{ (fibre axis)} \quad c = 9.14 \text{ \AA} \quad \beta = 62^\circ$$

In comparison, the usually accepted unit cell for cellulose I, obtained by Meyer and Misch [88], has the dimensions:

$$a = 8.35 \quad b = 10.3 \text{ (fibre axis)} \quad c = 7.90 \text{ \AA} \quad \beta = 84^\circ$$

During the process, various intermediate complexes form between cellulose, sodium hydroxide and water. These ‘soda-celluloses’ occur at well-defined conditions of temperature and sodium hydroxide concentration, as shown in a phase diagram drawn up by Sobue, Kiessig and Hess [89] (Figure 1.12).

X-ray diffraction studies show that a third form of cellulose, cellulose III, is produced by swelling in liquid ammonia and evaporation of the ammonia. However, this form is converted back to cellulose I in aqueous treatments [90,91].

Lewin and Roldan [90] produced a phase diagram of the ammonia–cellulose system, visualising the four major phases of cellulose at the corners of a tetrahedron (Figure 1.13). The base corners are cellulose I (I in Figure 1.13), cellulose III (III) and disordered cellulose (D).

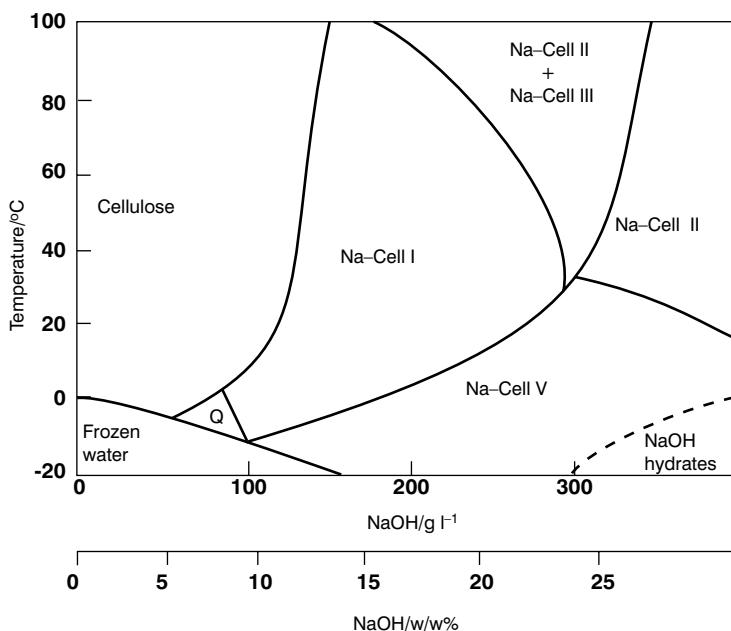


Figure 1.12 Sodium hydroxide/cellulose phase diagram [89]

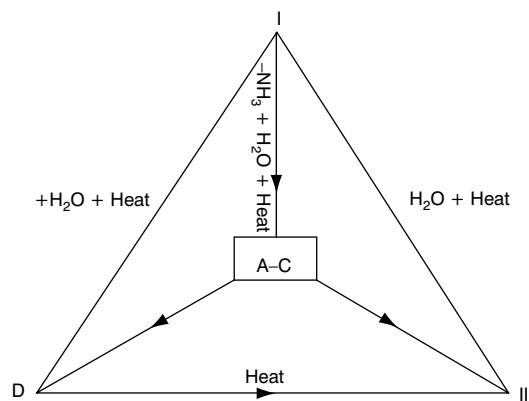


Figure 1.13 Ammonia/cellulose phase diagram [90]

The apex represents the ammonia–cellulose complex (A–C). Arrows indicate the direction of possible transitions; for example, transition from D to III is possible on the application of dry heat. The results of various experiments carried out by the authors are included in the diagram, showing interpretations of X-ray data.

1.11.6 Pore structure

Bredereck and Saafan [67] investigated the changes in supermolecular structure and

morphology of cotton fibres caused by liquid ammonia treatment, using X-ray and sorption measurements and examination of the fibre cross-section. They found some striking differences in comparison with the changes caused by mercerisation with sodium hydroxide. In X-ray measurements on industrially mercerised cotton, it was found that conversion from cellulose I to cellulose II was, in fact, very small, only about 9% of the cellulose being converted to cellulose II. In contrast, after a Sanfor-Set (ammonia-dry-steam) process, 35–38% of the treated material was in the form of cellulose III. Some conversion back to cellulose I took place after a further steaming or hot water treatment.

Iodine sorption, moisture content and water retention after a standard centrifuging treatment all showed distinct changes after the swelling processes (Table 1.4). Although moisture content is increased by both processes, mercerisation increases the water retention and ammonia treatment reduces it. Bredereck interprets this result by commenting that whereas both processes increase the surface area within the fibre, mercerisation increases, and ammonia treatment decreases, the total pore volume.

Table 1.4 Iodine sorption, moisture content and water retention after a standard centrifuging treatment on cotton fibres

Treatment	Iodine sorption (mg g ⁻¹)	Moisture content (%)	Water retention (%)
(a) Desized, scoured, bleached	40	7.5	50
(b) Mercerised	71	8.3	52
(c) NH ₃ treated	155	8.2	46
(d) NH ₃ treated	138	8.1	44
(e) (c) after 3 min steam	71	9.2	40
(f) (c) after 1 hr hot water	55	9.3	44

Changes in pore size resulting from swelling treatments on cotton have been examined in several studies at the Southern Regional Research Center, New Orleans. Rowland, Wade and Bertoniere [92] used a chromatographic technique, known as reverse gel permeation, to study the elution behaviour of a range of solutes of different molecular weights from columns of purified, sodium-hydroxide-treated and liquid-ammonia-treated cotton cellulose. The liquid ammonia was removed by evaporation. Measurements of the concentration changes of various solutions after passing through the columns enabled the accessible internal fibre water to be calculated. This was plotted against the molecular weight and diameter of the solute.

It was found that the sodium-hydroxide-treated cotton contained many large pores, defined as those into which sugars of molecular weight >800 or molecular diameter >16 Å are capable of penetration. Actual diameters of pores to accommodate these solutes would be substantially larger, by a factor of 2–4 according to Nelson and Oliver [93]. Bredereck and Saafan [94] concluded from equilibrium dye adsorption that pores having diameters in the region of 20–60 Å are of special importance relative to dye response.

In a later paper [95] the USDA study was extended to include not only sugars (bulky molecules) but also polyethylene glycols (more flexible, slender molecules) and glymes (long-chain ethers). Polyethylene glycols of molecular weights 300, 600, 1000 and 4000 (molecular diameters 16, 21, 27 and 54 Å respectively) were included. It was found that the ammonia-treated cotton was completely inaccessible to polyethylene glycol with a molecular weight of 1000, and all samples were inaccessible to the product with molecular weight 4000. Relative to scoured and bleached cotton, sodium hydroxide swelling resulted in increased accessibility for lower molecular weight glycols, while liquid ammonia resulted in a decrease in accessibility.

These results were said to have important consequences in durable press finishing, the chemical agents for which typically have molecular diameters around 10 Å. It was calculated that the sodium-hydroxide-mercerised cotton had approximately double the internal fibre volume accessible to molecules of 10 Å compared with the liquid-ammonia-treated fibres.

Bredereck and Blüher [66], using a similar method, examined the different pore structures resulting from the two variants of ammonia treatment – ammonia–water and ammonia–dry–steam. After the evaporation process, the pore volume was found to fall from 0.36 to 0.26 cm³ g⁻¹, and the average pore diameter from 36 to 24 Å with almost no pores above about 25 Å in diameter. In contrast, after the ammonia–water treatment, the average pore size decreased, this time from 40 to 31 Å, but a plot of accessible volume against molecular diameter showed that a significant number of large pores, up to 200 Å, were present.

The pore size, shape and distribution within the fibre are essential factors in determining reactivity in dyeing and chemical finishing processes. Internal fibre volumes and surfaces control dyeing rates, while pore sizes and shapes control the penetration of dyestuffs and chemicals into the fibre.

Hirschler [82] suggested that the internal light scattering was influenced by changes in pore volume. This comment was based on earlier work reported by Mattyus [83], who found increased K/S values for three direct dyes as a result of mercerisation, and attributed this in part to a reduction in pore volume. However, Mattyus gives figures for pore volume that are contrary to most reports: 0.40 cm³ g⁻¹ for bleached cotton, and 0.20 cm³ g⁻¹ for mercerised. Bredereck [67] considered that the increase in imbibition indicates an increase in pore volume on mercerisation. Mattyus' data contrast with the work of Berthoniere and King [95], who report figures for V_2 (the internal volume accessible to molecules similar in size to water) of about 0.3 ml g⁻¹ for bleached cotton, and 0.6 ml g⁻¹ for mercerised.

No work has been published on the effect of temperature of mercerising on pore size, and very little on its effect on dyeing characteristics. Bechter, Fiebig and Heap [14] used a direct dye, Sirius Light Red 5B, to examine the effect of temperature on the uniformity of mercerising. They compared surface colour depth with total dye uptake to obtain an index of uniformity. In their results, the depth of shade after mercerising at 60 °C was less than that after 20 °C treatment, under the same dyeing conditions. In a later study [96], Bechter used another direct dye, Chlorantine Light Green BLL (C I Direct Green 26), obtaining a similar result.

1.11.7 Changes in microscopic appearance

Cotton fibres exhibit certain characteristics under microscopic examination, many of which are modified after mercerisation. Raw cotton fibres have the appearance of a flat ribbon with a central canal known as the 'lumen'. During fibre growth, the lumen contains protoplasm and nutrients that are used to build up the inner wall of the fibre. In the boll, the fibre is swollen with water to a circular configuration, which collapses when the boll opens and drying occurs. During the drying stage, the collapsing tube twists in an irregular manner, forming 'convolutions'.

Under electron microscopy, the fibre wall can be seen to be built up from a large number of substantially crystalline elements called 'fibrils'. These tend to aggregate into bundles, which spiral around the fibre axis. Periodically along the length, the direction of the spiral changes at a 'reversal zone' [97].

Warwicker [75] has reported that when cotton is fully mercerised it swells and becomes almost circular in cross-section, and the lumen is virtually closed (see Figure 1.11). Mature cotton fibres lose most of their convolutions. On washing and drying, except for a change to a smaller cross-sectional area, the general features of the mercerised fibre remain the same. Under the conditions of commercial mercerisation, the morphological features of raw cotton are not greatly changed in the process. The fibrils may change their orientation or shape after mercerisation, but do not lose their identity. Reversal points are still present.

Most reports indicate that the appearance of ammonia-treated fibres is similar. However, Warwicker [98] observed that some fibres treated under tension-free conditions by the ammonia–water system appeared to have a greatly enlarged lumen, showing that at that stage the fibre is plastic and deformable.

1.12 TESTING

As with all testing, tests for mercerisation can be divided into two groups: qualitative and quantitative.

1.12.1 Qualitative testing

Hiibner's test [99]

The pattern, after having been freed from starch, is immersed for a few seconds in the following solution, along with a non-mercerised sample: 20 g iodine dissolved in 100 ml of a saturated solution of potassium iodide in water. The samples are now removed from the solution. After washing them a few times with water it will be seen that the non-mercerised cotton becomes white, whilst the mercerised sample remains a bluish-black colour, which only fades very slowly on prolonged washing.

Deconvolution count [100]

Cut the sample into lengths of 2 mm and immerse the cut fibres in liquid paraffin. Under the

microscope, count the number of fibres entirely free from convolutions. This number expressed as a percentage of the total gives the 'deconvolution count'.

Raw cotton has a deconvolution count of 2 to about 17; mercerised cottons give results in the range 17 to 80, but results in the 14 to 20 range must be regarded as inconclusive.

Differential dyeing

It is now known that swelling treatments affect the pore size of the cotton fibre, so that the relative dyeability of colorants will change depending on their mobility within the fibre. Mercerisation increases the pore size, so that large molecules can penetrate into the fibre more easily.

Goldthwait's red-green test [101] was intended to show differences in maturity in raw cotton, by differential absorption of two direct dyes, a red and a green. Vonhöne [102] showed that the test could also distinguish between unmercerised and mercerised cotton. Mercerised cotton dyes to a greener shade than unmercerised; the shade difference depends on the concentration and temperature of the sodium hydroxide used.

Dugal, Denter and Schollmeyer [103] described a cold-dyeing test for the characterisation of sodium-hydroxide-treated fabrics. Schollmeyer and Denter [104] described a test with Acid Red 151 and Direct Blue 10. This gives a blue colour on mercerised cotton. Bredereck and Buschle-Diller [105] observed that when the test is used on ammonia-treated cotton, the result is redder than untreated. In Goldthwait's test, ammonia-treated cotton dyes much redder than untreated. A similar result has been reported on ammonia-treated linen [69].

Organdie finish (sulphuric acid) can be distinguished from mercerised cotton by the Congo Red test. Swell the specimen in 18% sodium hydroxide solution. Wash it and stain it in saturated Congo Red (C I Direct Red 28) solution for 10 minutes. Organdie-finished cotton is dyed bright red, mercerised and untreated cotton is only lightly stained [106].

1.12.2 Quantitative tests

AATCC Test Method 89–1977 Mercerisation in Cotton

Mercerisation increases the capacity of cotton for absorbing barium hydroxide from aqueous solution. This is used as the basis for a quantitative indication of mercerisation as the 'barium activity number'.

Specimens of the mercerised material and an unmercerised cotton, after standard prescouring, are shaken in separate flasks with a standard solution of barium hydroxide for two hours. The residual solution is then titrated with standard hydrochloric acid to determine the amount of barium hydroxide absorbed by the cotton. The ratio of absorbed amounts, mercerised to unmercerised, multiplied by 100, is termed the barium activity number. A barium activity number in the range of 100 to 105 indicates no mercerisation. A barium activity number above 150 indicates substantially complete reaction between the cotton and the mercerising bath. Intermediate numbers indicate either incomplete reaction or use of a weak mercerising bath.

Iodine absorption

Schwertassek [107] used the increased absorption of iodine as the basis for a quantitative technique, by measuring the loss of iodine from solution by titration with sodium thiosulphate. Recently the use of radioactive iodine has been suggested as a refinement [108].

X-ray diffraction

The relative heights of the cellulose I and cellulose II peaks in an X-ray diffraction trace may represent a useful index for mercerisation. This has been suggested by several workers, among them Jayme and Knolle [109], Manjunath and Peacock [110] and Saafran and Sakran [111].

Infrared reflection

Ghosh and Dilanni [112] have developed a method for estimating the degree of mercerisation using a near infrared (IR) diffuse reflection technique.

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CHAPTER 2

Drying and setting

Leslie Miles

2.1 MECHANICAL METHODS OF WATER REMOVAL

Wet fabrics hold large quantities of water in the spaces between fibres and yarns and some of this water can be easily removed by mechanical means. Twisting by hand (wringing) of domestic washing was long ago mechanised, by using a mangle (wringer) and more recently by centrifuging. Finishers also developed the use of mangles, centrifuges and suction-slot machines, all capable of reducing the water held by an average cotton fabric from above 100% to about 50%. The efficiency of these processes is vitally important because of the much greater cost of evaporating water, due to its high latent heat of evaporation. Wyles [1] has quoted relative energy costs for the principal methods of mechanical water removal ('de-watering'), as compared with thermal drying (Table 2.1).

Table 2.1 Relative energy costs of de-watering and thermal drying [26]

De-watering	Energy cost	Thermal drying	Energy cost
Mangling	1.5	Drying cylinders	25
Centrifuging	2.5	Stenter	35
Suction slot	4.5	IR radiation	120

The method chosen for water removal will depend on a variety of factors, in addition to cost of energy. In the following sections the methods are reviewed.

2.1.1 Mangling

Fabrics processed in rope form are frequently mangled twice – in the rope form to facilitate opening to full width on a scutcher, and then in open-width to remove as much water as possible. It is clearly impossible to apply a high and uniform pressure to a twisted rope of fabric in a mangle nip and some manufacturers have used inflated rubber coverings (like tyres) on the mangle bowls, to achieve maximum uniformity and minimum abrasive effect on the fabric.

Mangles for maximum water extraction, sometimes known as water-mangles (see Figure 2.7), differ little in principle from pad mangles, designed for dye application. The objective, however,

is simply the removal of as much water as possible, as uniformly as possible. High pressures are applied to the ends of the bowls (so called because they were traditionally turned from tree trunks), which inevitably produces some deflection and less pressure in the middle. Figure 2.1 shows a roll in longitudinal section, showing a solid, central shaft (A) with end bearings (B), and a cylindrical shell (C) attached that can be stainless or steel with an elastomer covering (D). This construction reduces the deflection of the roll, which otherwise causes major variation in squeezing from side to centre on the wide-width machines in use today. Other methods of maximising uniformity across the width range from simply grinding an appropriate camber on the rubber covering, to very complex hydraulic loading systems [1]. Clearly there should be no creases passing through the nip and some type of expander is essential.

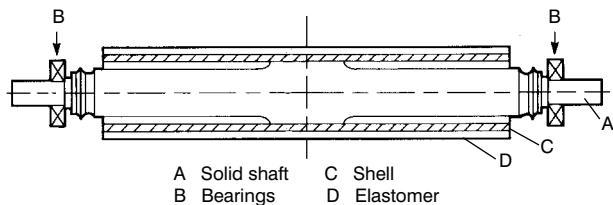


Figure 2.1 The anti-deflection roller (Modern Rollers Ltd.)

The essential principles of mangleing have been described very thoroughly in an early paper [2]. The water retention (percentage of water on dry fibre weight) by the fabric is reduced by:

- (1) increasing the pressure applied. This is usually expressed as total load divided by length of roll (kg cm^{-1}) or as pressure per unit area on the hydraulic rams. The actual pressure on the fabric is almost impossible to assess, and increases towards the centre line of the nip;
- (2) increasing the hardness of the roll covering, thereby reducing the deformation of the roll in the nip and increasing the real pressure. Clearly there is a limit, especially for non-compressible fibres and open fabric constructions, where hard rolls leave water in the spaces between yarns;
- (3) increasing the temperature of the water in the fabric, producing a reduction in viscosity and faster removal of water through the pores of the fabric;
- (4) reducing fabric speed, so that a longer time is available for expression of water;
- (5) reducing the roll diameter, thereby increasing the real pressure and, by reducing the nip width, allowing easier exit of water.

A significant reduction in water retention is obtained by using a resilient, porous covering for at least one of the rolls. Robert Oliver [3] discovered that a compressed fibre-covered roll, in which all the fibres are rubber coated, was practical and efficient. The efficiency is most apparent in the case of open structure fabrics of less compressible fibres, where water retention is typically halved. Because the coverings are compressible and relatively soft, water held in 'windows' between yarns is expressed and, when the pressure in the nip is reduced beyond the

centre line, more water is absorbed by the sponge-like covering. Water in the covering is, of course, squeezed out on re-entry to the nip. A similar mechanism would explain the better figures obtained with sycamore wood bowls, compared with solid rubber coverings.

Paper makers have used continuous felts to effect similar reductions in water retention and Monforts [4] have applied this approach in their Matex-Vac machine.

A major advantage of water-mangles is that they can be incorporated into continuous production lines, although they were traditionally operated as separate units.

2.1.2 Suction slot extraction

Many delicate fabrics are prone to damage if squeezed between the bowls of a mangle or spun in the cage of a centrifuge. There are other fabrics that are not easily damaged but are not efficiently de-watered by mangling. For both categories of fabric, suction extraction has been widely employed. A vacuum pump draws air through the fabric as it passes over a narrow slot and the water removed is withdrawn via a tap.

Table 2.2, comparing the efficiency of the three commercially important processes for selected fabrics, confirms that the suction slot can be more efficient than mangling.

Table 2.2 Typical water retention levels [1,5]

Method	Retention (%)					
	Cotton	Viscose	Acetate	Nylon 6.6	Polyester	Wool
A	45–50	80–100	30	15–25	12	42
B	45–70	60–100	40–50	20–40	20–30	58
C	40–55	70–80	27	14–29	15	84

A: Centrifuging 10 min, 700 g centripetal acceleration

B: Mangling 36 m min⁻¹, 0.6 kN m⁻² nip pressure

C: Suction slot 8 m min⁻¹, 1.2 mm slot, 94 kN m⁻² vac

The precise features of fabric structure that determine the water retention level have not been thoroughly investigated but, for woollen fabrics, a very low air permeability was characteristic of the fabric giving the highest retention.

In principle, the suction slot technique is suitable for inclusion in a continuous process line – immediately before a stenter, for example – but traditionally it has been used in a batch-to-batch machine. Experimental studies [7] showed that retention levels increased significantly with increase in speed from 6 to 9 m min⁻¹, so that in some circumstances a separate machine would give lower overall costs.

Maintaining a seal beyond the fabric edges is important and can be achieved with movable tapes. This method shows the highest energy costs because it is necessary to use a powerful pump to achieve a vacuum level of about 40×10^3 Pa (40 kN m⁻² or approximately 15 in Hg).

The mechanism of water removal is essentially one of pressure difference across the plane of the fabric, forcing water from the capillary spaces, followed by a flow of air pushing more water from discontinuous spaces. It also seems to be likely that some water is drawn by capillary forces from the larger spaces, towards the slot at a higher velocity than the fabric speed.

Related methods

Instead of using a vacuum to induce a jet of air to move through a fabric, air or steam pressure can be applied to force water out. A thorough assessment [8] of the Machnozzle, developed by the Brugman company – which accelerates steam to sonic velocity by passage through a narrow slit (Figure 2.2), before impinging on the moving fabric – concluded that it was economically attractive. More impressive would have been a comparison of the device with use of a Roberto roll in a mangle.

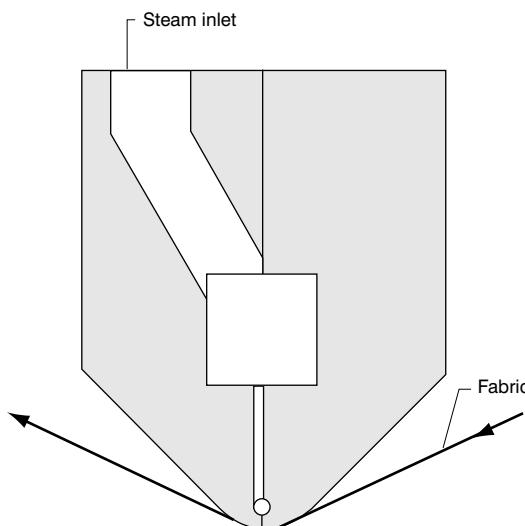


Figure 2.2 Cross-section of the Machnozzle

For tubular knitted fabrics, the use of a steam jet immediately above the suction slot has been recommended. A different approach [9] uses porous rollers to apply air or steam under pressure, for forcing water out and initiating the drying process.

2.1.3 The use of centrifuges

Industrial centrifuges, significantly larger than the domestic variety, are used to remove most of the free water from dyed garments, loose fibre, yarn hanks and fabric in rope form. Fabrics can be fed into the slowly rotating cage, to achieve a well balanced load; other loads can be hoisted in and out in net bags to keep labour costs down. The machines are heavy, consume a lot of power when accelerating to 1000 revolutions per minute or more, and must be properly suspended and mounted in substantial foundations [1]. A 120 cm diameter basket rotating at 1440 revolutions per minute will produce a 'g' value of about 1390, which will reduce the residual moisture in acrylic yarns or tops to 6–8% in a 10-minute cycle.

2.2 EVAPORATIVE DRYING

Having removed as much water as possible by mechanical means, the completion of the drying process requires the transfer of energy to the remaining moisture, to accelerate its evaporation. The textile material will still contain liquid water on, and between, the fibre surfaces as well as that held within the fibres, and the air within the structure will be saturated with water vapour. The energy is usually supplied as heat and the speed and economics of the process are determined by the mechanism and efficiency of the heat transfer achieved.

There are three fundamentally different mechanisms of heat transfer – convection, conduction and radiation – and we need to consider all three.

In addition to the transfer of heat into the textile, the removal of water vapour from the assembly of fibres is essential. This is a particular case of what engineers describe as ‘mass transfer’. Because most textile fibres are arranged in approximately parallel fashion, the capillary spaces between them provide a mechanism for the rapid transfer of liquid water from a wetter part of a yarn to a drier part. As drying usually starts at the most exposed surfaces, this is a significant mechanism of mass transfer during the first stage of the process.

The mechanisms of heat transfer and mass transfer in drying processes have been thoroughly described by Murphy [10] and Keey [11].

2.2.1 Convection drying

Any process of drying in which air carries heat to the fibres comes into the category of convection drying. Usually, fans are used to move the air over high-temperature heaters before it impinges on the wet fibres. Because the rate of drying is proportional to the difference in temperature between the air and the fibre, the process is accelerated. Such ‘forced convection’ also transfers heat faster than does ‘natural convection’ at the same air temperature – for example, in an oven with no fan circulation.

It is useful, at this stage, to consider the very simplest drying process, occurring when clothes are hung out and there is no direct heat from the sun. There will be no immediate heat transfer but the process starts with some mass transfer. Close to the wet fibres a thin layer of air will be saturated with water vapour (100% relative humidity). Further away the relative humidity will be, say 60%, and some water molecules will diffuse from the high vapour pressure (VP) region to the lower VP region. The saturated layer will therefore no longer be saturated and some water molecules will evaporate from the fibre surface. This evaporation leaves the remaining water colder than it was, as it supplied the heat required. The temperature of the wet fabric is therefore lower than that of the surrounding air, and heat transfer will start.

The two processes – evaporation, causing heat loss, and heat transfer from the air – proceed and soon reach an equilibrium in which the rate of heat loss is equal to the rate of heat gain. There will then be no further change in fabric temperature until the equilibrium is disturbed. The energy balance can be expressed thus:

$$(rate\ of\ heat\ loss) = (rate\ of\ heat\ gain) \\ Ak(P_2 - P_1)L = Ah(t_1 - t_2) \quad (2.1)$$

where A = surface area of evaporation/heat transfer

t_1 = air temperature

t_2 = wet fabric temperature

P_1 = partial pressure of water in the air at t_1

P_2 = vapour pressure of water at t_2

L = latent heat of evaporation at t_2

k = mass transfer coefficient of water vapour at t_2

h = heat transfer coefficient from air to fabric

This is the same expression as that used in the determination of atmospheric humidity by measurement of wet-bulb depression ($t_1 - t_2$) with a wet- and dry-bulb hygrometer [12]. The ratio h/k remains essentially constant if the air velocity exceeds 5 ms^{-1} , and psychometric charts provide the data to calculate P_1 for any values of t_1 and t_2 . A more useful presentation of the data is that shown in Figure 2.3. This shows that the wet-bulb temperature is largely determined by the absolute humidity rather than the dry-bulb temperature.

The same expression of an energy balance will describe what happens in any purely convection drying process, and fabric temperatures will correspond to the wet-bulb temperatures shown in Figure 2.3. Most drying processes, however, are not purely convective. The hot metal of the oven, stenter or other machine radiates heat that is absorbed by the moisture in the material being dried, leading to an increase in temperature.

Although the measurement of fabric temperature during a drying process is not easy, all the measurements that have been made confirm the analysis given above.

For example, a comparison of four very different heating systems gave the results shown in Figure 2.4. The plots of temperature against time show a common pattern of initial increase, a

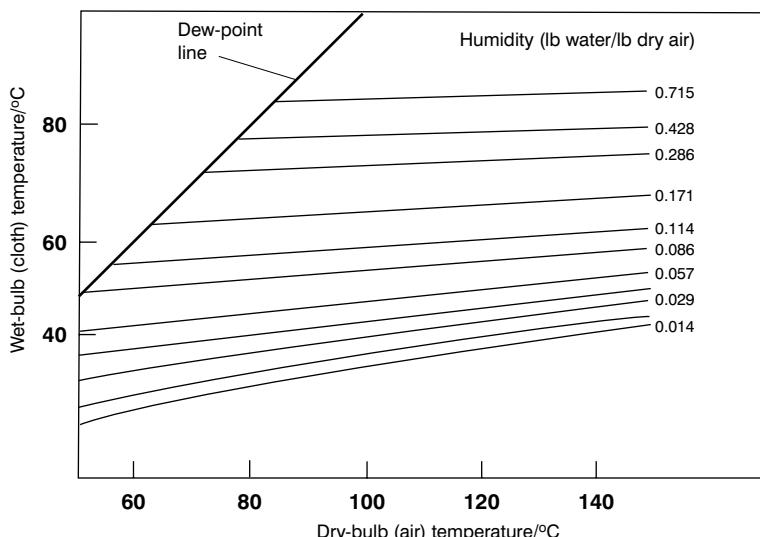


Figure 2.3 Effect of humidity and air temperature on wet-bulb temperature

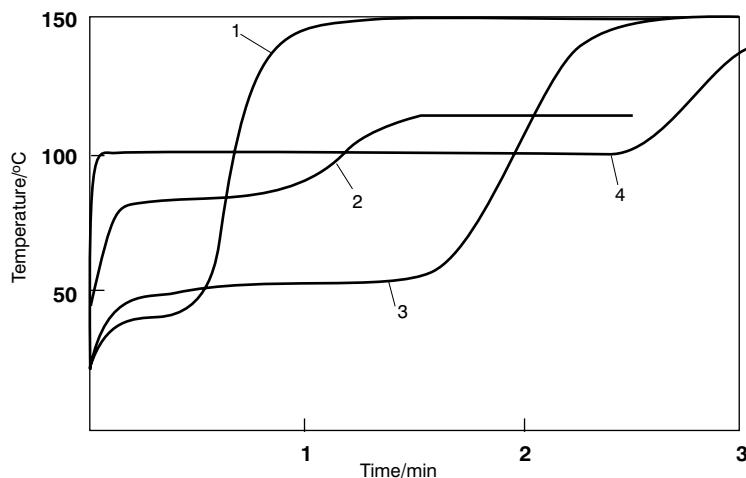


Figure 2.4 Fabric temperature curves for different drying conditions [12]: 1 Benz dryer, 2 Cylinders, 3 Lab. oven, 4 HT steamer

constant period, and then a rise to reach the maximum (dry) level. The difference in the constant period values of curves 1 and 3 is a clear indication of the much larger contribution of radiation from the oven walls in 3, moving the equilibrium temperature up about 10 °C. Curve 4 is not immediately relevant to drying processes but illustrates very clearly the extremely rapid heat transfer on entering a steam atmosphere, the dependence of the wet-bulb temperature on absolute humidity and the low drying rate in the high temperature (HT) steam.

During the constant temperature period, liquid water is able to move to the fabric surface, from spaces inside, so that all the evaporation can occur from the surface(s). Provided that the other conditions remain constant, the equilibrium between heat loss and heat gain is therefore only affected when this movement breaks down. This happens when there may still be small reservoirs containing water but the capillaries can no longer transport it. The migration of dye to the fabric surface also ceases at this critical moisture content, which is determined by yarn and fabric structure.

The kinetics

The rate at which convection drying proceeds is determined by the following factors.

- (1) The temperature of the air used. Wadsworth [13] has shown that rates of drying are directly proportional to the difference between air temperature and fabric temperature ($t_1 - t_2$ in Eqn 2.1), when other variables are held constant. In practice, because heat losses also rise, it is unusual to operate at above 140 °C.
- (2) The humidity of the drying medium (P_1). It is not impossible to operate dryers at 100% humidity, and at one time this was seriously advocated, but high temperatures are required to achieve practical rates. In the region of normal operations, the rate of evaporation is approximately inversely proportional to P_1 , because fabric temperature, and therefore P_2 ,

does not change significantly. In order to keep P_1 low, it is necessary to draw in large quantities of fresh air (or use a dehumidifier) and the heat consumed in raising its temperature makes the operation uneconomical (Section 2.4). An optimum humidity level of 10–20% provides a balance between economy and rate of drying.

- (3) The moisture content. Fibres containing polar groups hold water quite tenaciously, so that bound moisture is removed at lower rates than free water.
- (4) The values of h and k , heat and mass transfer coefficients, which depend on air velocity.

A typical rate of drying curve is shown in Figure 2.5. The drying starts during the short period of warming up, proceeds at a constant rate (and temperature) while evaporation occurs from the surface only, then at a decreasing rate when water cannot be transported to the surface and the

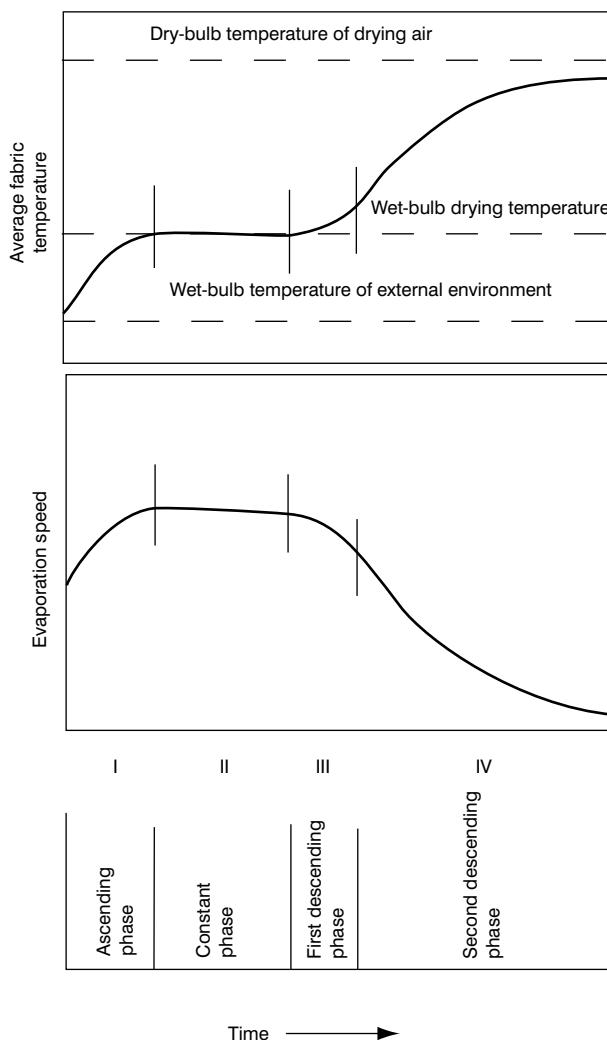


Figure 2.5 Fabric temperature and drying rate curves

plane of evaporation moves inwards. As the rate of heat transfer does not fall, the average fabric temperature starts to climb – the dry surface tending to reach the air temperature. For economic and technical reasons, the average moisture content should not be reduced below normal regain.

When moving air strikes any solid surface there is always a thin layer of stationary air that slows down the transfer of heat, in or out of the solid, to the speed of diffusion. Anyone who has worn stockings or 'long-johns' on a cold, windy day will have experienced the value of an increase in the thickness of the stationary layer. Conversely, stenter drying rates are greatly increased by using higher fan speeds to reduce the thickness of the layer. Engineers have measured heat transfer coefficients for many years, so that improvement in, for example, boiler efficiency may be correlated with fan speeds and metal surface characteristics. Heat transfer by convection has been shown to increase with velocity (v), with $h = 0.5v^{0.78}$ (approx.) and a heat transfer coefficient of $2 \text{ Wm}^{-2}\text{K}^{-1}$ in still air increased to $20 \text{ Wm}^{-2}\text{K}^{-1}$ in air at 26 ms^{-1} . In modern stenters, air velocities of 30 ms^{-1} are often used (Section 2.3.2).

The use of heat pumps for dehumidifying

Some yarn packages and clothing items such as hats have traditionally been convection dried in hot air chambers. Significant savings in total energy costs and in drying time have been achieved in such cases by introducing heat pumps.

The continuous reduction in the relative humidity of the drying air achieved by a heat pump (Figure 2.6), allows a closed system to be used and heat previously supplied to raise the temperature of incoming air is no longer required. The power required to operate the

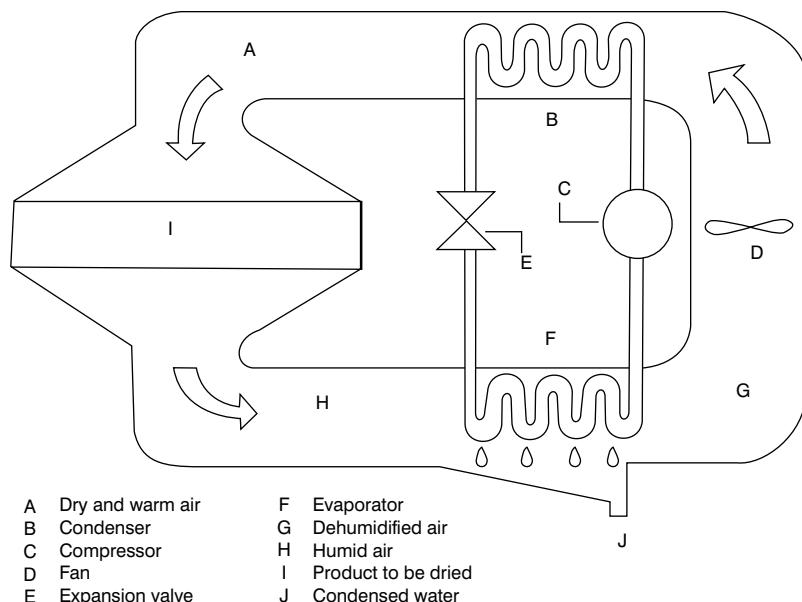


Figure 2.6 Principle of the heat pump as a dehumidifier

compressor of the heat pump is more than offset by recovery of the latent heat of the water removed. A lower air temperature will often be practicable, which also reduces heat losses and usually gives an improvement in handle. Total cost reductions of 70% have been recorded [14].

The domestic refrigerator employs a heat pump to extract heat from inside, transferring it to the hotter air outside. For dehumidifying, within a higher temperature band (for example, 35–80 °C), a different working fluid is chosen but the principle is unchanged. A heat exchanger provides heat from the cool humid air stream to evaporate the working fluid in the low pressure region of its cycle. The compressor then raises the pressure and temperature of the vapour, which will give up its latent heat in the condenser (a second heat exchanger) where the dehumidified air is cooler than the condensing vapour of the working fluid. The air temperature is thereby raised, perhaps 10 °C, and the air is moved back to pick up another load of water vapour from the textile material. Finally, the condensed working fluid passes through the expansion valve and back to the evaporator, starting another cycle.

The drop in temperature of the air stream in its passage through the drying chamber will not be large and this contributes to the high efficiency of the heat pump cycle (ratio of heat released in the condenser to energy supplied by the compressor). Clearly, the cost of electricity will be an important factor and in countries like France, that have a large nuclear generating capacity, interest will be high.

2.2.2 Conduction drying

Cylinders

Heat transfer by conduction has long been used in the highly economic method of drying on steam-heated cylinders (cans). Wet fabric carried on the moving surfaces of a series of stainless steel cylinders (Figure 2.7) is heated by direct contact with the metal, which is maintained at a constant temperature by the internal condensation of steam. The overall rate of heat transfer depends on fabric tension, to maintain contact with the metal, but a value of $120 \text{ Wm}^{-2}\text{K}^{-1}$ for the coefficient h is a reasonable one – much higher than in convection drying. As the rate of evaporation is usually not accelerated by air movement, the consequence is that fabric temperatures of about 80 °C (Figure 2.4) are likely. This makes the use of cylinders for drying acrylic fibre fabrics virtually impossible as they would be seriously deformed (stretched, flattened and glazed). At the other extreme, for woven cotton fabrics the method is attractive wherever some loss of width by crimp interchange is acceptable. Drying after bleaching, after dyeing and partial drying in front of a stenter frame are therefore very commonly achieved by passage over cylinders.

High fabric temperatures also lead to good fixation of reactive dyes in the pad-dry process. However, because evaporation is largely from the surface in contact with the cylinder there will be migration of dye to that surface. If the cylinders were run slowly this would lead to unacceptable differences between face and back surfaces, but at the normal speeds (60 m min^{-1} or more) no problem arises as alternate faces are in contact with consecutive cylinders.

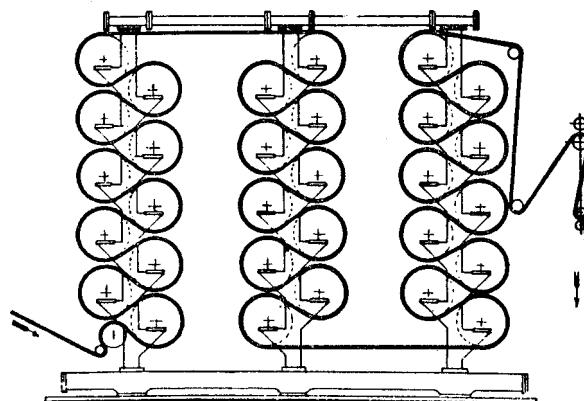


Figure 2.7 Vertical range of drying cylinders (Mather and Platt)

Migration to the surface occurs, and increases the colour value, to an extent that is usually acceptable. Some contamination of the cylinder surfaces with dye also occurs, and surface coating with polytetrafluoroethylene is advantageous.

The use of perforated cylinders for through-flow drying (Section 2.3.2) is best considered as a convection drying process of great value for loose-fibre and suitable fabrics.

2.2.3 Radiation drying

All hot materials radiate energy in the infrared (IR) region of the spectrum (Figure 2.8) and therefore transfer of heat occurs from walls to wet fibres in ovens and drying machines, as already indicated. When the temperature of a suitable material reaches the level that makes it visibly red, the radiation can be used for high speed heat transfer that requires no contact or air movement.

Electromagnetic radiation of higher frequency still provides dielectric heating, that is now of substantial importance in microwave ovens and radio frequency dryers.

Infrared

IR radiation units, either gas or electrically heated, are useful as a first stage in a drying process. The fabric temperature is raised to 100 °C in a fraction of a second, unless air is blown onto it to accelerate removal of water vapour and keep the temperature below 100 °C. Short wavelength IR (up to 1×10^{-6} m) penetrates well but is very colour-sensitive, whereas the far IR (up to 3×10^{-6} m), characteristic of gas-heated ceramic units, does not penetrate far but is less colour-sensitive. An intermediate wavelength (2×10^{-6} m) provides a good compromise and is absorbed very efficiently [15]. If the fabric moves slowly or inadvertently stops, there is a real fire hazard and it is essential to have automatic safety precautions.

The heat transfer rate (Q) is given by Eqn 2.2, where E , the emissivity, is about 0.94 and T_1 and T_2 are absolute temperatures (in K) of the radiator and the fabric respectively. As the

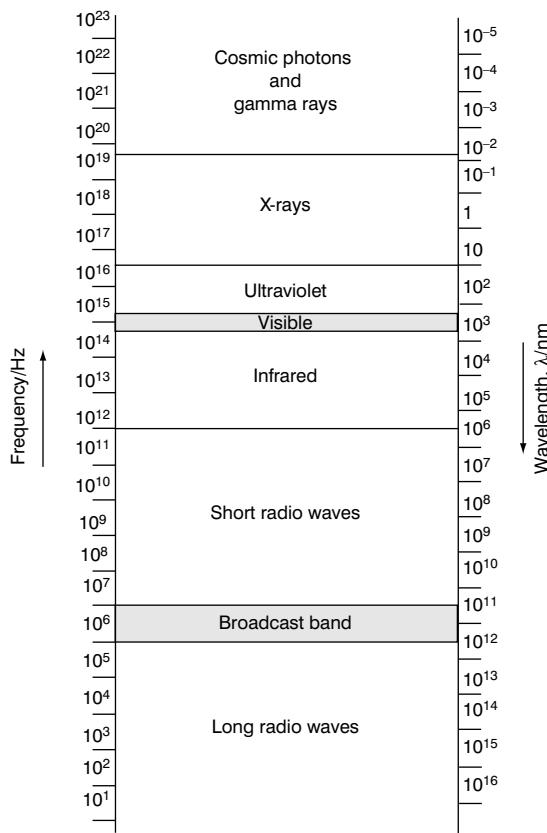


Figure 2.8 The electromagnetic spectrum

radiator temperature can be as high as 1000 K, the rate of heating may be twenty times that attained in convection drying.

$$Q = 5.669EA \left[\left(T_1 / 100 \right)^4 - \left(T_2 / 100 \right)^4 \right] \quad (2.2)$$

where A is the area of the radiating surface.

The application used most widely has been in the continuous dyeing of woven cotton/polyester blend fabrics, immediately after pad application of the dyes and before any contact with carrying rollers. Most of the drying will occur at the fabric surfaces and migration of dye therefore occurs, but it has been claimed that it is less significant than in convection drying. The most important advantage is that marking off of dye from the first carrying roller is usually eliminated.

Radio frequency drying

The hot air drying of yarn packages, wool tops and other bulky material is slow because heating occurs only from the outside, and the outer regions are overdried long before the inner regions

start to dry. The effect on wool, in particular, is obviously undesirable. In contrast, radio frequency (RF) drying effects immediate and uniform heating of any package and, by using a conveyor belt, the process is made a continuous one and is completed in minutes rather than hours [16].

The simplest configuration consists of two flat metal plates, with the wet package between them, and connections to the RF power generator (Figure 2.9). The electromagnetic field is oscillating in excess of 10 million times each second (13.56 MHz or 27.12 MHz) and the dipolar water molecules absorb energy as they are continuously re-aligned with the field. The energy absorbed by the fibre molecules is typically less than 1% of that absorbed by water, so that any wetter regions absorb more strongly than the drier regions.

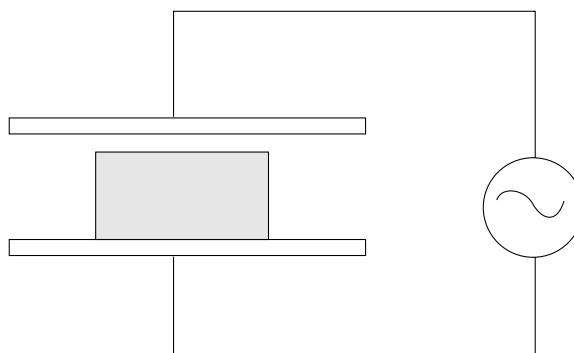


Figure 2.9 The simplest RF heating mode

It has been observed that the steam generated inside a wet yarn package pushes liquid water out of the package. It is possible therefore to omit centrifuging before RF drying but the normal recommendation is to centrifuge first, for minimum energy consumption.

One of the major advantages is that the uniformity of drying achieved, because of the preferential energy absorption by water, allows the product to be dried to the precise regain required. Energy waste in local overdrying is thus avoided. Energy required for heating up, and wasted when production ceases, is also eliminated. However, the fact that fibre temperatures during the drying process were at about 100 °C caused some problems, such as yellowing of white wool and deformation of acrylic fibres. These problems are avoided either by batch drying within a vacuum chamber or, more economically, by drawing a flow of cool air through the material being dried. As air cooling is employed in the RF generator, it has been possible to direct this air stream for use in this way. Not only is the drying temperature reduced but the rate of water removal accelerated.

When maximum drying rates are sought a combination of convection and RF drying has been shown to be effective, and practicable [17]. The RF heating moves water from inner regions to the surface, where it is efficiently removed by convection. Even a small RF proportion (10–15%) of total energy has been shown to shorten drying times dramatically.

Although the RF approach has been adopted primarily for loose fibre, hanks, tops, cakes, cheeses and other bulky packages, air-assisted systems are of interest for fabric drying. One type is a modified ‘staggered through field’ electrode system (Figure 2.10) using air flotation nozzles as electrodes.

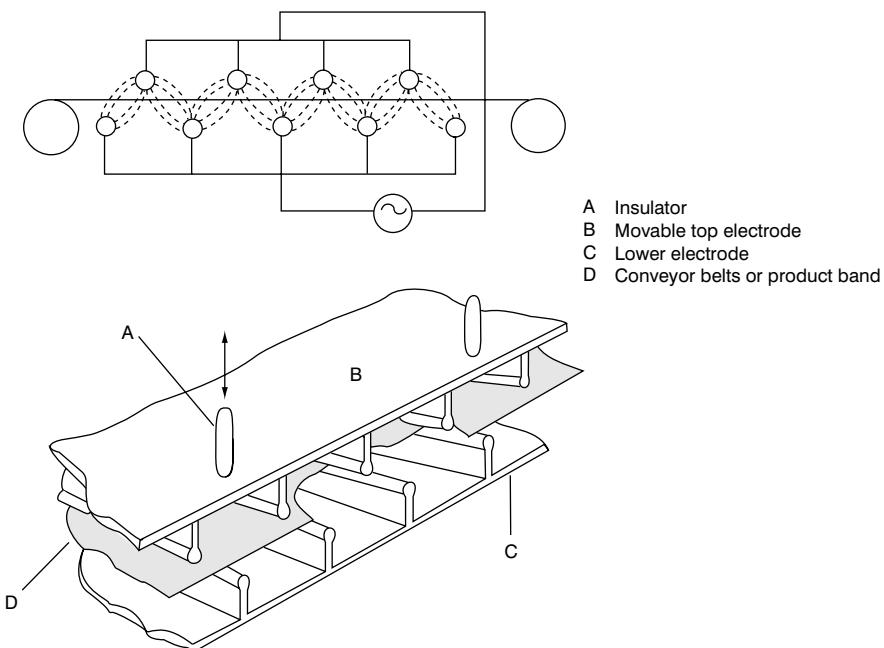


Figure 2.10 Staggered through field electrode system

Microwave drying

Radiation of higher frequency, the microwave band, can be used to achieve very similar dielectric heating as radio waves, and is familiar in its domestic oven application. The frequencies allocated to industrial, scientific and medical uses are 896 and 2450 MHz. They have not been adopted for use in drying to the same extent as RF frequencies, because of the higher costs of equipment, but they do have some advantages. A magnetron will generate power at 896 MHz with better than 80% efficiency, compared with an average 60% for RF generators. Transmission of the power must be through precisely engineered wave guides, however [18].

One very efficient applicator system, the cylindrical monomode cavity, has been adopted to dry up to six yarns passing through a horizontal tube 3 m long, at 20 m min^{-1} . Air is blown into the tube, to remove water vapour, in a counter-current manner. This dryer is part of a continuous processing system and its adoption eliminated the previous costs of double handling [19].

2.3 DRYING MACHINES

2.3.1 Machines for drying fibre and yarn

Wyles [20] and Gaunt [21] have reviewed the changes in drying machinery employed. Traditionally, centrifuging in a basket-type hydro-extractor was followed by hot air drying in a stove. The latter was a very slow process for packages of yarn, often taking 24 hours and occupying considerable space. By about 1950, the major package yarn dyers were using 'rapid dryers' (Figure 2.11), taking the complete carrier frame inside a pressure vessel. The process uses a blower fan to force compressed air (480 kPa or 70 p.s.i.) through the packages, from out to in, and push out free water. The air is then heated and circulated, from in to out, passing through a condenser unit to remove water vapour and provide a source of hot water. Drying cycles of 10 to 60 minutes are required, depending on the yarn, size of load and temperature used. By recirculating the compressed air, problems of energy consumption and contamination by dirt are minimised. Considerable power is, however, required to run the fan motor and drying uniformity is a problem because water drains to the base of the packages. The supply of hot water may exceed requirements, in which case a heat pump could be used to remove water vapour and save steam.

In more recent years, the alternative approach of RF drying following centrifuging has gained widespread acceptance. The extra handling necessitated has led to the adoption of robotic systems of package transfer. Both conveyor belt and batch drying units are used, and increasingly are of the LT (low temperature) or TC (thermo-controlled) type – that is, they use air circulation to control the drying temperature and to increase the drying rate.

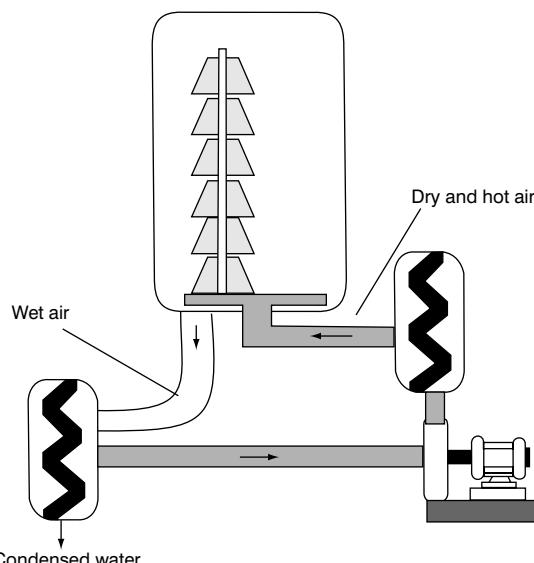


Figure 2.11 Pressure dryer for packages (diagrammatic)

The advantage of this approach is primarily the improved uniformity of drying achieved, with the elimination of energy and time lost in heating up and cooling periods.

In the case of yarn hanks, muffs, tops and similar material, the advantages of RF drying are more obvious as there is no equivalent of the rapid dryer. Staple fibre, after centrifuging in bags, can be dried on RF conveyor machines, after opening the mass of wet fibre with a spiked feeder. Alternatively, a Fleissner suction drum machine is used, drawing hot air through the bed of fibres to hold them on the perforated drum surfaces as they are dried. These systems are very much more efficient than brattice dryers, with drying times of about one minute (see also Section 2.3.2).

2.3.2 Machines for drying fabric

Stenters

The most universal fabric drying machine is the stenter, which is usually the most expensive and indispensable machine in the finishing works. Most finishers will need at least two stenters as the majority of fabrics have to be stenter dried, or heat set, at least once to establish dimensions and properties. In the Yorkshire woollen industry this machine is known as the tenter and commonly has two or more layers, for drying fairly heavy woollen or worsted fabrics.

The essential characteristics of a stenter (Figure 2.12) are the two driven chains carrying pins (or clips) to hold the fabric edges for passage through the enclosed drying compartments. Guiding arrangements are designed for accurate pinning of the edges, with provision for overfeeding the fabric to allow any required adjustment of fabric length while the width is increased to the precisely specified value. Clip stenters are useful for dense and heavy fabrics that tend to damage pins, but overfeeding is not possible.

The number of drying compartments, each typically 3 m long, depends on the speed required but is usually between three and eight. The tapering entry section is 5–7 m long and the delivery section another 5 m, to allow cooling to occur before removal for batching (or plaiting). A total length of 30 m, plus fabric feeding arrangements and batcher space, is therefore common and speeds of 100 m min^{-1} often achieved. More details of the mechanical arrangements have been given by Wyles [22].

Stenter drying provides the ideal opportunity to achieve weft straightening and edge uncurling, and the appropriate mechanisms are fitted at the entry end [23]. Sometimes the recovery of curled knitted fabric edges is not possible and a system of edge gumming and subsequent cutting and removal is fitted.

Efficiency and uniformity of drying demand attention to the air-flow. A powerful fan (or two fans) pushes air into two tapered ducts (Figure 2.13) and through precisely made nozzles to achieve high-impact velocity at the fabric surface. The slightly cooler air must then be directed into the return circuit, through a filter and the heating section (ideally an internal gas burner) to the fan. The Babcock Star-Jet nozzle system [24] is claimed to improve performance by 15%, because of its optimal air-flow pattern. Air temperatures in the region of 130–150 °C are used for high drying rates without excessive heat losses in the exhaust.

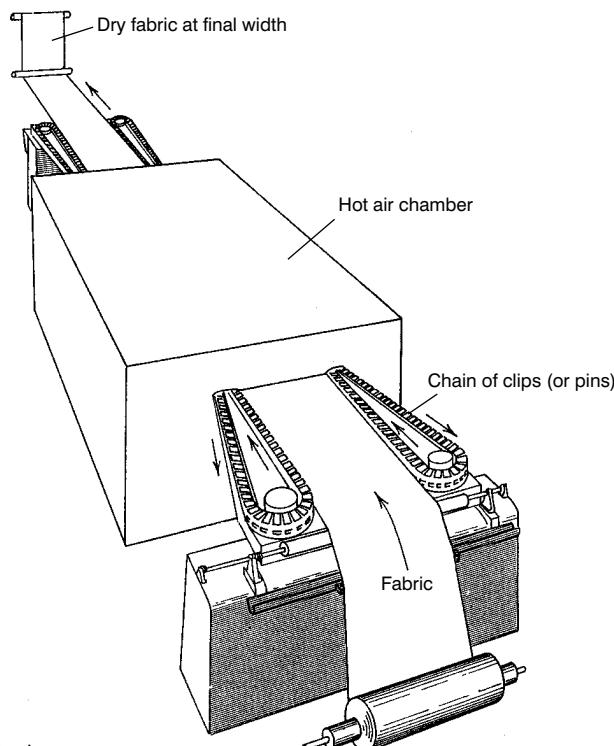


Figure 2.12 Clip stenter

For optimum thermal efficiency, it is essential to monitor and control the humidity of the drying atmosphere. It is possible to do this with a fluidic oscillator developed by Mahlo [25] and control of the exhaust dampers. Figure 2.14 [26] shows how dramatically energy costs rise when the humidity falls below 10% (0.1 kg water per kg air).

Reducing the volume of cold air entering (by exhaust damper control) reduces the energy required to raise its temperature, and it has been claimed that 30% savings in energy result when the humidity is increased from 5 to 10%. There is also a reduction in rate of drying, but an optimum balance can be found in the 10 to 15% region. In the future it may be that heat pumps will be used to maintain the optimum humidity, and eliminate exhaust losses.

Energy losses in the exhaust can be reduced by 50% by using one of several heat recovery systems [26]. Without attention to energy losses, in a stenter heated by steam in the traditional manner the useful heat (converting water to vapour) may be as little as 31% of the energy in the boiler fuel (Figure 2.15) [27].

Drying cylinders

When the control of fabric width is not essential, or when removing a substantial fraction of the moisture immediately before stentering, a cheaper method of drying will be chosen. For woven fabrics, this has traditionally been use of a set of cylinders filled with steam under pressure. Stainless steel cylinders are now universal and pressures of 210 kPa (30 p.s.i.) or even 600 kPa

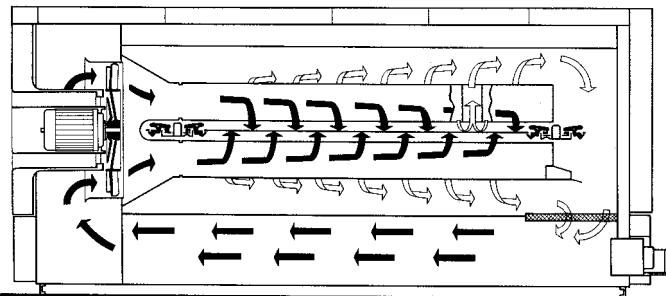


Figure 2.13 One method of air circulation in stenter drying

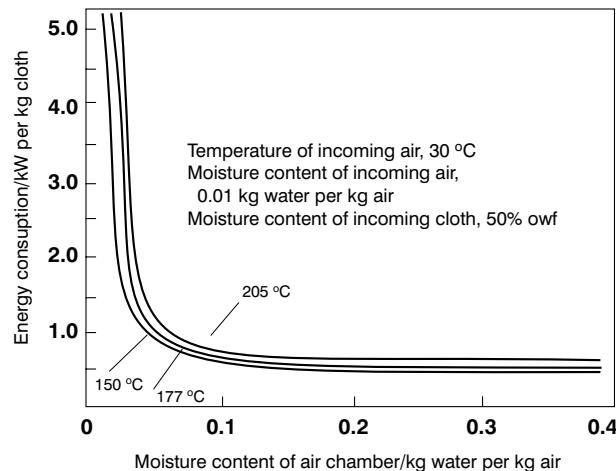


Figure 2.14 Stenter efficiency as a function of air humidity and temperature

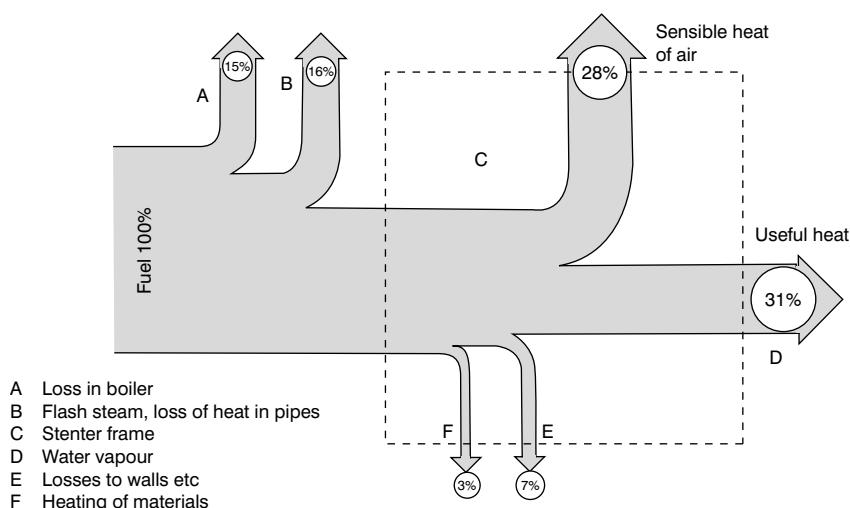


Figure 2.15 Thermal efficiency in a stenter drying process

are commonly used. Steam is fed into each cylinder through a hollow shaft and condensate removed continuously through a pipe extending to about 4 mm from the bottom (Figure 2.16). Air vents are fitted to allow the expulsion of air when heating up, and anti-vacuum valves permit air to enter when cooling down.

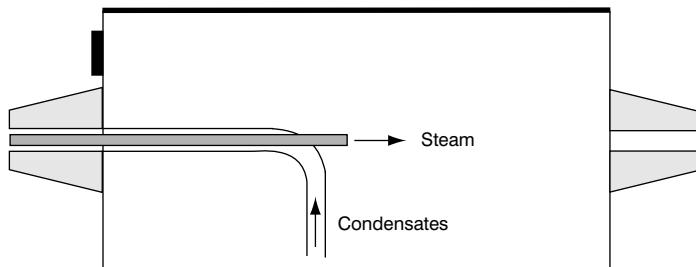


Figure 2.16 Cross-section of a drying cylinder (diagrammatic)

The fabric passes around each of the cylinders, which are staggered to obtain maximum contact, alternately in contact on face and back (Figure 2.7). Tension is necessary for good heat transfer and extension in length is inevitable, even though the cylinders are driven. A finish is therefore obtained that is similar to the effect of a hot iron, and may be desirable or not (Section 2.5.4).

High fabric speeds are usually possible and good thermal efficiency [25] means that overall costs are low.

Through-flow drying

For 50 years the Fleissner system of suction drum drying has been used for loose fibre (Section 2.3.1). In recent years, the importance of energy saving and a better understanding of convection drying has encouraged the application of this approach for drying a wide range of air-permeable materials, especially non-woven fabrics, but also selected types of paper [28].

Figure 2.17 shows the essential features of a typical perforated drum drying unit. A powerful fan creates a vacuum inside each drum, drawing air through the web fed onto its surface. No tension is applied, and by overfeeding it is possible to allow for shrinkage in drying. The web is transferred from each drum to the next automatically, with no need for a tape or leader. Air leaving each fan is heated, in any selected manner, and partially recirculated and partially passed on to the next drum. Counter-current movement of air provides easy control of humidity and high thermal efficiency. Drying rates are high because of the movement of air through the fabric structure. With the latest drum and fan system, designed for less permeable materials, specific drying rates of even $400 \text{ kg water m}^{-2}\text{h}^{-1}$ are claimed. Heat recovery from the exhaust is easily arranged.

In spite of the high power requirements of the fans, a total energy requirement of 3250 kJ per kg of water evaporated makes this system very attractive for those fabrics that are sufficiently permeable and not damaged by the contact with the drum.

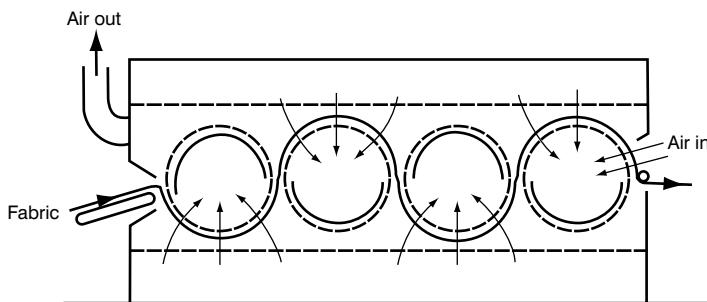


Figure 2.17 The Fleissner suction drum dryer

Relaxation dryers

When maximum relaxation during drying is required, to reduce shrinkage in washing and achieve softness of handle, it is not sufficient to apply overfeed. Agitation is required to maximise the freedom of fibre and yarn movements. Most of the shrinkage occurs in the period after the regain is reduced to 50% in cotton fabrics, so that initial drying can be achieved on suction drum units, for example.

Brattice, or conveyor, units have been used for relaxation, overfeeding on to the conveyor and agitating the fabric with jets of high velocity air from below and above alternately.

More recently the principle of the jet dyeing machine has been applied, using air instead of water to transport the fabric. The passage through a series of jets and relaxation scrays provides the mechanical compaction and random pressures for effective relaxation [29]. Both knitted and woven fabrics can, of course, be relax-dried in this way.

Short lengths of fabric can be dried in a tumble dryer used for garments.

Miscellaneous methods

At one time drying machines were made in which fabric was formed into festoons, or loops (as in a print steamer) within a drying chamber. In continuous dyeing ranges, so-called Hot-Flue dryers are often used, in which the fabric is conveyed on carrier rollers and air injected at relatively low velocities, to avoid causing creases. High drying rates cannot be achieved in such machines.

In contrast, high drying rates are achieved by the use of infrared radiators or lamps, preferably with some injection of air, but the energy costs are high and control is difficult (Section 2.2.3).

For small production units, where a standard stenter would be unjustified, large, single drum stenters may be used. Fabric width is maintained by toothed belts that may be carried flat on the surface of the drum after the fabric is impaled.

Tubular weft-knitted fabrics have, for many years, been dried by the passage of hot air from the inside as the tube is drawn over stretcher frames. They have the obvious advantage of not producing edge creases and well-designed stretcher frames can deliver fabric at the required dimensions.

A completely different approach is that developed by Hoechst for drying fabric after pad application of dye, and described as the Remaflam method. By incorporating an inflammable solvent, usually methanol, in the pad bath and passage through a radiant heater, the heat of combustion of the solvent produces *in situ* evaporation of water. When working properly, no flame is produced but attention must be paid to the flammability and explosive hazards. The advantage is less migration of dye to the fabric surface. Some dyers would, however, consider this a disadvantage.

2.4 THE ECONOMIC CONTROL OF DRYERS

Most of the factors affecting the cost of drying processes have already been mentioned, and may be summarised as follows:

- (1) mechanical removal of water must be maximised, and achieved as uniformly as possible;
- (2) drying should not proceed beyond the equilibrium regain of the fabric;
- (3) thermal efficiency of convection drying requires that optimum humidity of the drying medium be maintained;
- (4) air temperature should be high for speed of drying, but if taken above about 150 °C unit costs are usually increased;
- (5) air velocity at the fibre surface should be maximised – through-flow drying shows a clear advantage here;
- (6) losses by radiation and in the exhaust should be minimised – steam supply losses should be eliminated by direct heating within the drying chamber.

Point (2) is easily stated, but less easily achieved. When drying processes were slow and labour cheap it was possible to rely on judgement by hand to ensure that drying was complete, and not overdone. At the high speeds now fairly standard this is much more difficult because the fabric surface will be dry while significant moisture remains within (time for diffusion is significant).

At one time finishers relied on regain measurement, using either resistance or capacity devices. In practice, however, they were found not to be reliable, especially where different finishes were applied. The problem of control has therefore been frequently considered [11,30,31,32].

Analysis of the problem was simplified when it was observed [30] that for all fibres the difference between the fibre temperature and the wet-bulb temperature of the drying atmosphere, during the falling rate period, is correlated with the equilibrium relative humidity (e.r.h.) of the fibre. When the e.r.h. reaches 60% the fabric is at standard regain. For all the fabrics studied this was when the temperature difference was 9 °C. The problem was therefore resolved into one of making reliable measurements of fabric temperature and wet-bulb temperature of the drying atmosphere, at or near the fabric exit.

Fabric temperature can be measured directly with a contact thermometer but marking of the fabric is a hazard. Non-contact measurement with radiation pyrometers is well developed, but not cheap. The Monfor-matic unit [33] is indirect, but regularly applied to follow temperature

change. By measuring air temperature immediately before and after contact with the fabric, the temperature difference is obtained and can be correlated with fabric temperature.

Wet-bulb temperatures are reliably measured provided that the wick is kept wet. Harbert reports the use of a radiation pyrometer to measure both fabric and wet-wick temperatures, alternately. This novel approach eliminates some possible errors and was found to work well on a production tenter. Slater [34] has described an essentially similar system.

Once a measurement of e.r.h. or regain can be made, using it to control the machine speed is essentially straightforward. It is important to ensure that uniformity across the fabric width is maintained and, provided that it is, significant savings can be made by avoiding over-drying.

It is quite possible to measure fabric regain by a number of different methods. Beta-ray absorption has been used in the paper industry and microwave absorption instruments can be used to monitor both high (entry) and low (exit) levels [35].

2.5 HEAT SETTING

2.5.1 Definition and objectives

The most general reason for heat setting is to achieve the dimensional stability of a yarn or fabric containing thermoplastic fibres. In order to understand what is required, it is helpful to consider the stress in individual fibres. During drawing, spinning, weaving or knitting, and finishing processes the fibres are subjected to extension, twisting and bending forces that leave significant stresses in the fibres. As a result, any subsequent heat treatment or washing produces stress reductions (relaxation) that show up as shrinkage or change of shape (for example, of loops in knitted goods).

The objective of a heat setting process is therefore the achievement of a desired stress-free form of the fibres making up a textile product. It is rarely possible to achieve perfect setting but an acceptable degree of stability to garment making, wear and washing can be attained. The production of permanent pleats or creases in garments is a specialised form of setting.

A definition of setting [36] can be given graphically by a hypothetical experiment (Figure 2.18). A fibre is deformed to the point A in the stress-strain diagram. We can think of the deformation as elongation, although it could be bending or any other type of deformation. If the fibre is held at A for any time, the stress will relax – for example, to B. Release allows elastic recovery to D. If the fibre at A is heated and the segmental mobility of the fibre polymer chains increased, there will be a rapid relaxation of stress, reaching C under ideal conditions. Cooling, before release, allows the formation of new inter-chain forces and the deformation will be ‘permanent’. Although the experiment is a hypothetical one, it reflects what happens in practice. The production stresses get locked in until heat treatments – during dyeing, for example – allow partial relaxation and then heat setting provides the conditions required for stabilising the structure, with little or no stress left in the fibres, even though they have been twisted, stretched and bent.

The temperature reached in heat setting must obviously be below the melting point of the

polymer, but inter-chain bonds must be broken and significant losses in tensile strength are observed. The nature of the changes in structure and properties is complex, but thoroughly described by Statton [37].

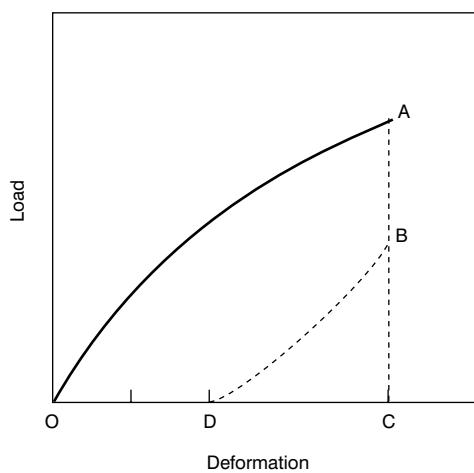


Figure 2.18 Load—deformation diagram illustrating the definition of setting

2.5.2 Setting on stenters

The pin stenter is an ideal machine for fabric setting, providing complete control of width and length. Sometimes – for example, for knitted nylon shirting fabrics requiring maximum stability to washing – stretching in both directions is desirable. In other situations the best handle and stability require maximum relaxation. Experiment is required to find the conditions giving the optimum result.

The heating time to achieve a setting temperature of 200 °C depends on the fabric thickness as well as air velocity, but will often be at least 20 seconds. If the fabric is being dried and heat set in one run, this means that the stenter speed will be low as the fabric temperature will not rise until drying is almost complete. Monitoring the fabric temperature is very desirable in these circumstances. When the setting temperature is reached, however, the time required is very short. Cooling before removing fabric from the pins is essential.

Temperatures of 200 °C (or more) in air can produce significant oxidation of some fibres; nylon especially may be seriously yellowed and the colour not easily bleached. Anti-oxidants incorporated in the fibre are helpful, but injecting steam into the stenter chamber has become the common solution to the problem. Most of the oxygen is thereby excluded and setting is accelerated.

In the case of blends with natural fibres the setting temperature will usually be limited to 150 °C (wool) or 180 °C (cotton blends to be finished white), to control the extent of damage and yellowing. When fabrics containing bulked yarns are set the temperature must again be kept low enough to avoid the complete loss of bulk. At these lower temperatures the setting

efficiency will be reduced, even when longer times are given. The alternative of setting in steam may be the best solution (Section 2.5.3).

The position of heat setting in the finishing sequence depends on the fabric structure, how clean it is, and the dyeing method. Setting after scouring is recommended when a fabric is heavily oil-stained or if setting makes size removal difficult. Setting after dyeing may significantly modify the colour.

Some recommended setting temperatures [23] are shown in Table 2.3.

Table 2.3 Recommended setting temperatures [23]

Fabric	Temperature (°C)
Nylon 6.6 (filament) – woven	200–210
Nylon 6.6 (filament) – knitted	220–225
Nylon 6 (filament)	180–190
Polyester (bulked yarn)	150
Wool blends	170
PE cellulosic blends	180–210
Acrylics	140
Tricel	190–210

2.5.3 Other machines for setting

For fabrics that are not easily extended, especially woven staple blend fabrics, passage over a set of heated drums has been much used in the USA. There is no control of dimensions, but the contraction in width can be predicted and allowed for, if the conditions are consistent. Because of the high heat transfer rate, running speeds can be high.

For smaller production levels and some restraint on fabric shrinkage, Palmer cylinder- and blanket-type machines have been used. Heavy industrial fabrics, which exert shrinkage forces too high for stenter pins, have been set on such machines.

High heat transfer rates are also attained on through-flow suction drum machines, exactly as those used for drying air permeable fabrics.

In the case of garments, especially halfhose and stockings, hot-head presses have been used, using formers to establish the garment dimensions. For optimum setting efficiency, it is often necessary to complete the process in steam, with or without removing the former.

Setting in a steam autoclave is a slow, but technically efficient method that was important from the earliest days of synthetic fibre production, and is still a valuable technique. An autoclave is a pressure vessel, large enough for a trolley carrying piles of pre-pressed garments, stockings on formers or rolls of tubular, knitted fabrics. Once the trolley is introduced, the door is closed and the air evacuated before opening the steam valve. Saturated steam at 110–140 °C, according to the fibre to be set, gives uniform setting in 10 minutes. Failure to evacuate before steaming produces a non-uniform result because pockets of air are trapped – between the garments in a pile, for example – that cannot be displaced by the steam.

The excellent setting, achieved at relatively low temperatures, is a consequence of the significant reduction in the value of the glass transition temperature (T_g) of the fibres. The segmental mobility of the polymer chains at a given temperature is substantially increased by the presence of water.

2.5.4 Effects of setting on properties

The reduction in stress produced by setting can lead to major changes in fabric handle. A woven nylon fabric, before setting, may have quite a stiff handle (especially in the wet state) because of the high inter-yarn frictional forces. The wet crease recovery will therefore be poor. Relaxation of stresses in setting, reducing yarn tension, can almost eliminate the frictional force and lead to low shearing stresses, soft handle and good recovery from wet creasing [38].

However, if the same fabric were to be heat set under tension these changes would be much less noticeable, and fabric handle may even be stiffer because of fibre adhesions.

Structural changes in most fibres during heat setting lead to a reduction in accessibility to dyes, especially the larger molecules. It is therefore essential that, when setting is carried out before dyeing, the uniformity of heating is good. The regular cleaning of air filters in pin stenters must not be overlooked as fibre temperature differences greater than ± 1 °C can lead to side-to-side colour variation.

Polyester fibre accessibility to dyes is setting-temperature sensitive. At 200 °C it is reduced, but at 220 °C dye uptake is usefully increased. Dye uptake by nylon fibres is also increased by setting in steam.

The shrinkage of unrestrained fibres during heat treatment is useful in that the heat setting of polyester staple blend fabrics produces a major improvement in pilling properties. The fibre ends not only shrink into the yarn structure, but tend to lock the fibres in place.

As stated earlier, however, the primary effect of setting is the stabilisation of yarn and fabric to subsequent heat treatment and washing. Woven fabrics are easier to stabilise than knit goods because they have clearly defined crimp intersections and small changes in yarn shape have minimal effect on fabric dimensions. Lower temperatures may therefore be used for setting woven fabrics. Many knitted fabrics are, however, very dependent on precise maintenance of the loop shape for dimensional stability [39].

The measurement of the residual shrinkage of yarn from a set fabric provides a valuable indication of setting efficiency [40].

2.5.5 Economic considerations

In order to attain the maximum safe running speed it is necessary to monitor fabric temperature. Regular checks with 'Thermopapers' attached to the fabric are better than nothing but measurement will usually save more money than it costs. Automatic microprocessor control of speed is now well established and ensures quality with economy.

Because setting temperatures are so much higher than drying temperatures it is essential to

control the amount of fresh air admitted and to recover heat from the exhaust. The combustion of lubricating oil from knitted fabrics can pollute the exhaust quite dramatically and contaminate the heat exchanger. The most economic solution is the complete combustion of pollutants in the gas flame of the stenter heating units. For stenters that are not gas-heated it is possible to install a combustion unit in the exhaust duct, before the heat exchanger. Where necessary, exhausts may be cleaned by liquid scrubber units.

Effective insulation and sealing of stenter housings is obviously more important in the setting than in the drying context.

Attempts to use infrared heating have usually proved to be unsatisfactory because of the difficulty of controlling fabric temperature. Setting in hot air, or steam, has the very real advantage of simpler control.

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CHAPTER 3

Application methods

P Greenwood and I Holme

3.1 INTRODUCTION

Following dyeing or printing, a textile fabric usually undergoes a further process or series of processes in order to confer or enhance the attributes required for satisfactory performance in its intended end-use. These may range from a simple application of starch to more sophisticated processes for crease resistance, water-repellency, handle improvement, shrinkage resistance or other properties that are obtained by means of a chemical treatment, usually from an aqueous bath. This chapter will consider the various methods available to the textile finisher for applying chemical treatments.

3.2 DIP AND NIP PADDING – THE PAD MANGLE

One of the most important and widely-used items of equipment in any finishing works is the mangle. Several types of mangle may be in use, either for removal of water after washing, or for removal of excess liquor in dyeing or chemical finishing operations. Pad mangles for chemical finishing applications are usually of a two- or three-bowl design. Machines with four or more bowls are available but the use of these is normally limited to dyestuff application.

The fundamental principles of the operation of mangling for liquor application and removal were set down by Potter [1] in 1955 and further investigated in research carried out by the Shirley Institute [2].

It was considered that the two main aims of mangling are:

- (1) uniformity of nip
- (2) efficient water removal.

When the primary purpose of the operation is to apply a dissolved chemical to the fabric then uniformity of the application is normally of overriding importance. To ensure uniformity, mangles for chemical padding are usually operated under lower pressure conditions than those that are used simply to express water.

Potter deduced a simple equation relating the take-up, T , to the minimum thickness of the fabric, t_m (Eqn 3.1):

$$T = \frac{t_m - w/\rho}{w} \cdot \sigma \cdot 100 \quad (3.1)$$

where σ = liquor specific gravity
 ρ = fibre density
 w = weight per unit area

Potter assumed that the amount of air contained within the fibre is negligible at the point of maximum compression – that is, the fabric is fully wet-out.

He further deduced that:

- (1) a greater load means less take-up;
- (2) for the same load per unit length of pressure area, bowls of smaller diameter give smaller take-up – in fact, the load required to produce a constant take-up is proportional to the square root of the radius of the bowls;
- (3) if we have n thicknesses of fabric passing through the mangle and if it requires a load, L_n , to produce a take-up, T , as compared with L for a single layer, then (Eqn 3.2):

$$L_n = \sqrt{nL} \quad (3.2)$$

The Shirley research showed that the effect of temperature variation is significant in the control of pick-up, giving as an example measurements of pick-up at two levels of liquor temperature. At 5 °C, pick-up was 71% on weight of fabric; at 65 °C, this was reduced to 58%, due, it was said, to the change in viscosity.

Cloth speed was said to have little effect, while increasing the load leads to diminishing returns due to the increase in the width of the nip. Changing bowl diameter or hardness can have effects depending on the resultant nip width.

The chief factor on which nip uniformity depends is deflection of the bowls under load, and ways of correcting or avoiding these are considered in detail. The requirements of mangles for water removal and for padding, and the extent to which existing and new designs of mangle meet these requirements, are discussed.

Methods of testing the performance of mangles are described in the same paper, although modern techniques – using load cells, for example – are not included.

3.2.1 Ensuring uniformity of application

For good uniformity of application, it is necessary to avoid bowl deflection due to non-uniformity of the applied load. Correction can be achieved by surface cambering, by skewing one of the bowls or by modifying the loading system.

Surface cambering

The object of surface cambering is to modify the shapes of the bowls so that, when deflection is present, the profiles of the bowls conform at the nip. The amount of camber required is best determined directly by measurement, or – less satisfactorily – by approximate calculation or by

trial and error, as is often done in industry. It is not necessary to camber both bowls even when both are deflected. Both deflections can be corrected by cambering one bowl, and it may be an advantage to camber the metal bowl, which is more or less permanent, so that the soft bowl can be ground parallel each time as it wears.

A serious limitation of surface cambering is that a particular camber can be correct only for one load. The camber has also to be applied every time the bowl is re-ground.

Skewing

If the axis of one of the bowls is skewed so that the bowl axes are no longer parallel, the bowls are wrapped round one another in the nip to a slight extent and this effect can be used to correct for deflection of straight-ground bowls. The required skew (distance between bowl axes perpendicular to original line of centres) at any point along the nip is given approximately by Eqn 3.3:

$$\text{skew} = \left[(D_1 + D_2) \Delta d \right]^{\frac{1}{2}} \quad (3.3)$$

where D_1 and D_2 = the bowl diameters

Δd = the amount of bowing with respect to the centre of the bowl face

Since the profile of the deflected bowl is almost circular, Δd is proportional to the square of the distance along the bowl face measured from the centre.

The required skew is thus proportional to this distance, which is exactly how the skew varies along the face of the bowl when it is applied by advancing the bearing at one end of the bowl and withdrawing that at the other end by the same amount. The correction for deflection by skewing is, therefore, equally correct for all points along the nip. The amount of skewing can be varied to suit the load applied and the bowl surfaces are, of course, ground parallel.

3.3 LOW WET PICK-UP

Typical measurements of pick-up in pad mangle application of chemical finishes are given in the literature. The figures given in Table 3.1 are percentages based on the weight of air-dried fabric.

Rüttiger [6] has pointed out that such levels of pick-up are unnecessarily high. He considered that application levels of 25–40% liquor pick-up could be advantageous, not only giving the opportunity for energy savings in subsequent drying, but also resulting in improvements in the finished product.

Considering energy costs, Goldstein [5] measured the energy consumption in finishing a 50/50 cotton/polyester fabric through a pad mangle, stenter, curing oven and batching unit, 60% wet pick-up, at a production speed of 3600 lb (1640 kg) per hour. The results are given in Table 3.2.

Table 3.1 Typical measurements of pick-up in pad mangle application of chemical finishes

Pick-up (%), based on the weight of air-dried fabric)	
Cotton	60–70 [3] 60–70 [4]
Cotton/polyester	55–59 [4] 60 [5]
Viscose	74–82 [4]

Table 3.2 Energy consumption in finishing a 50/50 cotton/polyester fabric, at 60% wet pick-up at a speed of 3600 lb h⁻¹ (1640 kg h⁻¹)

	Energy consumption (kcal × 10 ³ h ⁻¹)	Energy consumption (%)
Electric motors	163	12
Evaporation	628	48
Cloth heating	127	10
Air heating	359	28
Radiation losses	23	2

The total energy consumption was $1300 \text{ kcal} \times 10^3 \text{ h}^{-1}$, or 793 kcal kg^{-1} fabric, of which 48% is used in evaporation of water. Low wet pick-up methods, which can produce levels of pick-up below the range of a conventional pad mangle, can therefore yield significant energy savings. However, the need to have sufficient moisture in the fabric, to stabilise the fabric width [3,7], means that the practical minimum limit of pick-up is probably above 30%.

Potential product improvements resulting from the use of low wet pick-up techniques are considered in the next section.

3.4 UNIFORMITY OF DISTRIBUTION – CRITICAL APPLICATION VALUE

In the application of chemical finishes to textiles that depend on impregnation of an aqueous solution of the chemical, followed by removal of the water by evaporation, a high pick-up can lead to an uneven finish distribution, due to migration to the fabric surface [8]. This is illustrated in Figure 3.1 where the migration of liquor is shown to increase with the wet pick-up (WPU). Where high wet pick-up levels are used, the high rate of evaporation of moisture at the fabric surface leads to thermal migration of the liquor, concentrating the chemical finish at the fabric surfaces (that is, the face and back of the fabric) as the moisture evaporates. This leaves a lower finish level in the centre of the fabric structure.

It has been claimed that low wet pick-up finishing can lead to savings in the amount of chemical applied to the fabric. Low wet pick-up finishing has thus often been termed low add-

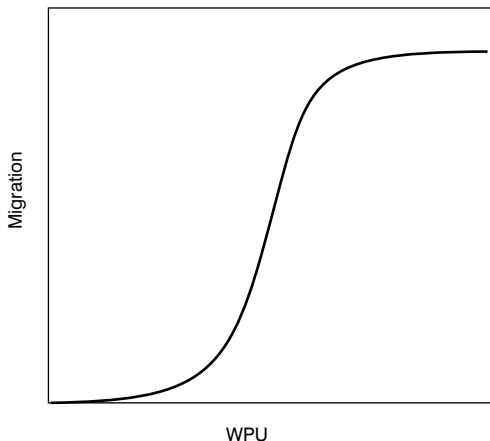


Figure 3.1 Thermal migration

on finishing, particularly in the USA, and these terms are essentially synonymous. The savings in chemicals arise from the more efficient and homogeneous distribution of the finishes to provide a higher technical performance than that obtained using a high pick-up followed by thermal migration of the finish liquor to the fabric surfaces during thermal drying.

It was considered [9] that the most promising development towards the production of 100% cotton easy-care fabrics would be to ensure that crosslinking is distributed as uniformly as possible within the fabrics and along each fibre. Such an effect appeared to be unattainable by the normal application method of dip and nip using a pad mangle, immediately followed by drying, as the conventional mangle is incapable of reducing the pick-up on cotton fabrics to a point at which migration does not occur.

Low wet pick-up application methods can be used instead of conventional padding to decrease the amount of water to be evaporated, so avoiding migration of chemical finishes to the fabric surface.

On the other hand, too low a pick-up can also result in an uneven distribution of chemical in the fabric [10], as the liquid phase is discontinuous. Heap [9] referred to these distributions as type-one and type-two non-uniformity respectively, and introduced the concept of the ‘critical add-on value’ (CAV). (This was later renamed ‘critical application value’ to avoid confusion with solids add-on.)

The CAV is defined as the lowest amount of finish liquor that can be applied to a given cotton fabric without producing a non-uniform distribution of crosslinking after drying and curing. This can be demonstrated by appropriate staining tests.

The CAV will vary according to the fibre type, the fabric construction, and the level of chemical pretreatment. If application levels below the CAV are applied then a spotty or speckled distribution of chemical finish may result, the uneven distribution being caused by the application level being not high enough to wet out and impregnate all of the fibres. In Figure 3.2 it can be seen that on cotton fabrics there is an optimum for technical performance in easy-care finishing when the low wet pick-up corresponds to the critical application value. This is the

value of wet pick-up sufficient to saturate all the fibres uniformly with the easy-care finish while avoiding migration of the finish liquor during thermal drying. In most cases the ideal fabric impregnation process would be a minimum application method that ensures that all of the fibres are wetted and impregnated uniformly with the chemical finish to leave the required add-on after drying, or drying and curing.

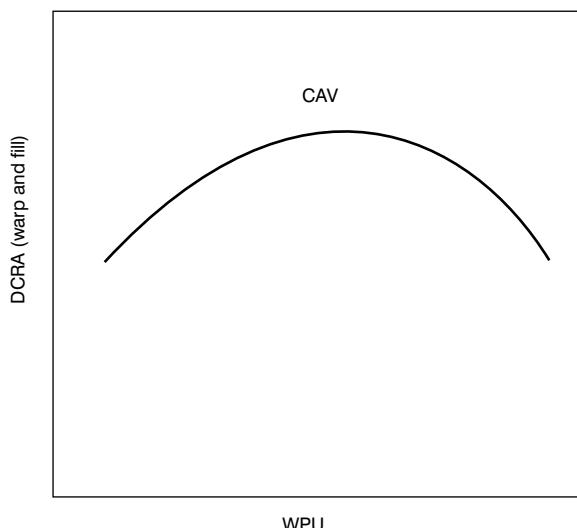


Figure 3.2 Migration vs pick-up

Hydrophilic fibres like cotton and viscose have high fibre saturation values and hence the minimum application levels (or CAV) are likely to be in the 35–45% wet pick-up range. However, hydrophobic fibres like polyester, with a fibre saturation level of only 4%, can be treated with much lower wet pick-up levels, provided that the solubility of the product being applied allows the chemical concentration and the low wet pick-up to yield the required add-on value.

The crosslinking agents used in the easy-care finishing of cotton fabrics are typically water-soluble, relatively low molecular weight compounds that readily migrate to the fabric surface during normal drying operations. It has been believed, since the early days of crease-resist finishing, that this migration should be inhibited as much as possible, to avoid the formation of excessive ‘surface resin’.

One of the earliest investigations into the effect of crosslink distribution on the properties of easy-care finished cotton fabrics was carried out by Shippee and Gagliardi [10]. Face-to-back differential distribution was produced by knife-coating a thickened solution of resin mix, and poisoning of the surface catalyst then effected by a spray or second coating operation using an alkaline reagent. Results showed that improvements in abrasion resistance were obtained for a given level of crease resistance, and a staining test using a direct blue dye showed that the crosslinks in the treated fabric were preferentially located in the interior of the fabric structure.

Aboul-Fetouh and Miles [11] investigated the effects obtained when drying was interrupted at about 30% regain, and there was a delay before the resumption of drying, so that back-diffusion was allowed to take place, leading to a more uniform distribution of the crosslinks within the fabric cross-section. It was found that significant improvements in crease recovery could be obtained, with relatively small reductions in strength and abrasion resistance. This technique was repeated in work carried out at TNO in Holland, where a staining technique was developed, using a mixture of CI Direct Blue 1 and picric acid [12], which confirmed that a uniform distribution was obtained, and indicated that below about 30% regain the effect of migration is practically eliminated. In later work at TNO, techniques were devised for the low-level application of crosslinking solutions, and the potential of these so-called 'low add-on' (LAO) methods for improving the balance of properties of treated fabrics was confirmed [13].

Other techniques for examining the distribution of crosslinks in a treated fabric were devised by Cooper and Roberts [14], Kokot and coworkers [15,16], and de Boer [17].

3.5 LOW WET PICK-UP APPLICATION METHODS

Two main types of low wet pick-up application methods have been developed. In the first type, the fabric is fully saturated with the finish liquor in the normal manner and then the excess liquor in the capillary spaces (or interstices) of the fabric is removed by a suitable method. Methods used for fabric de-watering (that is, mechanical drying) are widely used such as porous bowls (for example, Roberto bowl), or vacuum extraction (suction slot hydroextraction) or by blowing compressed air through the fabric. In the second type of low wet pick-up applicator, an exact quantity of the finish liquor is uniformly applied to the fabric using a lick-roller (kiss-roll), spray or foam application technique. In all of the saturation-removal methods and in the spray and foam application methods, any excess liquor removed from the fabric may be recovered and re-used, provided that only one finish liquor is involved. Where different finishes may be applied to the face and back of a fabric using spray or foam application techniques, mixing of the liquors may occur, preventing recycling of the liquor.

Both types of low wet pick-up application method offer energy savings of 30–40% in subsequent thermal drying, with the drying time being decreased by 25–50% or the drying speed increased by 20–66% according to the specific circumstances of the application method. As less water is used, costs for raw water treatment are decreased (for example, chemical softening). Decreasing the wet pick-up may allow treatment temperatures to be decreased and/or processing speeds to be increased without deterioration in the quality of the finished fabric. Expensive bath drops (for example, the full pad trough left at the end of a production run) may also be avoided. In some cases processing may be simplified – for example, by the elimination of infrared pre-drying.

The challenge of potential savings in energy costs proved attractive for machinery builders and research laboratories, and led to several new developments in application techniques. A comprehensive review of these was produced by the Textile Institute in 1986 [18].

Techniques included super-efficient squeezing, vacuum extraction, or the use of air-jets to

remove excess liquor – or truly low level application methods controlled by engraved rollers, lick-rollers, wet-to-dry cloth transfer, spraying and the use of foam.

3.6 SATURATION-REMOVAL METHODS

3.6.1 Porous bowl techniques

Conventional padding techniques utilise rubber-covered bowls (or rollers). However, porous bowls can be constructed from a mass of fibres with each fibre being coated with a thin film of rubber of microscopic thickness and then processed under carefully controlled heat and pressure to give a resilient and durable microporous structure. The use of Roberto bowls (Modern Rollers Ltd.) of this composition for low wet pick-up application of chemical finishes can decrease the wet pick-up on a woven cotton fabric to just under 50% for a Roberto bowl/steel bowl combination. This is achieved by the powerful squeezing action in the nip of the pad mangle together with a capillary suction effect. This is shown in Figure 3.3.

The fabric saturated with pad liquor is squeezed to express excess liquor. As the fabric exits from the nip, liquor from the fabric is sucked within the capillaries of the microporous bowl. The capillaries have been previously compressed in their passage through the nip under pressure, to remove entrained air and liquid.

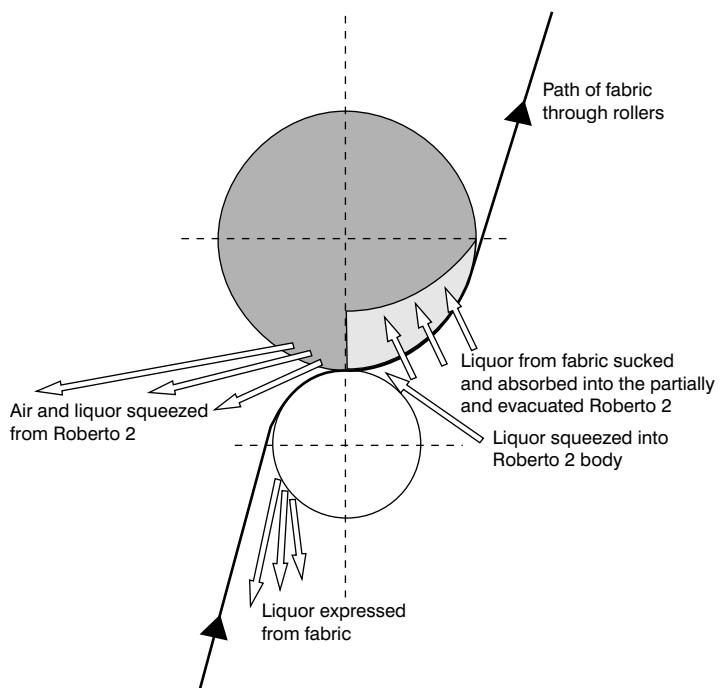


Figure 3.3 Principle of the Roberto 2 squeezing system

This compression and recovery of the highly elastic microporous bowl construction thus removes more liquor from the fabric to yield a lower wet pick-up than a conventional rubber bowl/steel bowl combination. Prestech bowls operate on the same principle of microporous construction.

Roberto bowls can be made to fit any existing pad mangle and the bowls are resistant to most chemicals except strong mineral acids and oxidising agents. The application of certain polymer finishes can, over a period, tend to clog the pores of a Roberto bowl. Where this occurs near the bowl surface it can be removed by re-facing and the bowl can be used again. The introduction of the Roberto 2 bowl is claimed to decrease the mangle expression (that is, the wet pick-up) by a further 12% on average compared with the original Roberto bowl, running against a steel bowl. Typical values of the mangle expression obtained by various bowl combinations in de-watering trials at 50 m min^{-1} , 54 kg cm^{-1} load, are given in Table 3.3.

3.6.2 VACUUM EXTRACTION [19,20]

Vacuum extraction using vacuum slot extractors (also termed suction slot extractors) is now a common method for applying chemical finishes to all types of fabric at open-width. However, the fabric must be permeable to air and the method is less effective on thick fabrics. The method is similarly unsuited to fabrics with an open construction that will not generate or support a high vacuum. Like many other saturation-removal methods the method is most effective on thin non-absorbent synthetic fibre fabrics such as polyester weft-knitted fabric on which wet pick-up values as low as 10–20% may be obtained. On hydrophilic natural fibre fabrics the method is less effective. On cotton fabrics, for example, the wet pick-up may range from 40–50%.

Table 3.3 Mangle expression (wet pick-up) obtained by various bowl combinations in de-watering trials at 50 m min^{-1} , 54 kg cm^{-1} load

	Roberto 2	Original Roberto	Rubber	Reduction in pick-up
100% Cotton (knitted)	55%	59%	78%	29%
100% Cotton (knitted-terry)	62%	69%	83%	25%
100% Wool (woven)	60%	66%	80%	25%
Cotton/polyester (40/60)	34%	39%	51%	33%
100% Polyester (knitted)	37%	47%	73%	49%
100% Cotton (toweling)	63%	68%	78%	19%
100% Cotton (120 g m^{-2})	63%	71%	79%	20%
100% Cotton (200 g m^{-2})	58%	64%	72%	19%
100% Cotton (70 g m^{-2})	66%	72%	91%	27%
Brushed acrylic	36%	52%	75%	52%
Microfibre	30%	35%	46%	34%
Wool/polyester (45/55)	37%	44%	57%	35%

The principle of the method involves passing the fabric into the pad bath and then over a vacuum slot to remove most of the pad liquor. On modern systems the extracted liquor is recirculated back to the pad bath. The applicator design is such that the fabric is held continuously in contact with the slot for optimum removal of the liquid. The vacuum slot design may be a straight slot or a herring-bone pattern of single or double rows. The design of the vacuum slot has to be engineered to take into account factors such as slot width, slot configuration and the vacuum applied. In addition, the fabric speed, fabric thickness and air permeability, and the fibre type are also of importance.

It has been demonstrated that for the normal saturation pick-up range the vacuum slot method can give a uniform low wet pick-up irrespective of minor variations in the saturation pick-up value. Thus the vacuum extraction step will correct any unlevelness in padding. The wet pick-up is dependent upon the slot width and design, fabric speed and vacuum pressure attained. Highly efficient edge sealing devices are used to maintain the vacuum pressure, and prevent a drop in vacuum pressure at the fabric selvedges. This would decrease the airflow in these regions and increase the wet pick-up value.

Synthetic fibre fabrics that exhibit low water saturation values can be very effectively de-watered to low wet pick-up values because the pad liquor continuum within the inter-fibre and inter-yarn capillaries in the fabric structure can be rapidly emptied by a single passage over the vacuum slot. The small amount of capillary liquid left in the structure does not then form a continuum and is present as pendular liquid droplets, or as menisci at points of fibre contact or crossovers. Thus the volume of liquid removed by a second vacuum slot is usually very small, the airflow passing mainly through the highly permeable fabric structure.

An increase in vacuum pressure can usually be attained only at the expense of higher energy costs because of the larger electric motors required for driving liquid-ring, positive displacement or stage-turbine pumps. Pump sizing criteria have been discussed by Adamzyk. A lower wet pick-up value can be attained by increasing the temperature of the pad liquor. This decreases

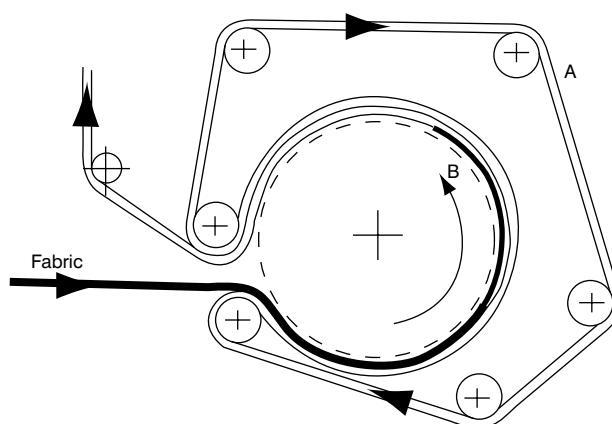


Figure 3.4 Monforts Matex-Vac system [18]

the viscosity of the pad liquor and should enhance the removal rate of the liquor from the fabric. However, not all chemical finishes can be applied in this way, and heating the pad liquor also increases the energy consumption, thereby decreasing the energy savings.

A vacuum extraction system operating on an alternative machine arrangement is the Matex-Vac system of Monforts [21]. In the Matex-Vac (Figure 3.4), wet padded fabric is fed in between an endless impermeable blanket (A) and a perforated drum (B), which is covered with an absorbent non-woven wrapper fabric. The liquor is absorbed by the wrapper fabric by capillary forces. Before the fabric emerges from the machine, the liquor is effectively extracted from the wrapper fabric by a vacuum operating within one segment of the perforated rotating drum. A similar system from Mohr consisting of an impregnator, vacuum extractor system and recirculation system in one complete unit has also been used.

Suction-roller extractors or vacuum-roller extractors have also been manufactured by Maier and Gaston County. The wet fabric is guided over a perforated roller with a vacuum slot inside the roller. The fabric distortion sometimes experienced by pulling a fabric across a vacuum slot is thus avoided by rotating the perforated roller with the fabric. Liquor extraction has been claimed to be more efficient than with conventional vacuum slot extractors, yielding wet pick-up values of 35–45% on cotton print fabrics and as low as 10–20% on knitted polyester fabrics.

A major advantage for liquor application to dry fabric (wet-on-dry application) is that some of the treatment liquor containing chemical finishes and so on can be recovered and recirculated to the pad bath, decreasing the chemical consumption and cost of the process. However, with some chemicals used in finishing there can be problems arising from polymerisation of the finish within the system. In addition, application of finish liquors to some types of non-woven fabrics may lead to excessive removal of fibre from the fabric. Lint filters operating underneath the vacuum slot may be useful in this respect especially for other fabric constructions containing staple fibres where a loss of short fibres may also be expected.

3.6.3 Air-jet ejectors

Air-jet ejectors work on a broadly similar principle to vacuum extraction, using compressed air to remove the excess liquor from the fabric. The advantage over vacuum extraction is that the pressure differential can be appreciably higher than that operating in vacuum extractors. In vacuum extraction this is limited to a maximum vacuum pressure of one bar, and in practice is always significantly less than the maximum value. By contrast, pneumatic ejectors have been operated in the 2–6 bar pressure range and consequently the method can be applied to fabrics with a very low air permeability.

However, the use of compressed air is more expensive than vacuum extraction and the advantage of using a higher pressure differential does not result in a substantial improvement in attaining an even lower wet pick-up value. Moreover, the energy consumption for attaining higher pressure differentials rises sharply with increased operating pressure. Another factor is that in general the noise levels using air-jet ejectors are high and consequently protective hoods may be required to absorb the sound to bring it below the acceptable working level of 86 dB. For

air-jet ejectors it is possible to recirculate the excess liquor removed from the fabric back to the application bath.

As energy costs have risen, air-jet ejectors have been used less frequently in comparison with vacuum slot extractors, which are widely used both for de-watering and for low wet pick-up liquor application. As with vacuum extraction, air-jet ejectors are more effective in removing liquor from hydrophobic synthetic fibre fabrics than from natural fibre fabrics. In the Pletec float-on-air system (Figure 3.5) the compressed air at high pressure is forced through a slit (A) into the wet fabric moving between two plates. This removes the excess liquor (C), which can be recirculated. The gap between the plates (B) could be adjusted according to the fabric thickness and on cotton and cotton-blend fabrics the wet pick-up range is as low as 40–50%.

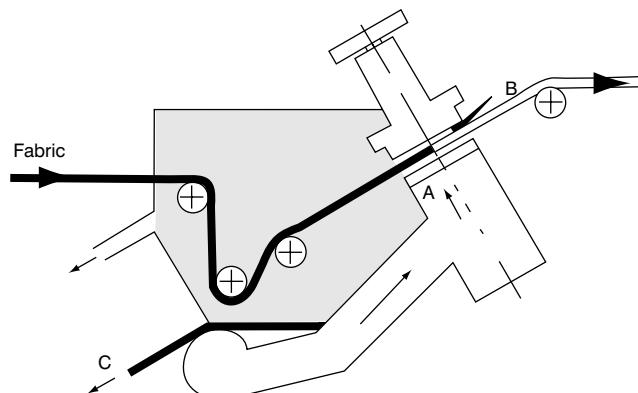


Figure 3.5 Pletec ejector [18]

Other systems operating on compressed air, like the Hikosaka Roller-Jet Squeezer have been described for liquor application but are more often used for de-watering fabrics prior to drying. The Brugman Machnozzle [22] operates on a slightly different principle using high pressure steam instead of air to remove excess liquor from the fabric. Weft-knitted fabrics or dimensionally unstable woven fabrics are more likely to be distorted where high pressure differentials are used.

3.6.4 Transfer padding – the Pfersee QS system

Transfer padding techniques take place in two stages; first the finish liquor is padded conventionally onto a suitable medium, and secondly the wet material is squeezed in a second nip in contact with the dry fabric for processing, so that some of the liquor is transferred. Two independent developments along these lines took place at about the same time.

In the Pfersee ‘Quetsch–Saugtechnik’ (squeeze–suck technique) [4], the conventionally impregnated fabric is passed into a second nip in contact with the incoming dry fabric, so that some of the padded-on liquor is removed from the fabric before drying. The second development was the loop transfer system, described in Section 3.7.1.

The Pfersee Quetsch-Saugtechnik, known as the QS technique, was developed by Rössler and Pusch and is ingenious in that it uses the fabric that is treated as its own transfer loop. A conventional three-bowl pad mangle is used (Figure 3.6), the incoming dry fabric being first partly pre-wetted during the final squeeze between rollers A and B in which it is in contact with the impregnated fabric. After passage over guide rollers, the partly wetted fabric is completely impregnated in the liquor bath. The wet fabric is now squeezed in the nip between rollers B and C to remove excess liquor and then passes again into the final nip between rollers A and B transferring more liquor into the incoming dry fabric. Within Europe it has been claimed to yield wet pick-up levels in the range 15–40%, although higher levels in the 60–75% range have been reported in studies in the USA.

Pfersee emphasised the energy savings, which could be obtained by the use of the QS technique. Table 3.4 shows typical reductions in pick-up on various fabrics. It has been estimated from these pick-up measurements that stenter speeds could be raised by 24–60%.

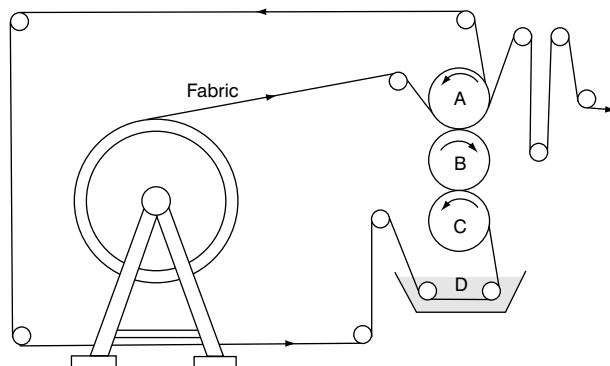


Figure 3.6 Pfersee 'Quetsch-Saugtechnik' (squeeze-suck technique) [4,18]

Table 3.4 Typical reductions in pick-up obtained by the use of the Pfersee Quetsch-Saugtechnik (QS technique) [4]

Fabric	Weight (g m^{-2})	Normal pad (%)	QS technique (%)
Cotton poplin	120	61	41
Cotton/polynosic poplin	131	75	54
Cotton/polyester 50/50 white	108	55	34
Cotton/polyester 50/50 dyed	108	59	36
Coat poplin cotton/polyester	232	58	45
Bed sheeting cotton/polynosic	175	77	61
Gaberdine cotton/viscose 70/30	265	65	43
Pocket-lining viscose	180	82	66
Decorative fabric cotton	310	67	48
Decorative fabric viscose	325	74	55

3.7 TOPICAL APPLICATION METHODS

Topical application methods are fundamentally different from the saturation-removal or expression methods. In topical application methods the liquor is transferred directly to the fabric or alternatively by means of an indirect transfer method. Typical topical application methods that have used commercially to provide a low wet pick-up application for textile finishes include:

- (1) loop transfer systems
- (2) engraved rollers
- (3) nip padding system
- (4) lick-rollers (kiss-rollers)
- (5) spray systems.

It is important to note that in all topical application systems a uniform distribution of the applied liquor can only be attained if the fabric is thoroughly prepared – that is, absorbent and wettable. The applied liquor must be able to wet and wick through the fabric structure in a uniform manner.

3.7.1 Loop transfer system

An alternative transfer padding technique, contrasting with the Pfersee method, is typified by the IIC system [23], in which a continuous loop of material is padded conventionally and squeezed in contact with the fabric for processing. The two materials are not necessarily the same, although the loop fabric should of course be at least as wide as the fabric for treatment. This is an example of a topical application method.

Loop transfer systems normally incorporate a loop fabric that picks up the finish liquor from the bath and then transfers the liquor to the fabric to be treated in a two-roller or three-roller machine arrangement. In the two-roller system (Figure 3.7(a)) the fabric loop (A) is passed continuously through the finish liquor and passed upwards into the nip formed between the top and bottom rollers (B and C). The fabric to be treated is squeezed against the loop fabric in the nip zone and some of the liquor is transferred into the fabric giving a wet pick-up typically in the range 15–40%. A roller bar may be run against the loop to decrease the amount of liquor passing into the transfer zone if a lower wet pick-up value is required.

A more sophisticated arrangement is offered by the three-roller loop transfer system (Figure 3.7(b)). Here the loop fabric (A) picks up the finish liquor as before and is squeezed between rollers B and C to control the wet pick-up in the loop. The loop then passes to the second nip formed between rollers C and D where a controlled amount of liquor is transferred from the loop into the fabric to be treated. The amount of liquor to be transferred can be decreased by using wiper or roller bars on the loop fabric and decreasing the pressure in the second nip. Increasing the pressure in the latter can increase the wet pick-up level, and values in the range 10–50% have been achieved on cotton and cotton/polyester fabrics.

Practical problems associated with the loop transfer system involve the necessity to use a

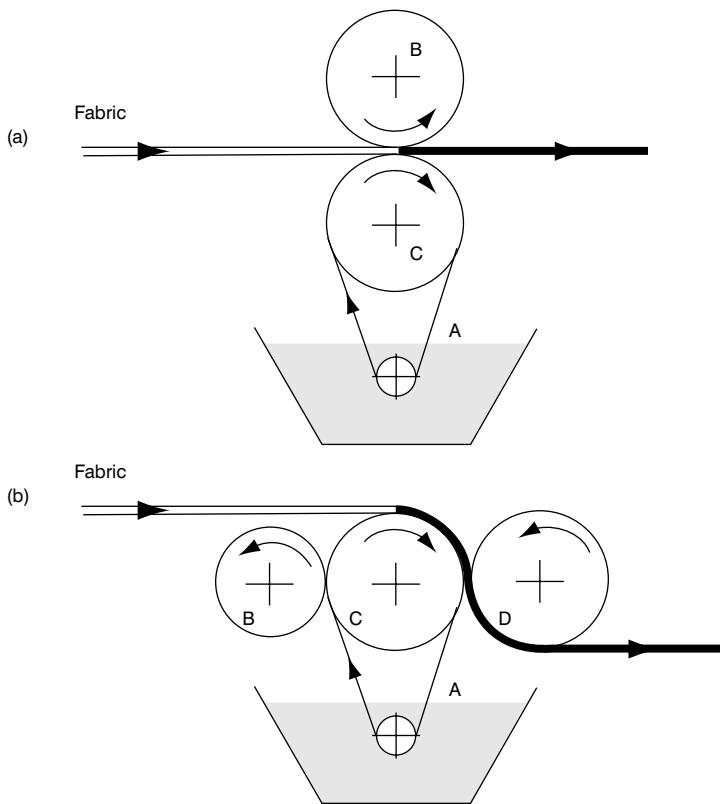


Figure 3.7 Loop transfer: (a) two and (b) three rollers [18]

seamless and dimensionally stable loop fabric that does not wear or become substantially compressed. Furthermore the finish chemicals must not build up within the loop fabric and the loop requires washing if the composition of the finish bath is changed for the next production run. The loop fabric must be maintained under a uniform tension to ensure that it does not wander from side to side of the rollers.

Normally it would be expected that most of the liquor would be retained on the padded material, so that the transfer loop technique would produce lower pick-ups than the QS treatment. This was found in trials carried out by Harper [24], who obtained pick-ups of 18–39% on cotton fabrics processed by this method.

3.7.2 Lick-roller (kiss-roller) applicators

The lick-roller, also known as the kiss-roller (USA) or slop-padder, is one of the simplest methods of liquor application, consisting in its basic form of a single roller rotating in the liquor. The fabric passes over the top surface of the roller, so that the pick-up depends on the degree of wetting of the roller surface and the absorbency of the fabric.

A form of the lick-roller, used for back-filling (one-sided application) mainly with starch, is known as the 'Betty Dodd'. The pick-up is often controlled by means of doctor blades, which remove any excess from the fabric surface.

The fabric may alternatively be carried through the liquor by the roller, and if the roller surface is cleaned by means of a doctor blade, the application may again be essentially one-sided. This type of back-filling machine is known as a 'Tommy Dodd'.

Lick-rollers have been widely used to apply a stiffening agent to the back of corduroy fabric while maintaining a soft pile on the face side. Three typical lick-roller systems that have been developed are illustrated in Figure 3.8. In the single roller system, Figure 3.8(a), a pad roller is partly immersed in the liquor bath and the film of liquor adhering to the roller surface is conveyed upwards, being doctored by a doctor blade to the requisite film thickness. Dry fabric is conveyed and pressed at an angle in contact with the surface of the liquor film, which wets the fibres and wicks into the fabric structure.

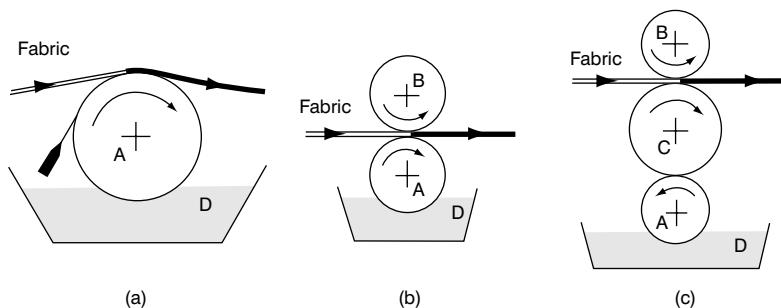


Figure 3.8 Three types of lick roller [18]

In the two-roller system, Figure 3.8(b), the top roller exerts pressure on the dry fabric to force the liquor film on the lick-roller into the fabric. Alternatively, a three-bowl system may be employed as in Figure 3.8(c). Here, the liquor on the kiss-roller (A) is transferred by the intermediate roller (C) to the fabric in the nip formed with the top roller (B). Lick-roller systems have been widely used in coating and the single lick-roller system can achieve a low wet pick-up of about 25% on woven cotton fabric.

By adding sophisticated control devices to the traditional lick-roller design, the Swiss research institute Triatex developed it into an application technique capable of producing a wide range of pick-up levels [25,26].

Figure 3.9 shows the Triatex MA (Minimum Application) system, now manufactured by Monforts. The lick-roller (A) rotates in the liquor bath (B) and moves in the same direction as the fabric passage. The moisture content in the fabric before and after passage over the lick-roller is monitored by two β -gauges (C). These fire a constant stream of electrons into the running fabric, and the intensity of the electron beam passing through the fabric is decreased as the fabric mass per unit area increases – for example, as the wet pick-up value increases.

Thus the difference between the readings on the β -gauges provides a measure of the wet

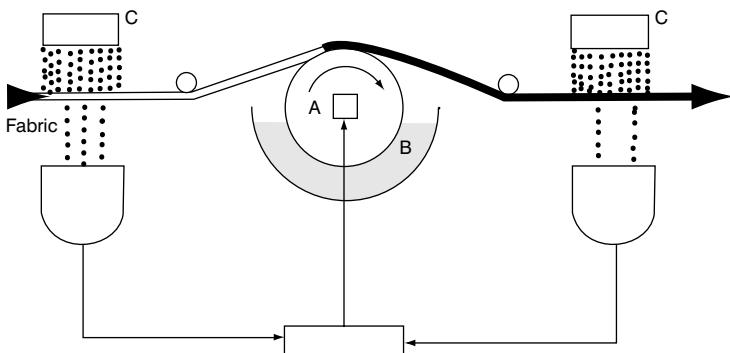


Figure 3.9 Triatex MA (Minimum Application) system [18]

pick-up value and this is used to control the speed of rotation of the lick-roller relative to the fabric speed, thereby controlling the amount of finish liquor applied to the fabric.

The use of the Triatex MA system can impart low wet pick-up values in the range 10–55% on cotton fabric, with 35% reported to be the optimum pick-up for uniform application. However, the fabric must be highly absorbent, and thus must be thoroughly scoured to ensure that satisfactory wetting and wicking in a one-sided application leads to the finish distribution being uniform on both the face and the back of the fabric. Bone-dry fabrics are difficult to treat on lick-roller systems and should be conditioned to improve fabric absorbency. One restriction can sometimes be that selected chemicals, finishes, dispersions and emulsions may not enable a uniform film of low viscosity to be generated on the lick-roller surface. In such cases it is necessary to add an additional chemical that will ensure that the appropriate film formation is attained.

Several studies on cotton fabrics showed that easy-care finishes applied by means of the Triatex MA machine, with pick-up levels below those attainable with a pad mangle, could have a better balance of properties; in particular, abrasion resistance was better at a given level of crease resistance [26–29].

Application of the liquor to both sides of the fabric in lick-roller systems normally requires a double lick-roller set-up. This approach allows a different chemical finish to be applied to the face and back of the fabric, and could be accomplished using two Triatex MA applicators operating a sequential treatment to the face and the back of the fabric respectively.

The control system used on the Triatex MA equipment is expensive. A similar lick-roller applicator with a different control system principle has been developed by the Research Institute for Textile Technology in Chemnitz. This is the Fimatron machine, marketed by Küsters Zittauer [30,31].

The Fimatron technique was developed primarily for wet-on-wet applications (Section 3.12), but can be used on dry fabrics; back-filling is also possible.

The control method employed by the Fimatron technique is distinguished by the fact that liquor application is automatically controlled as a function of fabric speed, according to a

defined relationship incorporating the parameters 'liquor viscosity', 'nominal add-on' and 'fabric area weight', without the fabric area weight and/or the delivered or applied liquor volume having to be measured.

Eqns 3.4 and 3.5 are used in an electronic circuit constituting the core of the control unit.

$$v_u = 1/k \cdot \ln(1 + C_s \cdot m_F \cdot b \cdot v_w / Q_0) \quad \text{when } v_u < 15 \text{ m min}^{-1} \quad (3.4)$$

$$v_u = C_s \cdot m_F \cdot b \cdot v_w / m + a / m \quad \text{when } v_u > 15 \text{ m min}^{-1} \quad (3.5)$$

where v_u = circumferential speed of lick-roller

C_s = nominal add-on

m_F = fabric weight per unit area

b = fabric width

v_w = fabric speed

Q_0, k, m, a are quantities of which the values for any ranges of m, v_w and viscosity are calculated according to the experimentally determined functional relationship.

It is also possible for the control of the lick-roller speed to be computerised.

3.7.3 Engraved roller application system [32,33]

A typical engraved roller liquor application system is illustrated in Figure 3.10. The engraved roller (A) rotates in the liquor bath (D), in which the cavities engraved on the roller surface become filled with the liquor. The excess liquor on the engraved roller surface is removed by an oscillating doctor blade (C). The remaining liquor contained in the cavities is then transferred from the engraved roller into the dry fabric, being forced into the fabric at the nip by the pressure of the rubber roller (B).

Critical factors in the operation of this process are the design and construction of the engraved roller because the volume of liquor delivered to the fabric per unit area is dependent upon the surface of the engraved roller, the number of cavities and their volume. Thus a specific

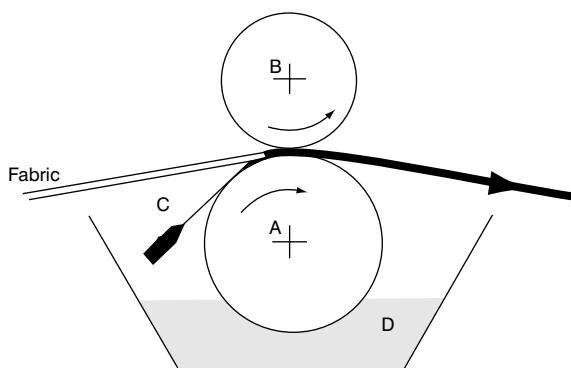


Figure 3.10 Engraved roller application system [18]

engraved roller will always deliver the same volume of liquor per unit area of the fabric. This is a disadvantage where the fabric mass per unit area is variable due to the processing requirements for different fabric types and mass per unit area to be finished. In order to achieve the same wet pick-up value on different fabrics it is necessary to use different engraved rollers with different cavity structures to deliver the requisite amount of liquid.

Engraved rollers are thus useful in large finishing plants where the same type of fabric is continually and continuously processed – for example, cotton denim. In practice, some problems can be experienced with clogging of the cavities in the engraved roller surface. Another problem relates to the application of high viscosity liquors where it is possible that some of the cavities are not completely emptied so that not all the liquor may be transferred to the fabric. Clearly the design of the cavities has to be engineered to provide the appropriate low wet pick-up value for the fabrics to be processed. The application of liquor to one side of the fabric must be followed by migration of the liquor throughout the fabric structure. Thus the chemical pretreatment of the fabric must be thorough to ensure satisfactory wetting and wicking of the applied liquor.

3.7.4 Nip padding

In nip padding, the liquor to be applied is maintained in a low volume trough, usually contoured to the dimensions of the furnishing or lick-roller. The liquor is picked up as a film of liquid on the surface of the lick-roller, which is doctored, in the Goller Eco-Pad system, by a magnetically-controlled doctor roller. The fabric to be treated is brought into contact with the film of liquor on the lick-roller surface and the liquor is transferred into the fabric under the pressure exerted by the pressure roller. The very low volume of the trough leads to less waste of chemicals and water at the end of a production run. A wet pick-up as low as 30–40% can be obtained on fabrics of 140 g m^{-2} , and this system may also be used for wet-on-wet applications.

3.7.5 Curved blade applicator

The West Point CBA system [34,35] has been used in the USA for application of chemical finishes using a topical low wet pick-up method. The principle of the machine is illustrated in Figure 3.11. The finish liquor is pumped into a manifold and emerges through a porous plastic foam to form a small reservoir of finish liquor that overflows down a curved blade forming the shape of a catenary. The uniform film of liquor flows over the surface of the blade until it reaches the tip of the curved blade, which is in contact with the fabric. The pressure of the tip and the angled path of the fabric ensure that the liquor is absorbed by the fabric. One-sided or two-sided liquor application is possible according to the machine design. The latter requires two curved blades each operating against a different side of the fabric.

3.8 SPRAY APPLICATION SYSTEMS [36]

Finish liquors may be sprayed in controlled quantities onto fabrics to give a low wet pick-up. In general, the liquor is sprayed through a manifold with spray nozzles. The concentration of the

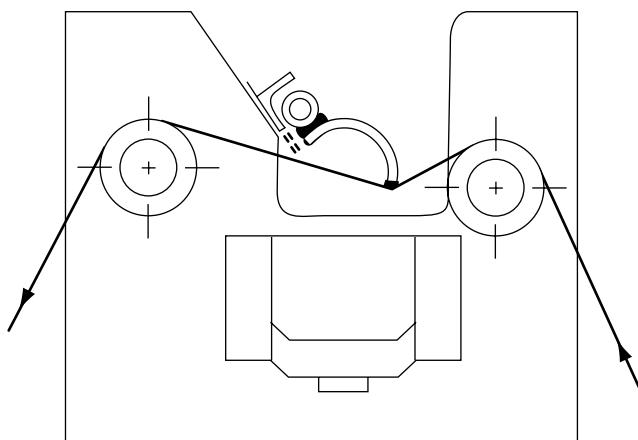


Figure 3.11 West Point Curved Blade Applicator (CBA) applicator unit [35]

liquor, the diameter of the nozzles and the pressure inside the manifold essentially control the amount of chemical deposited. Overlapping of the sprays can lead to an uneven distribution of the chemicals and careful control of the spray system is therefore necessary. Spray application systems are also widely used for conditioning fabric after overdrying.

An alternative spray application system is the WEKO applicator (Weitmann and Konrad) [37]. The liquor is pumped from a tank through an accurate metering device to the individual rotors, which are located in the rotor carrier. The rotors are run at about 5000 r min^{-1} , each rotor spraying a defined quantity of liquor in fine droplet form onto the moving fabric. A uniform spray application is ensured through the use of screens that control the application area such that all the rotors combine into one continuous spray band. Additional rotor carriers may be used to provide higher wet pick-up levels, which may vary normally for one rotor carrier between 10 and 30% depending upon the fabric mass per unit area. If additional rotor carriers are used either one or both sides of the fabric may be sprayed. Thus a different chemical finish may be applied to each side of the fabric.

Farmer Norton developed the spinning disc principle in their SD Liquid Applicator, illustrated in Figure 3.12. The fabric is pulled through the SD applicator by some other drive system – for example, a stenter drive system, by locating the SD applicator in front of the stenter. The fabric is passed in an N-shaped arrangement past two banks of revolving discs or rotors. The finish liquor is pumped and metered into the centres of the discs, which rotate at 3500 r min^{-1} and are spaced across the machine width. The centrifugal force disperses the liquor in the form of a fine fog of droplets, which is sprayed onto the fabric. Adjustable plates or baffles are used to control the direction of the spray, and the fabric may be sprayed on one side, or simultaneously on both sides. If only one finish liquor is used to spray the fabric, any excess liquor may drain to the bottom of the machine where it may be recycled.

In the Brückner Rotta-Jet spray application system, the wet or dry fabric is passed into an enclosed plastic unit. Here the fabric is charged through the action of a high electrostatic field.

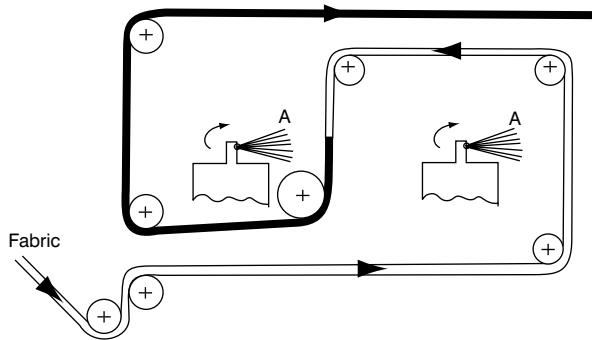


Figure 3.12 Farmer Norton SD applicator [18] (Farmer Norton products are now marketed by Parex-Mather)

The finish liquor is rapidly taken up by the charged fabric when it is sprayed either on one side or both sides by banks of high-energy spray nozzles.

In the USA, the Burlington Spraymiser system was developed in separate versions for open-width and for tubular fabric treatment respectively. Each spray nozzle is individually adjustable, a number of nozzles being mounted in a frame, with the spray controlled to prevent overlapping. The fabric is passed through a stainless steel chamber and may be sprayed either on one or both sides of the fabric to yield a wet pick-up value in the 18–45% range.

The MUWA Spray system (Mutschink) may be used for moisture conditioning or finish application and consists of an open mesh rotary screen that rotates in a small bath of liquor. A horizontal blade forces liquor into the open mesh of the screen, filling the holes of the mesh with liquor. Compressed air is supplied within a central supply tube and released into a larger pressure tube to be jetted through an orifice. The air blows the liquor in the mesh of the rotating screen as a fine spray against a moving fabric, and the wet pick-up can be controlled by the rotational speed of the rotary screen, the mesh size and the viscosity of the liquor. The spray of liquor droplets can be adjusted to the width of the fabric and the speed and size of the droplets are dependent upon the air pressure in the jet. The machine may be supplied in an open or fully enclosed construction with a manual or with an automated control system. The temperature of the liquor may also be controlled.

3.9 FOAM APPLICATION METHODS

The technology of treating textile materials in a foam as opposed to water probably commenced round 1900 for degumming silk and dyeing cotton cops. However, the advantages of foam processing did not become important until the early 1970s when the price of oil rose dramatically and energy costs in textile finishing increased rapidly. A major impetus was given to foam processing by the introduction of the Sancowad batch foam dyeing process of Sandoz in 1971 [38]. However, the major developments in foam processing have been concerned principally with continuous open-width finishing of textile fabrics, because the use of a foam enables fabrics

to be processed at a low wet pick-up, with considerable savings in water and energy consumption. As much as 95% of the water normally used to apply finishes to fabrics may be replaced by air, markedly decreasing drying costs.

As a result of developments in the early 1980s, the number of machine makers offering foam equipment and foam finishing machinery at ITMA (International Textile Machinery and Accessories exhibition) increased from two in 1979 up to more than 30 in 1983. Since ITMA '83 interest in foam finishing has declined with the rise of improved saturation-removal methods such as vacuum extraction. Nevertheless, practically all types of chemical finish can be applied to textiles in a foam medium provided that a suitable foam can be produced.

3.9.1 Foam structure and properties

A foam is an agglomeration of gas bubbles separated from each other by thin liquid films. It should be noted that most pure liquids do not foam and that the foaming ability is usually correlated with the surface activity of a solute dissolved in the liquid. Even liquids of similar chemical type and surface tension do not usually form a foam when mixed together. Persistent foams only occur with solutes that markedly lower the surface tension of a liquid, such as water, in dilute solution.

The conditions under which a foam may be generated and delivered to the point of application require close control to obtain uniform application to textile fabrics, both across the fabric width, and also continuously during the production run. Depending upon the fibre substrate to be treated and the foam application system, the foam must possess certain characteristics, and these differ especially according to the foam application system. Of particular importance are the foam stability, foam density (blow ratio), foam viscosity and bubble diameter.

Foam stability

When foam is first generated, the bubbles are almost spherical although slightly distorted by the effects of gravity. However, the foams used in textile finishing are unstable or metastable so that disturbing influences can lead to foam collapse. Small bubbles collapse to form larger bubble diameters and lead to the formation of more or less distorted polyhedral-shaped bubbles. Disturbances such as vibration, draughts, evaporation, radiant heat, temperature differences, dust and other impurities may hasten the collapse of the foam. The thin liquid films between the bubbles are termed lamellae.

When air is introduced into a dilute solution of a soap or a synthetic detergent, and the air/liquid mixture is mixed vigorously to form a dispersion of air bubbles to create a foam, the surface area of the liquid is markedly increased. Thus the Gibbs' Free Energy of the system is increased because it is proportional to the surface energy, σ , and the change in area ΔA , viz Eqn 3.6.

$$\Delta G = \sigma \cdot \Delta A \quad (3.6)$$

The surfactant molecules transfer from the bulk of the solution to orient at the newly formed liquid surfaces such that the hydrophilic head of the surfactant orients towards the water and the hydrophobic tail orients towards the air. Thus there is an energy balance in the foam. The Gibbs' free energy of the system decreases as the foam collapses, which decreases the surface area. However the transfer of surfactant molecules from the air back into the bulk of the liquid increases the free energy of the system.

Thus all foams are thermodynamically unstable and with time should collapse to the thermodynamically stable state – that is, collapse to the bulk liquid with the minimum surface area – the unfoamed state. The foams used in textile finishing must be appropriate to the substrate and the application system. If a foam is too unstable it may prematurely collapse, whereas if it is too stable it may be difficult to obtain uniform collapse of the foam through the fabric. The foams used in textile finishing are generally of the metastable type that have a half-life period ($t_{50\%}$) of between 30 and 45 minutes. The half-life period is the time in which 50% of the liquid volume contained in a foam has been drained. The shorter the half-life period, the lower the stability of the foam.

The bubbles of a gas such as air dispersed in a liquid are continuously in a dynamic state, ever changing and moving due to Brownian motion. Once a foam is generated, drainage of the liquid takes place leading to the formation of thinner films and to the discharge of excess liquid at the border, which is then drained down between undamaged bubbles. If three bubbles are joined, the three separating films meet to give a small triangular column of liquid known as Plateau's Border (Figure 3.13).

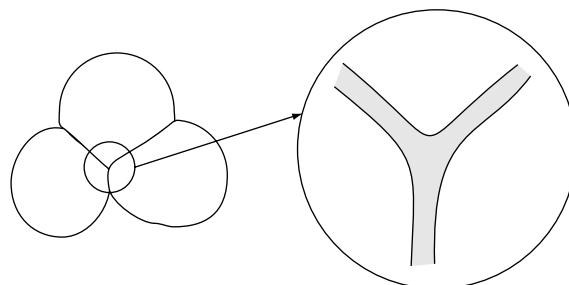


Figure 3.13 Plateau's border between three joined bubbles

The liquid in the border channel is at a lower pressure than that in the body of the film, and because of this pressure difference film thinning takes place. Drainage of the liquid leads to thinning of the foam lamellae and eventually this leads to random rupture of the film throughout the foam. In practice, foam drainage is caused by four simultaneous processes:

- (1) rearrangement of the films or lamellae between bubbles;
- (2) drainage of the lamellae
 - (a) by gravitational force
 - (b) by suction at the Plateau's borders
- (3) diffusion of gas through the lamellae;
- (4) bursting of the bubbles.

In most foam finishing systems a primary cause of foam drainage is the deliberate collapse of the foam usually by hot air drying, which bursts the bubbles.

Foam stabilisation is usually achieved by increasing the viscosity of the liquid in the walls of the bubbles to decrease the rate of thinning. Additives such as xanthan gum, hydroxyethyl cellulose and other thickening agents may be used to increase the viscous drag on neighbouring molecules, decreasing the drainage rate. High viscosity may also tend to dissipate mechanical shocks, thereby increasing the film stability. However, there are limits to this approach. Increasing the viscosity of a foaming system can make it difficult to remove entrapped air and to break down the foam within the time scale required in the foam finishing application.

Foam density

The foam density used in textile finishing applications is generally within the range 0.08–0.15 g cm⁻³ corresponding to a blow ratio range of 6.6 to 12.5. The foam viscosity depends upon the foam density as well as on the viscosity of the unfoamed liquor. In foam applications in which the foam density is used to control the wet pick-up, a decrease in foam density will result in a decrease in the wet pick-up. However, in other foam application systems the foam density is dependent upon the fabric mass per unit area and has to be increased as the mass per unit area is increased. A low foam density has been recommended for use on open-weave fabrics and a high foam density for tightly woven fabrics. In contrast, in the Gaston County FFT (Foam Finishing Technology) [39] direct pressurised foam application method, the foam density has to be decreased for heavy fabrics in order to increase the penetration into the fabric structure.

A more convenient measure of the foam density is the blow ratio which is defined as Eqn 3.7:

$$\text{Blow ratio} = \frac{\text{Weight of a given volume of liquid before foaming}}{\text{Weight of the same volume of foam}} \quad (3.7)$$

This is measured simply by filling a preweighed (that is, tared) container of a convenient size and volume – for example, a plastic cup – to the brim with the liquid and weighing this on an electronic balance. The same cup may be emptied, dried and refilled to the brim with the freshly formed foam and immediately reweighed. The blow ratio is then calculated. In the carpet industry the foam density of back-coating formulations is assessed using this method, which is sometimes referred to as the 'cup weight method'.

The foam density in foam finishing applications must be kept constant throughout the application to ensure that a constant wet pick-up is achieved throughout the production run. Accordingly the blow ratio is regularly monitored, either directly on the machine or periodically off-line. On many foam finishing application systems the flow of finish liquor and air into the mixer are kept at a constant blow ratio, in proportion to the mass per unit area of the fabric, but the flow of liquid and air are increased as the fabric production speed is increased.

Foam viscosity

It has been previously stated that increasing the foam viscosity by addition of agents such as xanthan gum or hydroxyethyl cellulose can aid in foam stabilisation. However, this is more often used in the foam dyeing and printing of tufted carpets than in the foam finishing of textile fabrics. Where viscosity additives are used it may be necessary to wash the finished fabric afterwards to remove any traces of the thickener or gum, and the fabric will then have to be re-dried. This increases the overall processing time and cost, and increases the water and energy consumption in finishing. However, in foam dyeing and printing processes it is necessary to wash off and dry as part of the normal processing sequence.

Bubble diameter

The shape and size distribution of the bubbles in a foam are influenced by the method of preparation (for example, by a static foam generator or a dynamic foam generator), the solution composition and the extent of drainage and breakdown. In general, bubbles with diameters in the range 20–100 µm with a sharp bubble size distribution give consistent creamy foams with the desired properties for foam processing. In practice, studies have indicated that the average bubble diameter of foams used in textile finishing, dyeing and printing may vary in the range 30–500 µm. Foam auxiliaries can be used to alter the bubble sizes considerably within a foam.

In general, the smaller the bubble size, the more stable is the foam. Smaller bubble sizes are obtained by using higher concentrations of surfactants. As the foam ages, the bubble size increases and the bubble size distribution becomes broader. Foams in which the bubble size is more uniform and the bubble size distribution is narrow are thus more stable.

3.9.2 Foam generation

Foam is generated by dispersing air in the finish liquor which may contain the finishing chemicals together with the foaming agent(s). There are two types of foam generator: static foam generation systems and dynamic foam generation systems.

In the static foam generator system, a stream of air under pressure may be introduced into the liquor to produce irregular-shaped foam bubbles. In the most common form of static foam generator (Figure 3.14) the liquor and air are both metered and fed through a chamber containing a number of closely-packed glass or stainless steel balls, stainless steel shavings (chips) or plastic chips, or having a series of sintered glass filters or an internal series of baffles. The

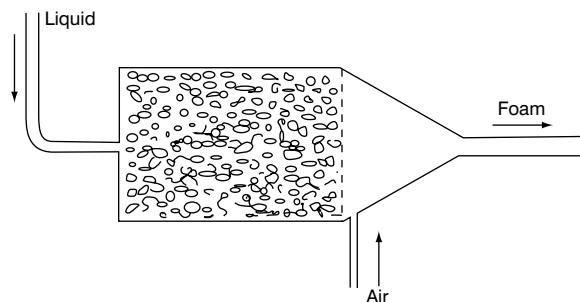


Figure 3.14 Static foam generator [18]

liquid and air are mixed in the static film generator head and the pressure of the air and the liquid then propels the foam to the foam application system where it is applied to the fabric.

Foams produced by a static foam generator are always the same in volume irrespective of the amount of air used. The foam properties may be changed by changing the packing in the chamber. Static foam generators, it is claimed, produce a more uniform foam with better consistency than that of the dynamic foam generator. They are less expensive and require less maintenance than the dynamic foam generator. However, there can be contamination problems with some chemical finishes and the static foam generator is generally less versatile than the dynamic foam generator system.

In a dynamic foam generator (Figure 3.15), air is introduced under pressure into a liquid, and then subjected to high shear forces in a mixing head. The system thus consists of a chamber or mixing head, a liquor-flow pump, and an air-metering unit together with a method for delivery of the foam to the desired point of application to the fabric. The chamber of the mixing head is capable of being pressurised and contains a rotor and stator mixing system. The rotor has a series of projecting pins or teeth, which are usually square-edged. These are mounted either radially or axially on its surface and are rotated between similar teeth on the surface of a stationary stator. When the liquor and the air are metered into the chamber and forced between the intermeshing action of the stationary and moving teeth, the high shear forces and turbulence generate the foam. By controlling parameters such as the speed of the rotor, the number and shape of the teeth, and the clearance between the stationary and the moving teeth, it is possible

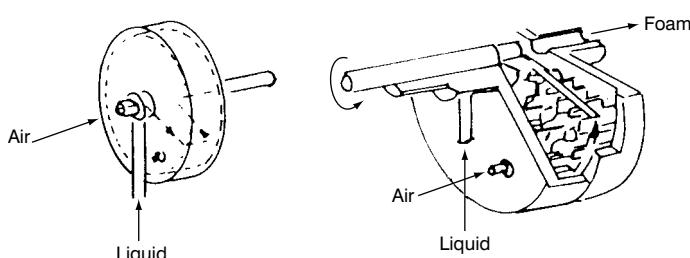


Figure 3.15 Dynamic foam generator [18]

to control the characteristics of the foam. The foam characteristics, however, are only uniform for a set of fixed parameters.

Twin rotor-stator mixing heads are also manufactured and, in applications such as foam backings for tufted carpets, the heat generated in the mixing head is dissipated by cooling the chamber with cold water, which is heated up and can be recycled in the plant. Modern dynamic foam generators are mobile units that can be pre-programmed to provide the required volume of foam at the correct foam density (that is, blow ratio). Campen, Cowie and Riding, Mondo-Mix and Oakes, amongst many other manufacturers, produce dynamic foam generators suitable for textile finishing. For laboratory scale studies, laboratory dynamic foam generators are supplied by Benz, Cowie and Riding, Oakes, and Werner Mathis.

3.10 FOAM APPLICATION SYSTEMS

There are many types of foam application systems available for applying finishes to textile fabrics. In the main, these are based upon modified padding, coating and printing systems together with the FFT (Foam Finishing Technology) slot applicator unit of Gaston County which is a direct pressurised foam application method.

3.10.1 Horizontal pad mangle

One of the first machines used for foam application was the horizontal padder or pad mangle, as shown in Figure 3.16(a). The foam is applied to both sides of the fabric by maintaining two foam banks contained in the nip of the pad mangle. The fabric passing vertically downwards through the foam picks up foam that is collapsed at the nip of the pad mangle, which ensures a uniform liquor application. Excess foam outside the fabric selvedges can be carried through the nip and may be prevented by controlling the width of the foam banks in the nip, or doctoring the excess foam off the rollers.

Foam stability is particularly important. An unstable foam can form an excessive amount of liquor in the nip, giving an uneven application of the finish liquor. More stable foam may tend not to collapse in the nip. This method is relatively simple to control and the fabric wet pick-up is controlled by the foam density and the nip pressure. A conventional horizontal pad mangle is easy to convert to a foam padding system suitable for woven fabric applications without a large capital expenditure. Wet pick-up levels of 30% can be attained on cotton and cotton/polyester fabrics using foamed chemical finish liquors.

3.10.2 Foam coating methods

There are many types of foam coating machines and techniques that may be used for foam finishing, and many are relatively simple to construct within the textile finishing plant. In the doctor coating system, Figure 3.16(b), foam is supplied as a foam bank that is built up on the face side of the fabric. The height of the foam is doctoring by a doctor knife and the foam height and the foam density control the wet pick-up. In the roller coater, the height of the foam

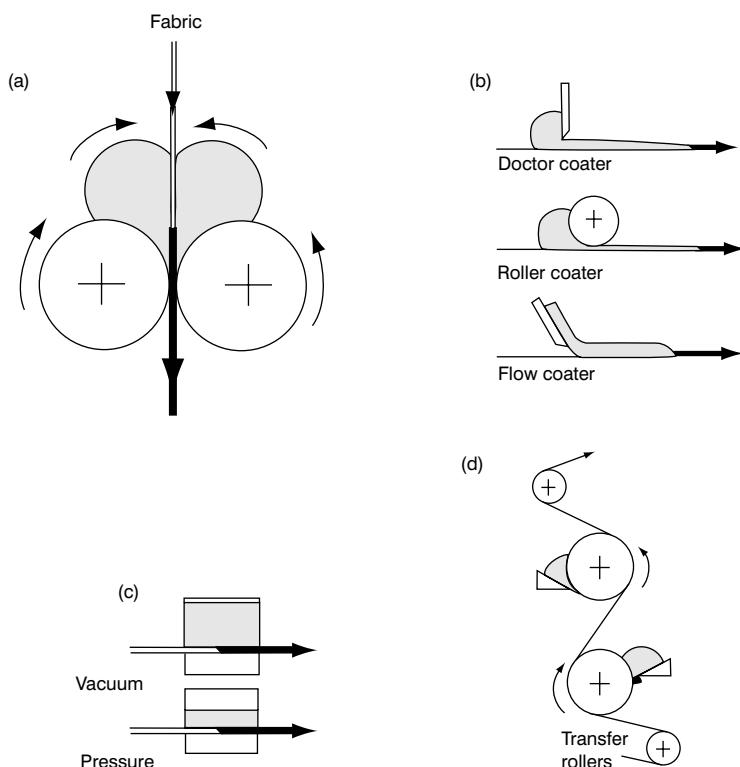


Figure 3.16 Methods of foam application: (a) horizontal padder; (b) doctor coating, roller coating and flow coating; (c) pressure or vacuum application; (d) transfer (double-sided) [18]

bank is doctored by a doctor roller, but the principles are similar to the doctor coater. Alternative coating systems based upon a flow coater, or the use of pressure or vacuum, Figure 3.16(c) have also been described for use as single-sided foam applicators. For double-sided foam application it is also possible to use a pair of transfer or kiss-rollers in the machine arrangement illustrated in Figure 3.16(d).

After the foam has been applied to the fabric, the foam must be broken down or collapsed to allow the liquor to wet and wick into the fabric structure. Capillary action withdraws the liquid from the foam into the fabric and is often used. However, the use of squeeze rollers, or pressure or vacuum application can also be employed (Figure 3.16(c)). Alternatively, methods involving temperature, presence of foam destabilisers, and shear forces have also been proposed. The capillary action, vacuum and squeeze roller methods are probably the most widely applied methods for collapsing the foam.

After the foam has collapsed, the liquor should completely and uniformly penetrate within the fabric. The wet pick-up may be adjusted by controlling the foam density, the volume of foam applied, the fabric mass per unit area, the thickness of the foam layer and the production speed.

3.10.3 Kiss-coating system

In the kiss-coating method, illustrated in Figure 3.17, foam is supplied to the trough and transferred to the fabric using a kiss-roller that rotates in the same direction as the fabric movement. Another kiss-roller system is based on the reverse roller coating principle and has been manufactured by Morrison Textile Machinery Co. (Figure 3.18). Here, the coating roller (A) is rotated in the opposite direction to the fabric movement. The foam picked up by the coating roller is then controlled by the metering roller (B) to deliver the correct amount of foam in the nip of the two rollers (A and C).

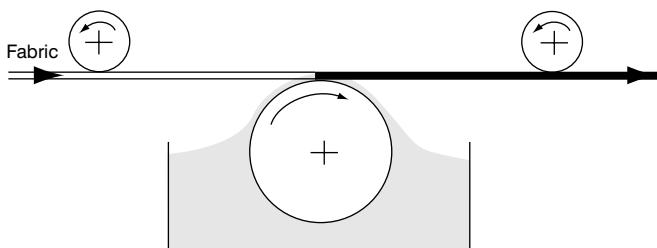


Figure 3.17 Kiss-coating system [18]

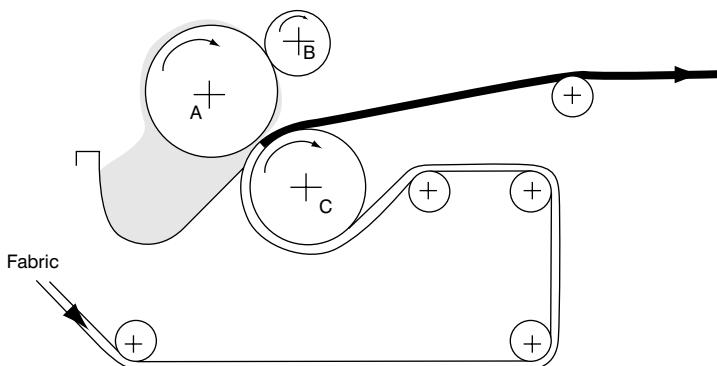


Figure 3.18 Morrison reverse roller [18]

3.10.4 Knife-over-roller coating systems

The knife-over-roller coating system is depicted in Figure 3.19. In this system, a relatively stable foam is used, which is applied as a uniform layer to the fabric surface either by a doctor blade (or knife) or a doctor roller as shown previously in Figure 3.16(b). The foam must be collapsed, because of its relatively stable nature, by a pair of pressure rollers or by the application of a vacuum. The knife-over-roller foam application system can be used for one-sided application, the wet pick-up being controlled by the foam density and the setting of the doctor blade or doctor roller.

When this system was used to apply a durable press finish to a 50/50 cotton/polyester fabric,

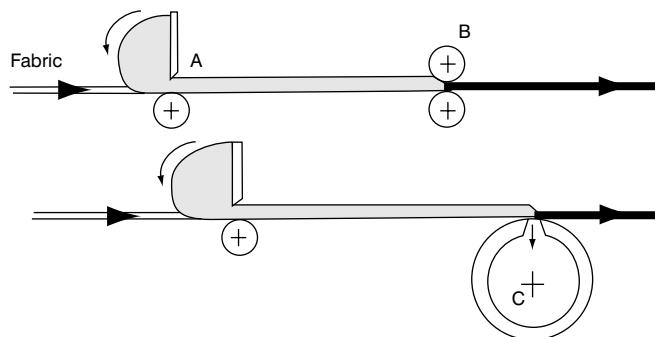


Figure 3.19 Knife-over-roller coating system [18]

using two pressure rollers to collapse the foam, the wet pick-up compared with conventional padding could be decreased from 60 down to 30%. As a result, the processing speed was increased from 30 to 38 m min⁻¹, the curing oven temperature was decreased from 177 to 107 °C, resulting in a gas saving of 74%. In addition, some technical improvements in fabric properties, such as improvement in durable press rating, crease recovery angle and shrinkage during washing, were noted.

Another version of the knife-over-roller coating system is employed in the Monforts Vacu-Foam [40,41] (Figure 3.20). A uniform layer of foam is produced by a knife-over-roller doctor blade (A) on an endless rubber blanket (B). The foam layer on the blanket makes contact with the fabric as both the fabric and the blanket pass around a perforated drum (C). Foam penetration into the fabric is then assisted by application of a vacuum as the fabric passes round the perforated drum.

The wet pick-up in the Monforts Vacu-Foam is controlled by the foam density and the knife clearance, as before, but the collapse of the foam is dependent upon capillary forces, the applied vacuum and the pressure of the blanket on the fabric. The use of this machine arrangement

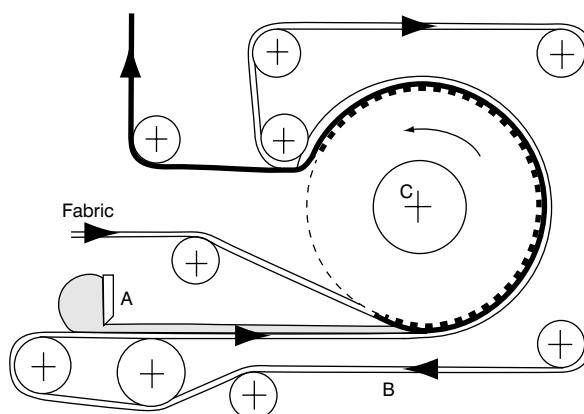


Figure 3.20 Monforts Vacu-foam system [18]

allows both single- and double-sided treatment of woven and knitted fabrics, and elastic warp knitted fabrics and pile fabrics have also been processed. The wet pick-up on cotton fabrics is about 35–40% and about 10% on polyester fabric.

3.10.5 Knife-on-air system

The knife-on-air, air-knife or floating knife system is illustrated in Figure 3.21. The amount of foam applied to the fabric is controlled and the foam is collapsed by the shearing action of the knife to give a wet pick-up of around 30–35%. The amount of foam applied to the fabric and the foam density are used to control the wet pick-up level.

A widely-used method in the USA has been the Valfoam process of United Merchants and Manufacturers (Figure 3.22). The fabric is passed underneath the foam bank and the doctor knife, being carried along by a moving conveyor belt. Foam collapse is controlled by pressure rollers to give a wet pick-up in the 10–40% range, and the system can be used to treat one side or both sides of the fabric.

A foam application method that has been used world-wide is the Texicon Autofoam [42,43] (Figure 3.23) originally developed by Dinting Engineering, now marketed by Beacon Controls,

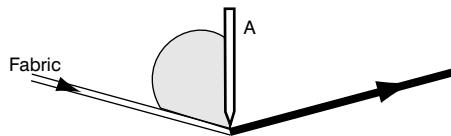


Figure 3.21 Knife-on-air, or floating knife system [18]

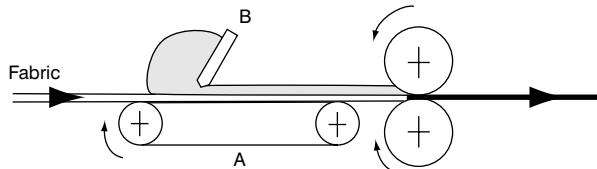


Figure 3.22 United Merchants and Manufacturers' Valfoam process [18]

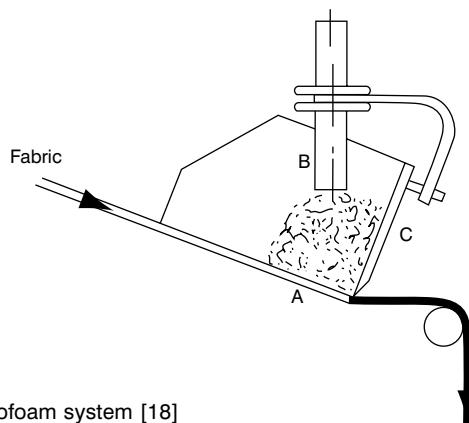


Figure 3.23 Texicon Autofoam system [18]

part of Datacolor International. Foam from the generator system is evenly distributed across the fabric width by a specially designed manifold system. The relative movement of the foam and the fabric create a roll of foam, kept to the fabric width by side seals and rotating against a specially-designed profile. This profile facilitates the transfer to the fabric of an accurately controlled quantity of foamed chemicals, at any predetermined wet pick-up level, typically 15–30%.

Careful design of applicator profile in the Texicon Autofoam eliminates any problems that could otherwise be caused by a proportion of the foam de-watering. This could give spent foam of increasing blow ratio that could combine with the new foam being supplied, to give a foam roll with varying foam ratios and hence uneven fabric treatment. The applicator profile is designed to eliminate such problems by controlling the release of spent foam beneath the profile, to ensure uniform fabric treatment irrespective of the type of fabric. Thus a constant foam volume is applied per unit area of the fabric allowing an accurate prediction of the blow ratio in relation to the mass per unit area and the required pick-up value.

Maintaining the foam roll at constant diameter by use of proximity probes, and automatically adjusting the blow ratio, overcomes any wet pick-up variation due to the non-uniform absorption of liquor from the foam roll. The controller requires three basic settings: the fabric weight per linear metre, percentage wet pick-up required, and blow ratio. The fabric speed through the applicator, which is determined by some fabric draw facility – for example, a stenter – is sensed and the controller then meters the correct volume of liquid and air to provide foam of the required blow ratio at a rate determined by the throughput speed. Once optimum processing conditions are established the controller can be set to automatic to maintain the quality of the foam application.

The advantages of foam finishing can be seen in comparative results obtained using conventional padding and the Texicon Autofoam system (Table 3.5). The more even distribution of the easy-care finish that results from foam application can lead to a 15% saving in the chemicals applied. The low wet pick-up in the foam application decreases the migration of chemical finishes during the drying stage.

Table 3.5 Comparison of conventional padding and the Texicon Autofoam system

Parameters	Pad route	Texicon Autofoam route
Wet pick-up (%)	60	25
Fabric speed (m min^{-1})	29	65
Energy costs per 100 m (pence)	49	22
Chemical cost per 100 m (pence)	77	66
Production per hour (m)	1740	3900
Labour cost per 100 m (pence)	40	19

Fabric: 33 $\frac{1}{3}$ / 66 $\frac{2}{3}$ cotton/polyester
 Finish: Easy-care finish (Dimethyloldihydroxy ethylene urea, 3% owf)

3.10.6 Screen printing systems

A wide variety of foam printing, foam dyeing and foam finishing techniques have been developed, many designed specifically for the carpet industry. A number of screen printing systems have been adapted for foam finishing of fabrics, and two well-known examples are the Zimmer Variopress system [44] and the Stork RSF (Rotary Screen Foam) system [45].

In the Zimmer Variopress system, foam is supplied by a foam generator to the Variopress unit (Figure 3.24). The foam is metered onto the fabric by the Variopress unit, which can be set at various heights above the fabric to provide either a controlled surface penetration or penetration of the foam to a controlled depth. Wet pick-up values in the range 15–40% have been applied in foam finishing.

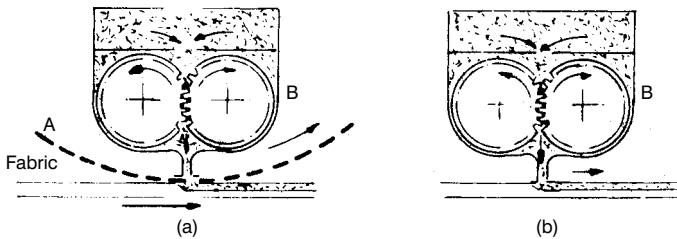


Figure 3.24 Zimmer Variopress system [18]

The Stork RSF (Rotary Screen Foam) system is illustrated in Figure 3.25. The foam from the foam generator is supplied to a chamber (A), which is formed by two stainless steel blades. The upper blade (B) has a tip of synthetic material and is pressed against the rotary screen (C) by air bellows (D). The lower blade (E) is pressed against the rotary screen by a combination of mechanical pressure and hydrostatic foam pressure. Foam is forced through the special 40-mesh Penta-screen, which has a circumference of 91.4 cm, a wall thickness of about 250 µm and an open area of 35%. The foam is forced into the fabric, which is held in contact with the rotary screen by passage over a counter-pressure roller.

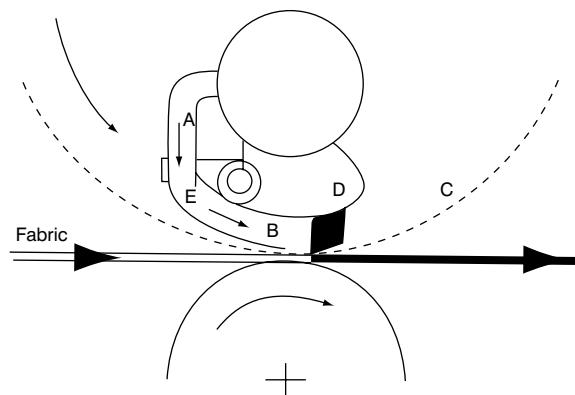


Figure 3.25 Stork Rotary Screen Foam system [18]

The amount of foam squeezed through the rotary screen mesh depends upon the squeegee setting. To decrease the amount of foam to the nip the upper blade of the squeegee may be set to a light pressure. Excess foam outside the fabric width is removed from the screen and the counter-pressure roller by a foam exhaust unit, which carries the foam back to the liquid reservoir to be recycled. In addition there is a counter-pressure roller cleaning system.

The Stork RSF system is a closed system and hence both unstable and stable foams may be used to provide low wet pick-up values in the range 15–40%. Optimum fabric penetration is achieved using unstable foam. The foam application is to one side of the fabric and thus the degree of penetration is mainly dependent upon the fabric mass per unit area and construction. A major feature of the Stork RSF system is that the control system ensures a constant foam supply independent of the fabric speed while the foam density is controlled electronically to give precise control over the characteristics of the foam supplied to the fabric. Thus the wet pick-up may be maintained at a constant value independent of the production speed, and is controlled by the foam density, squeegee pressure and screen mesh number. Because the surface speed of the rotary screen and the fabric are the same, and the squeegee inside the screen exerts a very low mechanical pressure, the foam delivery to the fabric is accomplished in a frictionless manner. This is an advantage for foam finishing of highly sensitive fabrics, such as plush, and even unstable fabrics such as knitted structures may be processed satisfactorily.

If desired, both sides of the fabric may be treated in a single passage by combining two Stork RSF units in a similar machine arrangement as that used in double-face printing. Wet-on-wet foam processing operations can also be conducted, avoiding the need for expensive intermediate fabric drying treatments. The use of the Stork RSF system on a viscose curtaining fabric (400 g m^{-2}) enabled the wet pick-up to be decreased from 80% down to 20%, the drying temperature to be reduced from 180°C to 120°C and the processing speed to be increased from 20 up to 60 m min^{-1} [46].

3.10.7 Slot applicator systems

The direct-pressurised foam application technique invented by Union Carbide and developed by Gaston County into the FFT (Foam Finishing Technology) system is based upon a slot applicator system (Figure 3.26), and many units have been sold since its appearance at ITMA '79. A foam generator supplies foam to the distribution chamber (A), and the foam emerges from the slot (B) onto the fabric. The foam is held under pressure in the chamber and the slot, and is applied directly to the fabric passing over the slot at an angle of between 15 and 25° . The special slot applicator design enables the slot width to be varied from 0.3 mm up to 25 mm. The angle of contact of the fabric with the inward taper of the slot is between 5 and 15° , and at this point shearing forces finally collapse the foam.

The applicator is constructed from stainless steel with a Flexiglass inspection panel directly under the application section. Photoelectric sensors control pneumatic edge seals and the slot applicator ensures that a uniform distribution is maintained. When the metastable foam contacts the fabric it immediately collapses and the wet pick-up value is dependent upon the

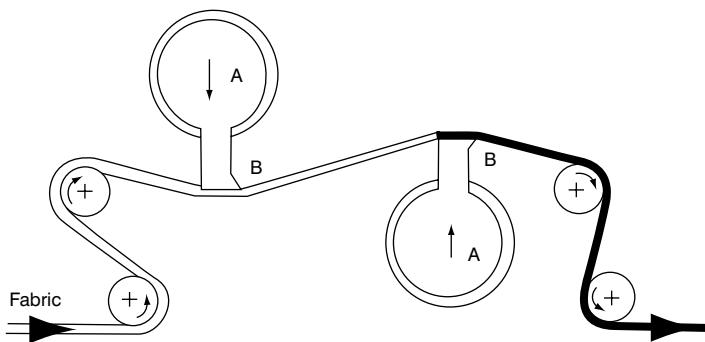


Figure 3.26 Gaston County Foam Finishing Technology system [18]

liquor flow rate, the fabric speed and the mass per unit area, so that it is independent of the foam density. The wet pick-up is maintained constant by controlling the rate at which the foam is applied relative to the speed by automatic means.

Lightweight fabrics (up to 140 g m^{-2}) may be processed using a single slot applicator FFT system. However, a dual application FFT unit enables both sides of the fabric to be treated with the same finish liquor, or alternatively if two foam generators are used, different finishes may be applied to the face and back of the fabric. A novel slot applicator has also been designed for the application of foam to open-weave fabrics. Wet pick-up values with the normal FFT system range from 10–25% on all-cotton and cotton/polyester fabrics, and 15–30% on wool. The FFT system can be used for back-coating and also for wet-on-wet applications. The savings in chemical costs are generally in the range 10–25% and energy cost savings range from 50–75%.

3.11 COMPARISON OF LOW WET PICK-UP APPLICATION METHODS

Saturation-removal (also termed expression) methods for obtaining a low wet pick-up are only suitable for wet-on-dry applications. They are not suitable for wet-on-wet applications because a low wet pick-up cannot be attained by this method. However, if the fabric is not very uniformly chemically pretreated, the saturation of the fabric may tend to overcome some of the wetting and wicking problems that can be experienced using topical methods. Saturation-removal or expression application methods can only decrease the wet pick-up value to the level achieved by the most efficient de-watering methods; that is, the wet pick-up level is determined primarily by the imbibition of the fibres when the fibres are fully saturated. Thus hydrophilic fibres like cotton and wool cannot yield low wet pick-up levels below the water saturation value for the fibres, and usually the low wet pick-up value, is above the water saturation value.

However, fabrics for low wet pick-up application should be well prepared and uniformly absorbent to provide satisfactory wetting, wicking and absorption of the liquor by all the fibres present. If the wet pick-up level is too low in topical application methods – that is, below the water saturation value of the fibres – the penetration of the chemicals within the fabric will be

incomplete. This can lead to an uneven finish distribution characterised by spots of adequately treated fabric surrounded by areas where the finish liquor has not been allowed to wick and spread across and through the fabric to the other side. In effect, the low wet pick-up has been preferentially absorbed by absorbent fibres in localised areas of the fabric.

Topical application methods of low wet pick-up finishing thus cannot be used on all types of fibre and fabric constructions, and there are certain finishing chemicals that cannot be applied using these techniques. However, some topical application methods can be applied both wet-on-dry and also wet-on-wet, and the methods can be used to apply a different chemical to the face and back of a fabric, opening up opportunities for technical innovation in chemical finishing. This is particularly of advantage where the pile fibre and backing fibres of certain fabric constructions require different chemical finishes.

One reported disadvantage of using a low wet pick-up is that treatment of tubular knit fabrics is not successful using this approach. Very low wet pick-up values can, in addition, create problems in stentering fabrics to width during drying, as the forces required are higher than with fabric conventionally treated with a high wet pick-up.

It should also be noted that application of pretreatment chemicals is usually carried out using a high wet pick-up – for example, 100–200%. The greater volume of liquor helps to stabilise peroxide bleach solutions and provides a greater liquor volume into which the impurities removed from the fabric may be dissolved, emulsified and dispersed. This facilitates their removal during washing and yields a higher standard of fabric pretreatment.

Wright [7] compared the effects produced by applying similar finishes by Triatex MA and Gaston County FFT foam finishing, from commercial experience gained in running both types of equipment at the Dan River finishing works in the USA. This confirmed that fabric preparation prior to MA treatment is most important. Very good and uniform absorbency is necessary. Wright mentions a problem observed with fabric containing undyed and dyed yarns. Differences in absorbency arising from the rigorous preparation prior to yarn dyeing led to variation in resin pick-up during finishing, which if sufficiently severe could result in differential shrinkage and fabric puckering in laundering.

Foam processing is less demanding on the pretreatment. The foam is effectively being pushed into the fabric, and the wetting agent required for foam generation counteracts any effect due to variable cloth absorbency. (A point worth noting here, although Wright does not specifically mention it, is that the wetting agent used in MA processing must be selected for non-foaming, as of course the deposit of foam bubbles on the fabric will result in uneven treatment.)

Fabrics with large open spaces, such as leno weaves, are not ideal for foam finishing. Seersucker is a problem fabric for both systems; the MA requires flat fabric, and foam needs uniform porosity; bone-dry fabric is not absorbent enough for MA treatment, and must be conditioned.

Advantages over conventional pad mangle application, noted by Wright, which are shared by both FFT and MA include:

- (1) energy conservation (Wright observes that by applying 35% of liquor in a low pick-up treatment, the fabric can be satisfactorily set to finished width in subsequent drying on the stenter);

- (2) less chemical migration, reducing chemical requirements by 10–20%, due to more efficient utilisation;
- (3) improved colour fastness, due to reduction in dye migration;
- (4) no build-up of loose dye in the pad bath, eliminating any possibility of fabric staining.

Kretschmer, reporting a similar comparison [47], mentions another advantage shared by both techniques over the pad mangle: the ability to treat pile fabrics without crushing the pile.

Machine manufacturers in the early 1980s were quick to see the potential advantages for the finisher of low pick-up techniques, and several concepts were shown at the 1983 ITMA exhibition. Jones and coworkers [48] at Cotton Incorporated extended their comparison to include two liquid film applicators (the Triatex MA and the CBA ‘Curved Blade Applicator’): engraved rollers; the Sando YS mangle; the Zimmer knurled roll; Toyoda NT; BTM Spraymiser; Farmer Norton SDE; WEKO and foam application.

Since the SAWTRI survey [18], interest has waned somewhat in low wet pick-up developments, and there has been little technological advance. Van der Walt and van Rensburg [18] wrote in their conclusion that:

‘... despite all the advantages offered by the low add-on and foam-application techniques, the conventional padder is still being used very widely today. There are various reasons for this, but the most important probably are its versatility, reliability (little or no maintenance being required), simplicity of operation, and low cost, compared with most other systems. It is therefore highly unlikely that the traditional padder will ever disappear completely from the dyehouse.’

Twenty years later, these comments are still valid.

It is possible that the main incentive for installing low pick-up equipment was the opportunity for energy savings, now less attractive due to improvements in heat recovery at the stenter. For certain applications, there has even been some interest in high liquor add-on [49].

3.12 WET-ON-WET APPLICATION

To avoid the expense of a drying stage between bleaching or dyeing and subsequent application of a finishing treatment, some finishers would like to remove as much water as possible from the washed fabric – for example, using a high-pressure mangle or vacuum extraction, followed by impregnation with finish liquor. This is termed ‘wet-on-wet’ application.

A serious disadvantage of the pad mangle in wet-on-wet processing is the difficulty in keeping the concentration of the treatment at a constant level, due to interchange between the treatment liquor and the water carried into the system by the incoming fabric.

Reiker and coworkers [50] have published equations (Eqns 3.8–3.11) showing the effect of liquor interchange on product add-on. These include the ‘liquor exchange coefficient (α)’

introduced by Rüttiger [51], which is the proportion of the incoming water that is replaced by treatment liquor during the process.

Wet-on-dry:

$$P = C_B Q_D \quad (3.8)$$

Wet-on-wet:

$$P_1 = C_B (Q_2 - Q_1) = C_B \cdot Q_D \quad (3.9)$$

$$P_2 = C_B \cdot \alpha \cdot Q_1 \quad (3.10)$$

$$P = P_1 + P_2 = C_B \cdot (Q_2 + Q_1) + C_B \cdot \alpha \cdot Q_1 = C_B \cdot (Q_D + \alpha \cdot Q_1) \quad (3.11)$$

where P = total product pick-up (g kg^{-1} *)

P_1 = product pick-up by differential pick-up (g kg^{-1} *)

P_2 = product pick-up by liquor exchange (g kg^{-1} *)

Q_1 = water content of the incoming goods (l kg^{-1} *)

Q_2 = liquor content of the exiting goods (l kg^{-1} *)

Q_D = differential pick-up (l kg^{-1} *)

α = liquor exchange coefficient

C_B = actual product concentration in the impregnation bath (g l^{-1})

*calculated on air-dry material

The liquor exchange coefficient is reported to be normally between 0.3 and 0.6 [31], but should be determined empirically for each system. A value of $\alpha = 1$ indicates complete liquor exchange in padding, while a value of 0 indicates no exchange of liquor.

Eqn 3.12 shows how, in a normal wet-on-wet padding operation, the bath concentration changes over time, due to liquor interchange [31]. In slop-padding, it is claimed that there is no liquor interchange ($\alpha = 0$) and there is no difficulty in keeping the finish liquor at a constant concentration.

$$C_B = C_0 \cdot e^x + \frac{X_2 - X_1}{X_2 - (1 - \alpha) \cdot X_1} \cdot C_N \cdot (1 - e^x) \quad (3.12)$$

where C_B = bath concentration after time t

C_0 = initial bath concentration

m_F = fabric weight per unit area

b = fabric width

v = processing speed

t = processing time

V_0 = liquor content of trough

X_2 = moisture content after impregnation

X_1 = initial moisture content

C_N = concentration of feed liquor

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CHAPTER 4

Mechanical finishing – traditional and modern

A P Lockett

4.1 INTRODUCTION

It has been known and noticed by the earliest producers of textile materials, both woven and non-woven, that simple physical or mechanical treatments could considerably change the appearance and the properties of those materials.

The simple process of wetting and drying a fabric could alter it; shrinkage occurred making the fabric more stable and, in some cases, thicker. If heat was also employed the combined effect of moisture and heat made it more likely that the fabric would be altered, especially when mechanical processes were used. The treatments involved simple static pressing or prolonged mechanical agitation such as beetling or fulling. The use of beetling on cotton fabrics – a batchwise process involving repetitive crushing between wooden blocks – produced a fabric with a special feel or handle more dense and shiny in appearance. With wool fabrics a similar process was used to felt or shrink the fabric into more stable, dense and robust products.

These early finishers noticed that the use of naturally occurring products, such as gums, starches and certain mineral deposits, could change fabric properties quite radically. These changes could give enhanced properties or produce aesthetic effects suitable for clothing or household decoration. Surface treatments by the use of hand tools were employed to alter the face of a fabric; the cloth surface could be raised to give a pile effect with the aid of a dried flower head such as a ‘teasel’, or a form of corduroy could be achieved by selective cutting with a sharp knife or scalpel.

Nowadays, the general objects of traditional finishing are many and varied, but in the simplest case the finisher is able to confer a more pleasing appearance and handle or to render the fabric more suitable for the intended purpose or end-use.

The slow and batchwise historical processes, usually based on simple mechanical treatments, have now been replaced by continuous treatments capable of producing finished fabrics at high speed. Control of all the machine parameters is possible, resulting in fabrics being finished consistently to close tolerances.

Traditionally, textile finishers were classified separately from bleachers and dyers; often they were called ‘dry finishers’. This term arose because, although these finishers used water-based finish liquors, the amounts of water used were small and in general the finishing mill conditions were comparatively dry, in strong contrast to a dyehouse or bleach works where fully saturated

cloth was often seen, especially in the rope form, being transferred from one process machine to another, with the resulting impression of excessive use of water.

Apart from the mechanical, physical processes, the dry finishers found that the application of certain finishing agents could confer quite drastic changes in fabric properties. For example, a soft cotton cloth could be treated to produce a very stiff fabric with quite different properties, or an open-weave cotton could be treated to produce fully filled, completely opaque fabric with low air porosity. Equally, a cotton fabric could be processed so that when it was subsequently mechanically treated a tough, flexible finish was achieved, as in a bookcloth, or a highly glazed or glassy finish, as in a cambric. A cotton fabric could be prepared with 'secret' mixtures and then treated on a calender in which the heat and mechanical pressure produced a translucent fabric for use as tracing cloth.

These examples illustrate the kinds of specialist finishes produced by quite small companies, which proliferated in the past. Many of the so-called 'secret' finishes were carefully guarded and passed down from father to son. An entire industry developed to produce all types of finishes using only naturally occurring products, and the chemical ingenuity of these textile chemists is legendary.

The early finishing industry – the traditional 'dry' finishers – were dependent on these natural products until the true chemical finishing industry was developed, when chemical products were applied to fabrics, reactions with the fibres took place and permanent finishes were achieved. Chemical finishes were applied that were fast to washing and so made domestic procedures far less demanding. For example, the traditional starching of shirts and prolonged use of the 'smoothing iron' has largely died out because of the use of durable easy-care fibre-crosslinking finishes, which produce fabrics that require minimum ironing.

The advent of such new synthetic chemical finishes and man-made fibres saw the production of such a range of fabrics that it changed the old dry finishing industry completely. The use of most natural products gives interesting and occasionally quite remarkable finishes, but they suffer from their lack of permanency and as they are removed by aqueous treatment they have restricted use or require refinishing during their useful life. The traditional industry has therefore diminished in size, but it has also seen great improvements in productivity through more efficient equipment and the introduction of control systems. There are still many finishers using the older types of finishes, which have the advantage of low price, and this branch of the finishing sector still produces many metres of finished cloth for highly specialised end-uses, including disposable industrial use and the specialist but fickle fashion market.

The use of calenders to flatten or compact or to produce polished fabrics is still important. The brushing or raising of suitable substrates to produce pile fabrics – velvets and corduroys, and so on – is still demanded by the fashion trade. Mechanical compressive shrinkage is still used to produce non-shrink garments without the need for chemical treatment. Although the cotton and cellulosics finishing industry has evolved to depend less on the traditional and more on chemical finishes, many of the traditional finishing processes for wool are still carried out, for there is no better finish to produce the 'right' handle; so that blowing, decatising and pressing

are still in demand. The machines have better control systems but the basic finishing processes have not changed.

The original commercial organisation of the cotton industry, especially in the UK, was based on the 'horizontal' system of commission processors. The complete processing of a fabric after weaving could involve many individual processes, some quite complex, carried out by small, independent, highly specialised private companies, usually situated in the locality, who did not own the cloth but who processed it according to instruction and charged for the process.

The change from this horizontal industry to complete in-house vertical integration led to the demise of many small companies. The incorporation of small, highly specialised companies within a vertical set-up has also seen some spectacular failures. The volume of business in a vertical organisation was often insufficient to satisfy the economic production demands for very specialist processes, which can only be satisfied by a wholly commission company. It is surprising how many spinning machines are required to feed a loom and how many looms are required to keep a stenter in production for 168 hours per week when it is capable of 120 metres per minute. Outside the UK, commission finishing is rare and the role of the independent merchant finisher is important in other areas of fabric processing, especially where development work on new finishes is involved.

The structure of the world's finishing industry is changing. The size of world markets has meant that the production of commodity textiles can now be organised into the most efficient system where economy of scale is of paramount importance. Nowadays, one production line can produce one specific textile product on a continuous basis, resulting in highly efficient processing using modern statistical control methods. The old system, in which a number of companies all produced similar product mixes, is disappearing. The small traditional commission finisher has a future only in highly specialised finishing or in the production of short runs to specific instruction where the cost of processing is of secondary importance.

4.2 FINISHING WORKS MANAGEMENT STRUCTURE

The traditional finishing works consists of several distinct departments. One of the failings of the UK industry was the surprising lack of effective communication between companies, and even between departments in the same company. However, the effective and profitable operation of a company in the modern economic climate demands absolute cooperation by all staff.

The usual company set-up is as follows:

- (1) Office – for general management, including all elements of order processing, order chasing, sales and production planning, purchasing, invoicing, personnel, payroll and all aspects of financial control including the many legal and environmental requirements;
- (2) Grey room – the department responsible for the efficient unloading and recording of all cloth deliveries;
- (3) Finishing department – the actual processing of cloth will be carried out in a number of individual sections;

- (4) Making-up room – the department where the finished cloth is put into a form suitable for the ultimate customer or for further onward processing; this department is also responsible for order despatch.

There are many local variations; for example, the despatch may be controlled from the office.

There are two other most important departments; the laboratory and the maintenance department. The laboratory can be office-run or controlled by the finishing department; or occasionally the laboratory is a law unto itself. Most finishing works also have the traditional maintenance department, which is responsible for the efficient running of all the equipment from the boilers through to the making-up equipment.

This traditional works structure is still the basis of the modern factory, but there is now very close liaison between all departments. Forward planning of regular maintenance and improvements are now vital if efficient running with the minimum of downtime is to be achieved.

The use of computers has helped enormously both in production planning and in the assembly of information in databases. It originated in the processing of accounts, but has now spread to the laboratory, the making-up room and the whole area of production planning.

The importance of the grey room has been neglected in the past; the following section indicates its role in an efficient company.

4.3 GREY CLOTH DEPARTMENT

The 'grey' or 'greige' room has the responsibility for the reception of cloth, the storage and identification of the goods and the retrieval and sewing down of each individual processing order. The easily recognisable individual orders are then taken to the correct location for processing. At all times the goods have to be protected from unnecessary soiling.

In many works, it is the responsibility of the grey room to take representative samples of loomstate cloth, so that tests can be carried out to determine the correctness of the fabric or to identify chemical contaminants – such as 'PCP' (pentachlorophenol) [1], for example – that may cause environmental problems. In the future, it is likely that each processing order will have to be analysed for its potential 'chemical oxygen demand'.

Identification of individual processing orders is of paramount importance and various methods of marking cloth have been used over the years, usually based on black indelible inks, asphalt or tar-based materials. Now that computer production planning is becoming more common, magnetic markers have been tried for identification purposes, with qualified success. Automatic readers for bar-coding systems are available, which incorporate all the information needed for the processing and tracking of an order through all its various processes. The criteria for successful identification are that the markings are permanent, readable, and do not mark off in processing onto the bulk of the fabric. With high-speed equipment the recognition of the start and end of different orders is also of importance.

With modern processing equipment capable of high running speeds it is essential that

continuous cloth movement occurs with the minimum of downtime. The modern grey room will identify the cloth for each order and it will be sewn into continuous lengths either on stillages or trucks, but more likely it will be rolled into 'jumbo' rolls or 'A' frames. This process allows for inspection and the detection of 'cuts' or 'throughs' which, if undetected, could cause major production problems if a machine runs out of cloth.

There are many patents relating to sewing machines, but there are only two types; these are the 'chain stitch' and the 'butt end' sewing machines. Each has its own advantages, so any particular works must decide which of the two best serves its production requirements.

The earliest chain stitch machines were based on Heatons Patent. The design involved a mechanical device for passing a thread through the cloth structure using a needle, the thread forming a long loop held in position by a looper as the thread was withdrawn. The cloth then moved forward and the needle was reinserted through the 'held' loop to form a chain stitch. Some of these machines were extremely well built and ingenious. Either mechanical treadles or electric motors were used to provide the necessary motive power. The main advantage of this sewing was its strength, simplicity and ease of use on virtually any fabric, both wet and dry. There are two disadvantages. The sewing can unravel if the final sewing is not tied back. This of course could happen inside a machine during processing, causing major production problems. The other drawback is that the sewing can be double or treble the cloth thickness and with some processing, especially that involving nips, this is a major problem.

The butt end sewing machine solved most of the problems of the chain stitch machines in that the two pieces of cloth to be joined are automatically trimmed level and the sewing process involves the formation of thread loops in the warp direction. The tension on the cloth pulls the sewing, resulting in the 'butt end' or flat sewing. These machines are not cheap and need regular maintenance and adjustment for different fabrics. The number of stitches per inch can be adjusted for the cloth construction, as can the depth of stitch. For a normal sewing, each metre of sewing width uses up to 10 metres of sewing thread, and often the cost of producing good sewings is not realised.

The efficient running of a grey room is vital to the profitability of a company where the value of the cloth processed can be many times that of the processing cost.

4.4 TRADITIONAL FINISHING

A long history of works practice taught textile workers that all types of substrates – for example, furs, leathers, woven fabrics and felts – could be altered by the application of various treatment agents and processes. The treatments could produce improved technical properties, or the aesthetic appearance could be altered to enhance the fabric appeal.

It was found that the application of naturally occurring products could produce quite dramatic effects and new fabric properties. The life of a fabric could be extended, or vastly improved properties, such as water-repellency or increased strength or durability, could be achieved with simple or quite complicated finishing treatments.

Nowadays, many of these finishes are carried out for very specific purposes in that they give

special properties for specific end-uses, and in most cases the cost of processing is extremely competitive. Most of the end-uses are industrial, where the life of the product is short term – for example, rotary polishing mops for the metal industry. In many cases, the finishing effect does not need good mechanical or washing properties as the final product is never to be given a wet treatment.

Traditionally, a wide range of naturally occurring chemical compounds has been used including starches and gums.

4.4.1 Starch and similar natural products

There are numerous sources of ‘starch’ and these include the seeds of wheat, rice, maize and so on; the piths of plants, such as sago; roots, such as tapioca; and tubers, such as farina from the potato tuber. The preparation of useful products can be complicated where, for example, adventitious matter such as soil or plant residues have first to be removed. In the case of wheat starch, the presence of protein material can alter the final properties of the starch mix.

The starch grain is normally insoluble in cold water and the process of purification involves mechanical rupture of the plant cell form, followed by washing and subsequent separation of the starch grains, and drying. The starch grain usually contains a number of carbohydrate compounds, the principal ones being ‘amylose’ and ‘amylopectin’, the amounts of each component being different depending on the source and the presence of other polysaccharides. Each source of starch can be identified by the structure of the grain and there are many references in the literature. Starches have two big advantages; they are freely available and relatively cheap.

As well as the starch-based natural materials, there are a large number of other natural products based on plant exudations; the adhesive properties of the gums are well documented, especially for their use in textile printing. The various gums have different properties; some are soluble in water and some are not, and there is a range of properties in between. The gums have a number of disadvantages in that their separation and final preparation are complicated, the quality is variable and costs are high, but low add-ons are used. The various gums and their sources are listed in Table 4.1. Heat and other chemical treatment of animal waste products produce a range of glues or bone sizes, and these have specialist outlets usually as adhesives.

Table 4.1 Starches and gums

Gums	Starches and flours
Gum tragacanth	Wheat flour and starch
Gum arabic	Farina (potato starch)
Gum senegal	Rice starch
Gum karaya	Maize or corn starch
Indian hog gum	Sago
	Tapioca
	Arrowroot

The main types of starch may be distinguished by microscopic appearance (Figure 4.1). The principal property of all starch grains is that at a certain temperature during an aqueous heating cycle the cell wall of the grain bursts and the starch becomes gelatinised and so produces a viscous liquid. Each individual starch has different gelatinisation and viscosity characteristics (see Table 4.2 and Figure 4.2). The presence of other components in the starch mixture can alter the film properties and it is normal for the final processing liquor to be a mixture. The final fabric property depends on a number of factors as well as the effect of the individual starches.

It was also found that these various sources of starch and gums could be chemically treated to produce products with changed properties – for example, fully soluble starch that gives clear films on drying, or products with adhesive properties or flexible films. The production of these thin or clear boiling starches increased the range of finishes, especially as their application to coloured goods does not affect the colour. Two of the best known chemically produced products

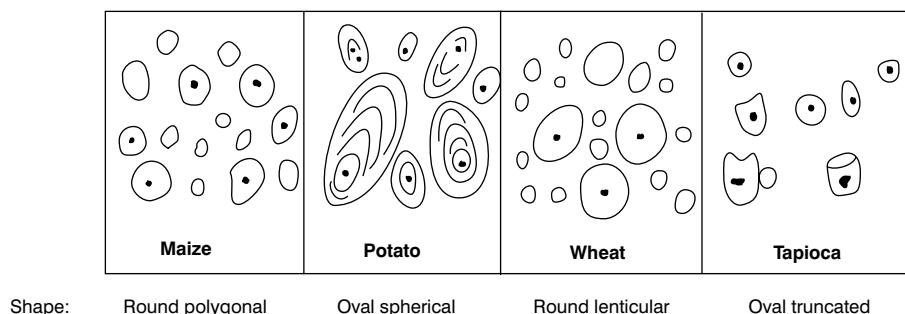


Figure 4.1 Microscopic appearance of starch grains

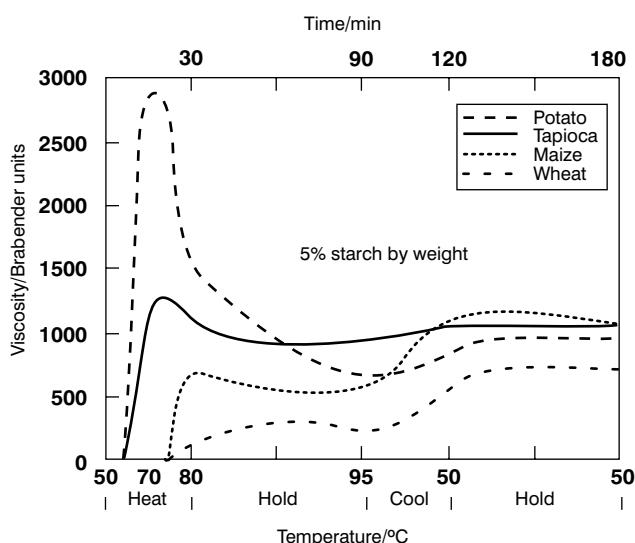


Figure 4.2 Brabender viscosity curves of native starches

Table 4.2 Gelatinisation of starch

Starch	Gelatinisation (°C)		
	Rupture clearly marked	Gelatinisation begins	Gelatinisation complete
Rye	45.0	50.0	55.0
Maize	50.0	55.0	62.5
Chestnut	52.0	56.3	57.7
Barley	37.0	57.5	62.5
Potato	46.2	58.7	62.5
Rice	53.7	58.7	61.2
Tapioca	50.0	62.5	68.5
Wheat	50.0	65.0	67.0
Buckwheat	55.0	68.7	71.2
Acorn	57.5	77.5	71.2

are dextrin or British gum, with low viscosity and good adhesive properties, and glucose. The preparation of thin boiling starches enabled very high solid content processing liquors to be made; usually, the maximum workable concentrations are in the order of 5%, whereas 40% solid contents are possible with these ‘modified starches’. The usual methods of treatment are hydrolysis, heat treatment, oxidation with various oxidants and esterification, or combinations of these treatments. These various chemical treatments can also be applied to cellulosic materials to give appropriate properties designed for specific end-uses. For example, cellulose esters, cellulose ethers, cellulose hydroxyethers and many other specific compounds have been produced for specialised end-uses.

It is obvious that the range of mixtures of the various products is enormous and the production of processing liquors to give specific fabric properties can be difficult to quantify. The recipe for any finish will depend on the fabric and the finishing machinery to be used.

In the past most of the known materials were used extensively but now because of price and the need for constant quality the starches based on farina and maize (corn) represent the major usage. The use of starches for finishing is also very closely allied to their use as sizing agents for textile yarns. Similar structural and mechanical properties are called for, and occasionally the requirements for the sizing process are at odds with the operation of efficient chemical processing of the final woven fabric.

4.4.2 Filling or weighting agents

The predominant use of agents for the filling and weighting of fabrics is in the finishing of cellulosic fabrics; little weighting of wool is carried out but, depending on the state of fashion, silk can be similarly weighted.

Table 4.3 lists the substances that have been traditionally used as filling or weighting agents.

There are a number of other products that have been traditionally used, but they are now found only in specialist finishing works. Table 4.4 lists some of the products that have been used for specialist end-uses.

Table 4.3 Weighting and filling agents

Magnesium sulphate – Epsom salts
Sodium sulphate – Glauber's salt
China clay
Barium sulphate
Barium chloride
Titanium oxides
Tin salts (for silk fabrics)

Table 4.4 Other finishing agents for special effects

Carragheen moss extracts	Softening agents
Sulphonated oils	Softening agents
Various soaps	Softening agents
Oleine oil	Softening agent
Tallow and paraffin wax in various emulsion forms	Handle and lustre modifiers
Glycerin	Softening by hygroscopicity
Glucose	Softening by hygroscopicity
Pigment blues aquamarine	'Blueing' agent
Antiseptics	
Silica products	Anti-slip finish

All the substances listed in Tables 4.3 and 4.4 were used in great quantities by the old traditional finishers; many hundreds of tons were used annually. However, the introduction of new synthetic finishes with highly specialised properties and a change in finishing styles have seen their usage decline considerably.

In the past, the composition of finish liquors was quite complex and surrounded by severe professional skill and jealousy, even to the extent that 'journeymen' starch mixers travelled from works to works making-up their special mixes. Old finishing books such as Percy Bean [2] contain many specific recipes, but the following sections indicate the types of mixings used for a variety of the more common finishing styles.

Starching to alter handle

Starch mixtures have been used to improve the handle of dyed and printed goods; bleaching can cause the fabric to become quite soft. The light application of starch can improve aesthetic appeal or it can give the fabric a temporary handle to aid making-up into the final article. Fabrics with some degree of dimensional stability can be handled much more efficiently by sewing machinists.

For example, a handkerchief is always sold with a crisp finish. A light application of farina starch enables the fabric to be folded with a neat crease to produce an attractive looking product at the point of sale. Coloured woven dusters, bleached or printed tea towels and damask style tablecloths are treated in the same way. As the finish has to be temporary and has no technical value it must be cheap, and so starch is used.

Where fabrics are incorporated in the manufacture of other products – for example, in the shoe trade – small patterned components are cut out prior to assembly. Handling can cause fraying of the cut edges, which can be reduced by the application of a starch solution to stick the yarns together for the machining process. Some of the stiffness is removed during assembly.

Fabric used for component manufacture is often finished at the full cloth width, then slit into narrower component widths. A simple anti-fray finish is applied to ease the slitting process and to stop the cut edges from breakdown during handling. The ‘bias binding’ market is considerable for the clothing, household and furnishing and furniture trades. The anti-fray process can of course include other finishing effects such as stiffening or tinting to indicate cloth quality. Typical processing routes are given below:

- light stiffening – up to 5% of farina starch with the addition of gums or softening agents applied by nip or slop padding, and dried;
- anti-fray – up to 5% of dextrin or thin boiling starch applied by padding, and dried; gums can also be used.

Components for industrial and engineering tools and products often contain textile materials, which have special properties. Fabrics treated with starch and starch mixtures to give abrasive properties are made into polishing mops for a variety of end-uses especially in metal polishing.

There is a need for fabrics with a very stiff handle where the structure of the fabric is more like rigid sheet than a flexible cloth. Such fabrics are used for their support properties. Cotton drills were used traditionally as the inner support for belts and all types of accessory manufacture. Much stiffened fabric is used in the manufacture of millinery and hats. A starch-stiffened fabric of cotton or jute can be steamed to give the right shape (plastic materials do not have this property). A buckram fabric either of cotton or jute can be manipulated with the aid of steam into quite complex shapes. A typical process is given below:

- heavy stiffening – up to 5% of farina and/or maize starch with the addition of 10–20% of dextrin or other clear boiling starches; many specially formulated recipes; often multiple padding applications are used.

Starching to give added weight

Traditionally, woven cotton fabrics were treated in the loomstate with mixtures of starches and china clay. This had the effect of increasing the weight of the fabric, blocking the fabric interstices, removing creases, stiffening and so stabilising the cloth structure, and providing anti-fray properties. The shoe trade still uses fabrics from light to heavy weights finished by this route. The final goods not usually being visible, the cheapest products are used.

There are end-uses where the visual appearance of the final product is important and in these cases high quality filling agents such as barium compounds and even titanium dioxide are used. Large amounts of bleached fabric are padded or coated with these mixtures for the label trade; after coating, the fabric is often heavy calendered prior to printing and slitting. The production of drawing or tracing cloths involves multiple padding on a medium weight but

finely woven cotton fabric, with a mixture of starches, dextrans and gums with the addition of waxes and soaps. After drying, the filled fabric is subjected to hot calendering where the action of the heat and pressure on the starch and waxes produces a translucent shiny pliable sheet.

A finish with good visual appearance but complete opacity is required in the manufacture of 'shroud' cloths. The bleached white fabric has to be treated to give complete opacity with a degree of resistance to handling. The application of these finishes cannot usually be carried out by simple padding as the add-on levels required are not possible by this method. Traditional coating methods were developed which were quite different from those used by the usual finishing trade. Two legendary pieces of equipment were developed for the heavy coating of cotton fabrics – the Betty Dodd and Tommy Dodd machines. Details are given in Figures 4.3 and 4.4.

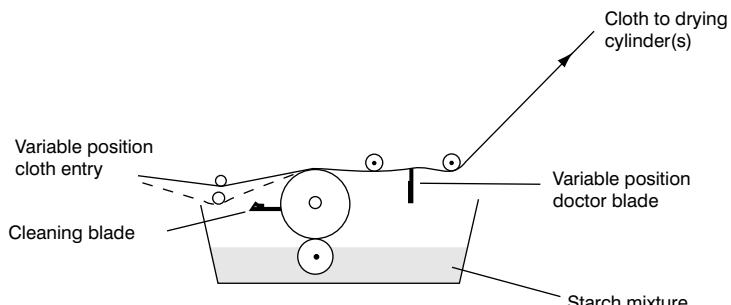


Figure 4.3 Betty Dodd back-coating machine

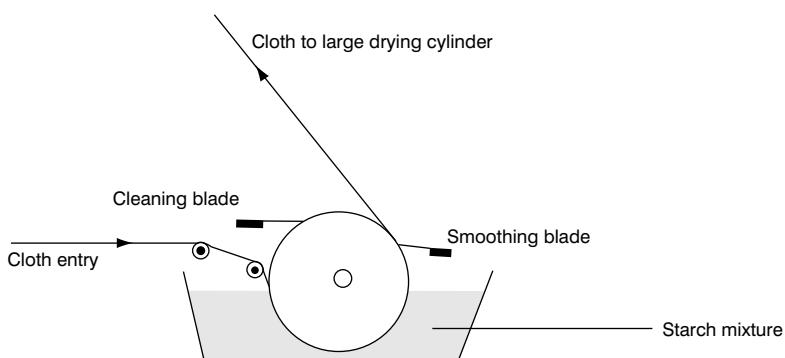


Figure 4.4 Tommy Dodd back-filling machine

Some speciality finishes

In Table 4.3, the use of Epsom and Glauber's salts for the weighting of fabrics was mentioned; however, there is another use for these salts. Fabrics treated using mixtures of these salts with china clay in different proportions can be made into polishing mops for the metal treatment industry. The different metals need different combinations of cloth and finish, and high consistency of cloth and finish is required.

The proportions of prepared starch solutions have been described and the use of their viscous

nature and stiffening and filling properties indicated. The modified starches and gums also have significant adhesive characteristics and this property has been employed in the combining of fabrics. The two fabrics to be combined can be treated in a whole variety of ways depending on the final end-use. A combined fabric exhibits quite different mechanical behaviour compared to a single fabric of similar weight and thickness.

Combined cloths to act as stiff supports are usually treated first with a starch mixture to seal the cloth surface and to give a degree of stiffness. The two fabrics are then brought together through a 'dry' nip after receiving a coating of adhesive on the inside surfaces. Usually, the base cloth is coated with the adhesive. Where the face fabric is to be the decorative side then only the back base fabric is wet processed prior to the combining stage. After the combining or laminating nip, the fabric is dried to complete the process. Traditionally, a wide range of prepared starches, gums and glues were used for these processes. Today, newer modified starches and synthetic adhesives are often incorporated.

Very light scrim fabrics are often combined to paper products to act as supports for further processing and moulding. The production of book cloths is an old established industry using cloth and paper products often with multiple processing routes. In many cases, the finish liquors contained pigments so that the coated fabrics could be coloured.

The production of jute buckram is carried out in a similar manner. The jute fabric is multiple padded with modified starch products to give a stiff finish with adhesive properties; 20–30% add-on is achieved. Two layers of the stiffened hessian are then passed through a calender nip with the application of steam. Under the effects of pressure and steam the starch mixture becomes softened and adhesion between the two layers occurs. After cooling, the bonded fabric is capable of being slit into narrow widths and steam moulded.

- hessian buckram finish, for hat components and furnishing accessories – 40% modified starch, padded, dried, steamed and calender combined.

The production of fabrics with a 'nice face' is achieved by padding fabrics with a mixture of gums and emulsified tallow or paraffin wax. When these fabrics are calendered lightly with a little heat, lustrous smooth finishes are obtained.

A number of coloured woven fabrics of higher value need to be finished but the surface of the fabric would be spoiled by a wet treatment such as occurs when a fabric is padded. A stabilising or handle-improving finish can be obtained by applying a finish to the back of the fabric without wetting the face. The 'Betty Dodd' type of machine (Figure 4.3) was commonly used for this purpose. The more expensive gums were used, and many sateen and jacquard cloths were finished by this route.

Flame-resistant finishes

There is still a large market for flame-resistant finishes even if the finishes have no fastness to water or washing. There are many traditional flame-resistant products that have been used for many years with varying degrees of success. Many are based on the ammonium salts of a variety

of well-known acids. The flame-resistant properties are good, but there is a tendency to 'chalk' marking because of surface deposition of the finishing agents and their hygroscopicity. Fabric tendering due to the acidic nature of the flame-resisting compounds can occur in storage or in sunlight. The best known flame-resistant finishes are those based on boric acid and borax, of which large quantities were used at one time. These borax mixtures have the problem of 'afterglow', where the charred fibrous mass remains incandescent for a period and can cause further potential flame generation. However, the tendering effects shown by other products are not encountered with borax and its mixtures. Nowadays, for a finish with minimal effect on the handle, low propensity to effloresce and zero afterglow there are a range of mixed phosphates and ammonium polyphosphate products.

Softening processes

Often, the structure of the cloth resulted in the need for the liberal use of softening agents. Some were based on moss extracts – for example, Iceland, Irish or carragheen mosses – which were stable to Epsom and Glauber's salts, and the resulting finish was leather-like, especially after calendering. Soaps and sulphonated oils were used for softening fabrics or for removing the harshness of finished cloth. Glycerin and glucose were sometimes used for their hygroscopic properties, which imparted a softer handle. Softeners are now produced for all fibres from a wide range of chemical types.

Some traditional finishes

Shower- and water-repellent finishes were usually based on the production of wax and oil emulsions, which – when applied to the substrate and dried – resulted in the formation of a layer of wax on the fabric surface. These finishes were acceptable for performance but were prone to marking.

One of the traditional finishes for waterproofing involved the application of large amounts of wax, and the development of the modern waxed or oiled cotton jacket is an interesting technical but more probably a marketing development. Specialist cotton fabrics with good strength but soft handle are dyed and then given a light cuprammonium treatment. This treatment serves three purposes: it chemically singes the fabric surface, it gives a waterproof coating and it provides a degree of rotproofing. After this treatment, the fabric is passed through a bath of molten paraffin waxes so as to coat both sides evenly. A wax addition of the order of 40% is made to the fabric. Garments made from this material are truly waterproof, windproof and silent, and do not suffer the effects of cold weather, as do the synthetic coated materials.

Over many years, fabrics have been finished in a variety of ways, often with a form of trademark to indicate the finish or the export market. Some of these have resulted from ingenious chemical and application methods. Although many have been superseded, it is surprising how many are still used albeit with some modern innovations. In many cases, the reason for the success of these processes lies in the economics of processing for highly specific

end-uses. Often, the actual final presentation of the finished goods is of vital importance. There have been many fancy and intricate forms of making-up, which have enabled the final customer to benefit from rapid conversion of the goods with minimum waste.

4.5 CALENDERING

It had been noticed from the beginning of fabric manufacture that the application of pressure could alter the properties of fabrics. Initially this procedure was carried out in a simple batchwise process, with either a simple hot iron or screw press, with a chesting press or by a form of roller calender. With the roller calender, the cloth was rolled on to a pole that was then subjected to a rolling or static load between the calender rollers. The resulting pressure in the presence of moisture and other finishing agents gave quite interesting results, varying from compacted to supple handle effects and forms of optical effects. The original watermarking finish was produced in this manner; the fabric was treated with starch products, and rolled in a damp condition onto a wooden roller, which was then placed between two horizontal rollers. The cloth roll and the other rollers were then rotated and the rolling action caused yarn slippage in a distinctive way. The cloth was then unrolled and dried. This process could be carried out more than once to produce the desired effects. Obviously this batchwise process was extremely slow and the simple continuous application of a rolling pressure was developed into the present-day process of calendering, which is often at high speed.

In the past, the size and type of calender were often of great significance in terms of commercial value and professional pride. The greater the number and size of the calender bowls, the higher the professional status of the owner. Modern calenders have developed mainly through the introduction of modern materials and modern control systems – the principles of the processes remain the same.

The various parameters affecting the calendering process, and the effects produced, are listed in Table 4.5.

Many papers have been written, and research projects undertaken, concerning the effects of calendering, but because of the large number of parameters involved it is difficult to be specific, and only the general effects will be considered here. It has been found by the author's company that a production run of different fabrics at the same calender settings can produce vastly different final effects, and herein lies some of the so-called 'mystique' of calendering.

The alteration in properties depends on the ability of the fabric to be mechanically changed. So, a soft fibre or a soft spun yarn that has been woven with an open weave will be affected much more easily than a hard fibre, spun tightly and in a close-weave construction.

A light load calender with a soft bowl and low temperature will produce soft, smooth, lustrous handle on light open-weave fabrics. Increasing the temperature or the loading causes more compaction and this leads to smoother surfaces but with more leathery handle. In many cases, this type of finish – often called 'swizzing' or 'swissing' – is all that is necessary to give a fabric the correct final handle. Harsh fabric effects, especially from stenters, can be removed very easily and quickly and give the finished fabric good point-of-sale appeal.

Table 4.5 The calendering process

Parameters affecting the calendering process
Cloth construction
Fibre content
Finish applied
Moisture content
Temperature of the bowls
Running speed
Differential bowl speed – degree or ratio of friction
Pressure applied
Bowl composition
Repetition of the process
Effects of the calendering process
Reduction in fabric thickness
Compaction of the weave structure – alteration to the fabric porosity
Change in the handle – softening effect, stiffening effect
Change in appearance – effect on lustre

The effect of moisture and chemical treatments can also drastically affect the result. A fully dried fabric will not be affected as much as a fully conditioned fabric or a fabric containing a softening agent. The deformation of a fabric under the compressive load will determine the calendering effect; a soft, easily deformed viscose fabric will be altered far more easily than a hard linen fabric or resilient fibres such as wool and polyester. Obviously, the application of increasing pressure or temperature will affect wool more than polyester, but when there is moisture, temperature and pressure the polyester polymer can be drastically altered even to the point of fusion and full fibre bonding leading to a paper-like effect. The same mechanism can apply to the application of finishes, which – under the influence of moisture, temperature and pressure – can be caused to react to produce a whole range of finish effects. The chintz or 'Everglaze' finish was world-renowned and involved padding the fabric with a mixture of resins (usually urea-formaldehyde resins or melamine resins), softening agents and wax-based glazing agents. The fabric was dried carefully so as to prevent overdrying. Moisture contents in the region of 10% were obtained. Heavy calendering or friction glazing caused the surface of the fabric to become very highly glazed. This glazed surface was made permanent by a baking or polymerisation treatment. Subsequent washing removed a little of the glaze but it was fast to washing and many metres have been – and are still – finished for the curtaining and upholstery markets.

A highly glazed finish can be achieved by high temperature and pressure treatment on untreated fabrics but the result can be too papery and of course it is not fast to washing. However, there are many markets where the glazed finish offers a cheap but highly effective finish. The cambric trade for cushions and pillows uses a glazed finish where the 'shiny' glazed side is used inside the pillow; the feathers or filling do not protrude through the fabric because

of the compacted low porosity and shiny surface. There are many other examples of this type of finish.

Many industrial fabrics are finally calendered to give the correct fabric properties. Fabrics to be coated can be calendered to a specific thickness, so that the coating process can be better controlled. A light-pressure, low-temperature calendering offers a fast, cheap method of removing creases caused by packing and transport, especially in the bale form – far cheaper than the use of a wetting and stentering process.

Fabrics and felts for the filtration industry are calendered under carefully controlled conditions so that the right porosity is achieved and at the same time a shiny surface is imparted that then gives good 'cake' release. Filter fabrics made from synthetic fibres in monofil, filament or staple spun yarns can produce highly effective and consistent products.

Calenders and calendering have in the past been regarded as extra processing only to be carried out if absolutely necessary. There have been examples of multistage equipment but the process has normally been of a stand-alone system so that close control of the final finish can be achieved.

4.5.1 Engineering aspects of calenders

Simple swissing calenders

The early calenders had the basic structure shown in Figure 4.5, where two or more rollers were mounted – usually in the vertical plane – in a closed, solid cast iron frame with basic bearings. Obviously, it is not usually possible to run two metal rollers together because of the risk of cloth damage. Most calenders consist of a system of hard metal rollers and a composition softer bowl, and it is usual for the term 'calender bowl' to mean the softer non-metal bowl. There are many combinations of calender configuration. A system of levers was used to load the top bowl, and the bowls were usually driven by electric motor. A system of entry rails was used to guide and tension the cloth through the nip formed by the two rollers. A batching-up arrangement rolled the fabric after treatment onto boxes, which were then taken for further processing. This simple description covers the general construction but there are many calenders with more than two bowls, and during running one or more nips may be used.

The standard three-bowl heavy friction calender shown in Figure 4.5 was built with closed frames for extra rigidity. The compound levers were designed to apply a very heavy pressure to the bowls. The calender could also be used 'dead-set', for heavy work such as book cloth, by locking the top levers to the frames with pins and applying the pressure with the top handwheels. The calender was fitted with a steam-heated, top-chilled iron bowl, then usually a fibre bowl and finally a close-grained cast iron bowl at the bottom. For certain finishes, the fibre bowl was replaced by a harder fibres paper bowl.

Various drive systems have been used, but the primary drive was usually to the top bowl. For friction or glazing finishes, the top bowl and the bottom bowls were directly linked either by gear wheels or chain drives to give the differential speeds needed for the friction effect. Auxiliary drives were present on some calenders to allow for threading up procedures.

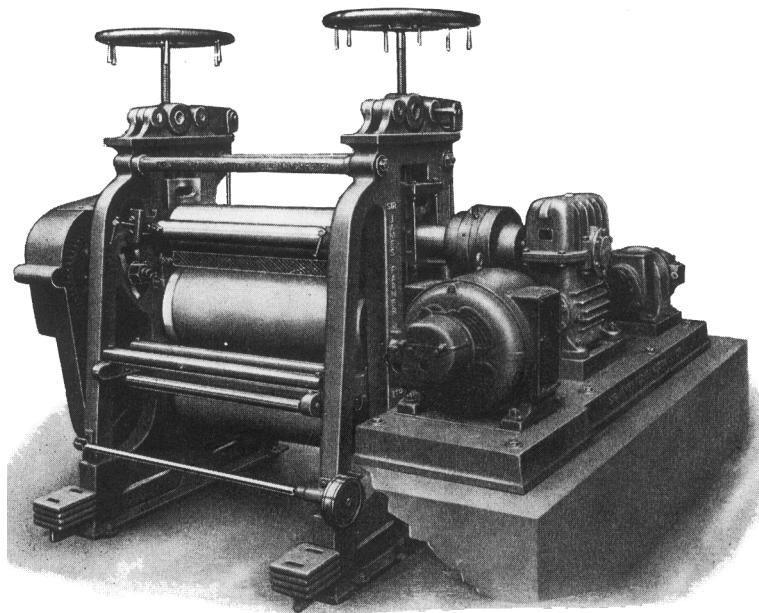


Figure 4.5 Early Farmer Norton three-bowl friction calender with lever loading

These early machines were batchwise and so had a low level of productivity, running from box to box with low yardage because mechanical handling and large 'A' frames were non-existent. As a result, fixed speed motors were acceptable, and manual guiding was the norm. The calender bowls were made out of a variety of materials with each bowl manufacturer offering specialised bowl coverings for different fabric treatment. In many cases, the calender frame was made by one maker and the customer would specify the type of bowl that he preferred. These machines were heavily engineered, often involving civil engineering work in reinforced concrete to a depth of four feet. The torque and loading produced by a 60 horsepower motor with high ratio speed reduction are considerable and not to be underestimated. There were a number of light-pressure calenders made, which needed only low power motors and in the past line shafting was often used for driving the rollers.

One of the major problems with calendering is potential bowl damage, usually caused by 'bad' sewings where more than one layer of fabric is present. The hardness of the calender bowl needs to be high so that the correct finish can be achieved without too high a pressure loading, or excessively elevated temperatures or low production speeds. However, at the same time the bowl must be resilient enough to allow for cloth variations. The surface hardness is measured by driving a small, hardened probe into the surface and directly measuring the load applied through a spring dial. The choice of hardness was a factory choice balancing the need for an acceptable finish against the risk of downtime for bowl treatment. The range of 75–90° Shore hardness is normally that found in most finishing works.

The construction of most calender bowls is illustrated in Figure 4.6. The central shaft or mandrel is covered progressively by the bowl material, which is fitted in circular sheet form from

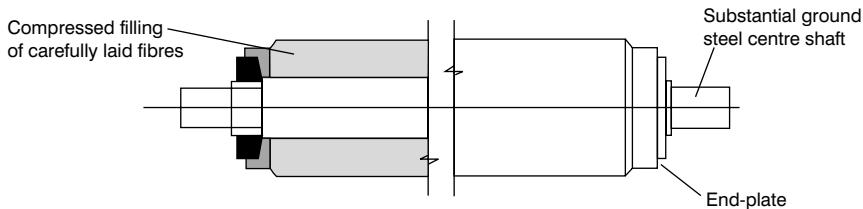


Figure 4.6 Typical filled calender bowl

one end, and the covering is compressed. When the covering, after compression, has the correct hardness the loose end-plate is fitted (or refitted, as the mandrel can be often re-used). The bowl surface is ‘skinned’ or machined to give a perfectly smooth surface with the correct profile.

The composition of the bowl can vary widely but the usual substances used are cotton paper or wool paper or a mixture of each. Cotton paper gives a harder surface offering higher lustre but once marked is difficult to repair. Wool mixtures give a more resilient surface, which can be more forgiving when processing coarser types of fabrics and surface marks can be more readily repaired. Various plastic coverings have been considered, usually based on polyamide and polyurethane materials, and the use of easily removable sleeves has been pioneered by a number of calender manufacturers. The usual construction of the metal bowl is high-quality steel, often case hardened and highly polished, or fine cast iron. Chrome or nickel-plated steel bowls have been produced for certain end-uses where high gloss is required without the resort to friction systems.

The major problem with calender bowls is bowl replacement, its frequency and the related downtime, and the ease of the engineering. Modern calenders have ‘open cheek’ structures where the bowls are located by means of bearing carcasses on the side of the calender frame, making removal of the bowls relatively easy. In the older closed-frame calender, with its great strength, the whole machine had to be dismantled to remove the damaged bowl. Many finishing works had an overhead gantry system so that the calender bowls could be easily lifted out and moved for transport to the bowl maker. Few finishing works had their own bowl repair facilities.

The original closed-frame calenders had open ‘white metal shell’ bearings lubricated by heavy grease for the bottom bowl, and simple phosphor bronze float or block bearings for the other bowls. Modern calenders have enclosed forced lubrication bearings, which can be easily accessed and replaced.

4.5.2 Control of calender parameters

The following parameters have to be accurately controlled if the calendering process is to be consistent on a day-to-day basis:

- (1) pressure, and distribution of pressure, across the nip;
- (2) temperature of the bowls;
- (3) speed, and relative speed, of the bowls.

Application of pressure

The traditional method of applying pressure to the bowl set-up was by a system of levers or direct screw loading. The lever system allowed thicker sections of cloth to go through the nip with minimal cloth or bowl damage but the pressure level was relatively low. The screw system allowed very high 'dead-set' pressures to be achieved but there was always the greater risk of fabric or bowl damage. The modern method of pneumatic or hydraulic pressure systems has altered the calender set-up. Lever or screw systems always work on pressure being applied from the top of the machine, whereas hydraulic systems usually raise the bottom bowls to give contact with a fixed top bowl. Pneumatic systems give a more resilient system, while hydraulic systems are similar to the dead-set screw method. Pressure change can be easily achieved with these systems and many calenders are fitted with rapid pressure release devices, the so-called 'seam' or 'sewing-jumpers'. The device detects a sewing and momentarily lowers the bowl pressure to minimise damage; however, it also reduces the calendering effect either side of the sewing.

The effect of a loading force applied at the ends of the calender bowls causes the bowls to deflect, which results in the nip pressure in the middle of the nip decreasing. Figure 4.7(a) shows a typical representation of a calender nip under light loading and Figure 4.7(b) under heavy loading. A heavier loading, a greater bowl width and a smaller bowl diameter all increase the propensity to deflect, and many devices to compensate for the deflection have been devised. The same problem is also found with mangle bowls and similar remedies have been sought.

The obvious remedy is to have a bowl whose diameter varies along its length, so that the lifting in the middle is compensated by a greater diameter here. However, the correct setting only applies to one specific loading and where different cloth widths are processed problems can arise. Figure 4.7(c) shows the principle of 'cambering' where the softer composition bowl is usually 'ground' in a lathe to give a middle level surface for the width to be calendered and then cambered to the edges to allow for the deflection under the normal processing conditions.

Another method that has been used to solve the problem of bowl deflection involves 'skew' positioning of the bowls. Instead of the bowls being in parallel configuration they are in a skew position, as shown in Figure 4.7(d). The deflection of the bowl is compensated by the skew. The cloth path into the nip has of course to be altered, as it has to be at right angles to the nip and not to the bowl centre line. The use of special bearings is necessary and surface scrubbing of the bowl filling can occur.

Modern lathes can grind a bowl to a parabolic configuration, which gives a larger pressure tolerance. Other loading systems, where the load is applied through cranks to minimise the deflecting effect, have been suggested. The most famous of the devices to give a perfect nip distribution is the swimming roll, in which a series of independent loading sources are located inside the roller. These systems have been described in Sections 2.1 and 3.2.1 – on water removal and padding, respectively – where the same problems have arisen.

A number of calender bowl developments have been made, and the Bentley heat dissipation system is a novel answer to the problem of bowl damage when using high temperatures to achieve fashion, or technically demanding, finishes. These conditions are often found in the

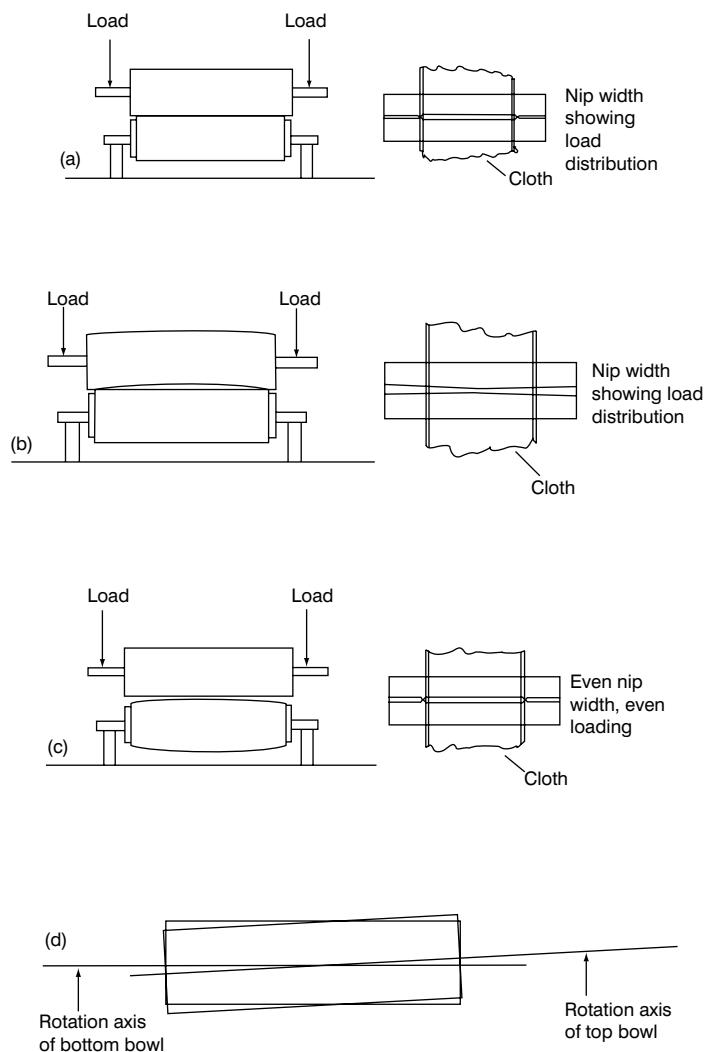


Figure 4.7 Side view of a calender nip under showing the results of various load distributions:
(a) light load; (b) heavy load; (c) cambering; (d) skew positioning

production of high glazed or chintz finishes. Figure 4.8 illustrates the heat dissipation system, comprising a series of thin copper discs dispersed at regular intervals within the fibrous filling material of the composition bowl, which is in contact with the fabric and the high temperature metal bowl. The diameters of the discs, which are in contact with the copper-plated centre shaft, remain below the minimum useful diameter of the bowl and do not affect its resilience. Copper rods are inserted axially into the bowl filling though the steel end-plates at each end, and are positioned at carefully determined intervals in order to affect an even transfer of heat from the

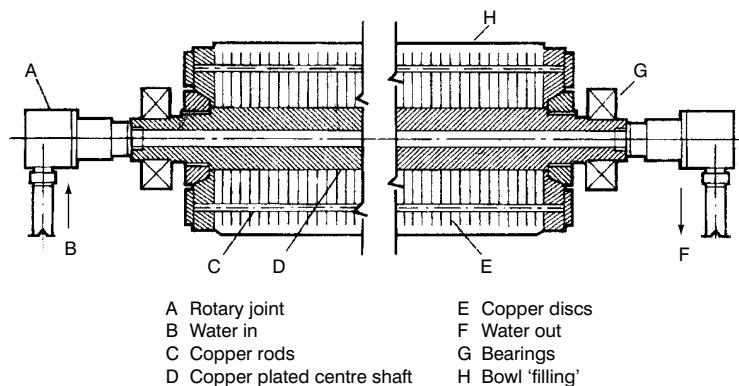


Figure 4.8 Bentley heat dissipation system for calender bowls

filling material into the end-plates and copper discs. To complete the system, the copper-plated bowl centre, which again improves heat transfer, is bored through to allow the circulation of cooling water, thus removing transferred heat from the centre shaft.

Temperature control

Accurate control of the metal bowl temperature is vital for consistent results and this is achieved by gas, electric, thermal fluid or steam heating. Gas and electric heating need very accurate control whereas steam or fluid heating gives level heating profiles. The choice depends on local circumstances. The temperature can vary between ambient for a light smoothing finish, to 190 °C for full lustrous calender finishes. Modern hand-held infrared pyrometers now offer far more accurate temperature assessment compared with conventional surface probes. Normally, only the metal bowls are heated though some composition bowls have heating systems. When extremely high temperatures are used for processing synthetic materials or high glaze resin systems – for example, for sail cloths – cooling coils can be incorporated in the body of the composition. Water can be passed through these coils via rotary joints to decrease the surface temperature and hence the risk of surface scorching of the bowl.

Speed control

Modern thyristor motor controls give highly accurate speed control, which until recently was only achieved by large DC motors or expensive AC motor controllers. The production speed of calenders depends on many factors previously described. In general, the slower the speed the longer the fabric is in the calender nip and so the greater the effect on the fabric. Speeds can normally vary from very slow (in the region of 5 metres per minute) to a top speed of 75 metres per minute. Some machines can process faster than this, but there are many production problems associated with high speeds, such as dust generation and accurate variable tension control.

4.5.3 Friction calendering

To achieve the maximum surface change, a glazing calender is used. The main difference between a simple swizzing calender and a glazing calender, apart from the machine being generally heavier, is the use of a gear system to drive the smooth metal bowl faster than the softer composition bowl. The peripheral speeds of the two bowls may vary by a factor of up to three times, the metal bowl being the faster. The fabric enters the nip and tends to stick to the softer bowl; the faster-moving metal bowl then imparts a glaze or highly lustrous surface to the fabric. Apart from the lustrous effect, the cloth handle can become quite papery and thin. Creating the chintz finish involves close control of all the calender parameters as well as the correct presentation of the fabric to be treated. Incorrect fabric conditions can lead to unacceptable handle that cannot be corrected; most probably, more damage is caused by incorrect moisture content than by any other factor.

4.5.4 Schreiner calenders

One of the problems with friction calendering in producing a lustrous, smooth, drapeable fabric is the potential for papery thin handle and this problem was solved by the use of a ‘Schreiner’ calender. ‘Schreinering’ is a form of embossing whereby fine lines engraved on a metal roller are transferred to the fabric by passage through the nip between the heated engraved roller and a filled bowl. Instead of using friction to achieve a lustrous effect, the metal bowl is engraved with very fine lines at an angle so that when the fabric is calendered these lines are impressed on the surface of the cloth. With the correct cloth construction and the correct line direction of the engraving, a soft lustrous handle can be achieved, and many metres of Schreinered cloth have been – and are being – produced, mainly on sateen fabrics.

The finish, of course, is not fast to washing, but it produces a fabric with good point-of-sale appeal, often called the ‘silk’ finish. A production problem with these calenders is the ease of damage to the engraved bowl and also the pick-up of lint in the very fine engraving, which naturally spoils the optical effect.

With the correct cloth, and engravings of up to 500 lines per inch at an angle of 20° to the weft, extremely lustrous fabrics can be obtained. Nowadays, plain fabrics are given an imitation Schreiner finish using a bowl with only 150 to 200 lines per inch.

The cloth to be finished must be correctly pretreated; good bleaching and dyeing must follow the singeing process and a light softening treatment is followed by drying to the required moisture content.

For Schreinering, the engraving is so fine that the filled bowl is not usually positively driven and rotates by contact with the metal roller. Thus a filled bowl can be used against different Schreiner lines, whereas in true embossing a filled bowl, once impressed with a specific embossing design, can only be used with that particular design.

Broadly speaking, the cross-section shape of the engraving is either a V-shape or a U-shape. V-shapes give more sparkle of light reflection, or ‘character’ of lustre, whereas the nearer to a U-shape the engraving cross-section is, the nearer is the lustre to that of a normal calender glaze.

All Schreiner finishes reduce fabric tensile strength and the loss is greater with deep V-type engravings.

It is a first principle that the angle of the engraving should follow the approximate angle of the line of the twist of the yarn. As yarn twists are either S or Z, it follows that the line of engraving will incline to the left or to the right. Thus for a weft-faced fabric, the inclination will be either left or right and at an angle of 15–25° from the horizontal. For warp-faced fabrics, the same principle applies: according to the yarn twist, the direction is either left or right but the angle is usually confined to about 15° from the vertical.

An exception is a purely vertical line – that is, perpendicular to the roller axis. This has the merit that on warp faced-fabrics it can be used with either S or Z twist. It can also be used successfully on plain square-weave fabrics irrespective of S or Z twist.

Once a fabric has been finished with a particular Schreiner line, it cannot be refinished with the same line, as this may cause a ‘moiré’ or ‘watered’ effect. Watering may occur even if the previously finished fabric has been re-dyed and no apparent line is visible on the re-dyed fabric. Commercially, if refinishing is necessary, a different line is chosen for the second finish, varying as far as possible in lines per inch and in angle.

Process conditions

For any Schreiner line, the result is governed by:

- (1) moisture content of fabric; dry fabric cannot be finished satisfactorily and it is essential that the moisture content be not less than the standard regain, which is 9–15 % for cotton, for example; this is usually ensured by pre-damping;
- (2) temperature – 120–160 °C;
- (3) nip pressure – 3.5–5.0 Bar;
- (4) speed – 2–10 m min⁻¹.

Note also that the darker the colour of a fabric sample the better it shows the lustre of a particular Schreiner line. Conversely, on a white fabric, quite different Schreiner lines appear to give the same lustre, not much different from a normal calender glaze.

4.5.5 Embossing calenders

The production of engraved Schreiner bowls was related to the manufacture of fully engraved bowls, and in the past much cloth was processed by this route. The embossing calender usually consists of two bowls; the top metal bowl is engraved with a suitable pattern and the softer composition bowl has a surface that will accept the embossing pattern.

For true embossing, the filled bowl has to be first impressed with a specific, deeper, reversed version of the design on the steel roller; this can only be done if the filled bowl is positively driven at the same peripheral speed, so that the impression remains in register. These bowls are specially made with super-resilient properties and often both the bowls are heated.

The embossed bowls were, and are still, quite expensive to produce and the embossing process can be quite slow. Originally, these calenders were used to produce imitation leather cloth and book cloths. A moiré embossed effect can be produced by an embossing roller but of course there will always be a repeat to the effect. The application of an embossed crepe design on easily deformed viscose fabrics gave a whole family of creping effects.

4.5.6 Moiré calenders

The moiré effect is an optical effect produced when a tightly woven fabric with very fine yarns is subjected to a surface pressure that distorts the weave structure by yarn movement or yarn self-compression. It resembles the watermarking effect produced by repeated damp rolling techniques, as previously mentioned (Section 4.5). The moiré effect can only be produced when the fibre being treated is capable of being deformed; for example, wool does not produce bold patterns because it has good resilience and springs back after deformation in the calender nip.

The moiré effect is in demand for a number of styles, including heavily moiréd cotton and synthetic fibres for curtaining use where the moiré effect is produced on plain dyed materials. Similar fabrics are used for wall coverings to produce subtle patterns that hide any wall imperfections. Acetate and viscose fabrics are given a moiré treatment and used in presentation boxes and as the lining in purses and handbags.

A number of moiré calenders have been produced, having two or three bowls. Cloth feed arrangements allow two layers of cloth to be passed, one on top of the other, through the heated nip to give the desired effect. The finish is usually carried out twice with the cloth turned over for the second run. This evens out the gloss produced by the metal bowl.

Some extremely attractive results have been produced and there are many jealously guarded secrets as to how the best moiré is produced. Clever cloth guiding devices to give traversing movements and so alter the effect are recorded. The use of a Schreiner calender with cloth traversing also gives a watermarking pattern.

Moiré effects are still produced for special uses and the refurbishment of ‘stately homes’ often requires the reproduction of finishes as they used to be produced, and this can tax the ingenuity of many a works finisher.

4.5.7 Chasing calenders

As many generations of finishers have been aware, when two or more layers of fabric are passed through a nip, useful changes to the fabric handle occur. One of the early cotton finishes was that of beetling, which was related to felting in wool. Repeated compression with wooden hammers produced a soft handle on linen fabrics. As linen was regarded as one of the best fibres in existence, there were attempts to finish cotton with linen properties. Multiple passage through the various nips gave linen-like slub effects and, with some fabrics, watermarking and moiré effects.

As a result, calenders were and are made with multi-bowl configurations of different bowl types – some heated and many with clever loading arrangements – with the number of bowls related to the commercial status of the company. The cloth path allows the fabric to pass from nip to nip from top to bottom of the stack; it is then returned to the first nip and passes down the stack as a double layer until it emerges at the bottom for rolling up. One of the problems with this type of arrangement is that it is batchwise. Although clever cloth passage arrangements are available to give continuous running, they are very space consuming.

Chesting calenders have been produced, usually with five bowls. The fabric is run progressively through the nips but it is allowed to run onto the top bowl and build up. Again, this is a slow batchwise process but gives special thready finishes.

The majority of calenders now in use for commercial production require high throughput. They tend to be of simple construction but will be extremely well-engineered with full control of all the parameters discussed. Two- or three-bowl calenders are the norm but they are capable of producing special effects to satisfy aesthetics or high technical specification.

4.6 EMERISING

Emerising (also known as sueding or sanding, in the USA) is a process in which fabric at open-width is passed over one or more rotating emery-covered rollers to produce a suede-like finish [3]. Woven and knitted fabrics and also laminated fabrics may be emerised, the surface appearance, texture and handle of the treated fabric being altered according to the emerising conditions [4]. Woven cotton denim fabrics may be given a suede-like finish while polyester and nylon microfilament fabrics have been given a peach-skin finish which can impart a soft luxurious handle, especially if chemical softening agents such as amino-functional polysiloxane softeners have been applied.

The major change in the fabric after emerising is the production of a very low pile – that is, short fibres protruding from the fabric surface [4]. The handle will differ according to the type of fibre(s) present, the fibre linear density and the intensity of the emerising action on the fabric. In general, the handle of a fabric is much softer after emerising and the softness can be greatly enhanced by using fine microfibres ($<1 \text{ dtex f}^{-1}$) together with chemical softening agents to give a peach-skin finish in which short fibres protruding from the fabric surface simulate the soft handle and appearance of natural peach-skin [5–9].

Emerising of microfibre fabrics should be carried out prior to dyeing [6–9]. Experience has shown that emerising a dyed fabric can result in very slight unevenness, and especially stripiness [9,10]. A further problem arises from the coloured dust generated by emerising the fabric. This dust settles in the fabric and must be removed. Where grey fabric is emerised, however, the subsequent wet processing – that is, dyeing and rinsing – may be used to remove the dust.

4.6.1 Multi-roller emerising machines

The most versatile and common form of emerising machine is the multi-roller type, which

typically may have 4–8 rollers [4,5,9]. Each roller is independently driven and may be rotated in a clockwise or anticlockwise direction, causing the rollers, covered with emery paper, to turn with or against the direction of the fabric run.

The surface character of the rollers can be varied within wide limits. For example, the grade (grain or grit) size on the surface of the abrasive emery-covered cylindrical rollers may be varied according to the fabric requirements [4,5]. The napping action of the multi-roller machine subjects the fabric to the abrasive effect of the emerising rollers, varying pressure being applied through adjustable idle rollers that lower the fabric to a greater or lesser degree into contact with each abrasive cylinder.

Essentially, the emery-covered rollers function as a cutting tool, severing the protruding fibres to produce a velvet-like, very short pile or nap [5]. The effect on the fabric may be finer or coarser depending on the emery grade (or grain) size. Microfibre fabrics are usually emerised using fine grade emery-paper-covered rollers followed by relatively coarse grade emery-paper-covered rollers [5,8]. However, many fabrics are emerised by operating in the opposite order to yield satisfactory results. Entry and exit drive rollers transport and control the tension as the fabric progresses through the machine.

In the multi-roller machine, the emerised or sueded effect obtained is dependent upon the degree of mechanical action on the fabric. This depends upon the following parameters [5,9,11]:

- (1) the number of rollers in operation;
- (2) the direction of rotation of the rollers (that is, with or against the fabric);
- (3) the fabric tension;
- (4) the fabric wrapping angle on the rollers;
- (5) the fabric speed;
- (6) the grade of abrasive grit used in the emery-paper-covered rollers;
- (7) an additional device may be fitted that also sues the reverse side of the fabric.

The multi-roller type emerising machine is generally considered to be more flexible and versatile in terms of the range of surface effects that can be obtained on a wide variety of fabric structures. The multi-roller machines are also more productive than single-roller emerising machines and are particularly effective on spun yarn fabrics.

Operating speeds on multi-roller sueding or emerising machines are generally higher on woven fabrics than on knitted fabrics; typically of the order of 12–15 m min⁻¹ on microfibre fabrics, up to 15–25 m min⁻¹ on spun yarn types of woven fabric, and 10–20 m min⁻¹ on similar knitted fabrics [9]. Precise tension control is required to transport the fabric through the machine at open-width without folds or fluttering [5]. Pre-set tension control must be indicated and maintained constant. Automatic tension re-adjustment must be incorporated on the machine to ensure constant tension should the textile fabric stretch. An absolutely crease-free state is essential, otherwise the abrasive action of the rollers can lead to the formation of holes in the fabric.

Compared with the single-roller sueding or emerising machine, however, the multi-roller type

can have some drawbacks [4,5,9]. For example, the mechanical action is such that yarn knots are often missed so that emerising and opening does not occur. The emerising rollers also hardly heat up so that a longer time is required in the emerising zone, and the mechanical energy is dissipated because of the large number of emerising points. Nevertheless, the multi-roller machine offers the possibility of greater potential variation in surface effect. Individual rollers may have different grades of emery paper (grain or grit size) and may be run in different directions. This versatility offers advantages to textile finishing companies that operate with constant changes in fabrics and specific customer requirements [5]. The generation of fibre dust as a result of sueding or emerising is dealt with by incorporating a self-cleaning dust exhaust and collection system on the machine [9].

4.6.2 Single-roller emerising machines

Single-roller emerising or sueding machines generally consist of one abrasive-covered metal roller and one rubber-covered compression or pressure roller [4,5,9,11]. In some machines, water is circulated through the interior of the metal cylinders to help prevent the abrasive-covered roller from expanding as heat is generated from the friction created by grinding against the cloth. In more recent machine designs, the abrasive-covered metal roller may be refrigerant-cooled, particularly where emerising of high-friction synthetic microfilament fabrics of polyester or nylon is carried out [9].

The compression or pressure roller is micro-adjustable and is used to press the fabric against the abrasive roller. Thus, the abrasion and cutting of the fibres on the fabric surface takes place in the nip formed between the pressure roller and the abrasive roller [4,5,9]. Compared with multi-roller machines, the single-roller emerising machine is less productive, with a typical operating speed of about 7.5 m min^{-1} on microfibre fabrics [9]. Imperfections in the fabric surface caused by slubs or knots on the back of a spun yarn fabric can lead to damage and holes. Where the fabric selvedges are thicker than the cloth, as a result of shuttleless weaving, this can lead to over-treated selvedges on single-cylinder machines, a fault that does not usually occur on multi-roller machines. On certain styles of fabric, the single-roller machine may be utilised to develop a directional pile effect on the cloth, whereas the multi-roller machine may be operated with the emery-paper-covered rollers rotating in opposing directions, thus eliminating this effect.

The single-roller machine, however, is used especially on fabrics with terry loops on the face that must be broken, and also on difficult fabric styles where the fabric surface must be effectively shaved – that is, cleared of fibre to produce a polished or burnished effect [4]. In addition, an engraved roller can be employed in place of the rubber-coated pressure roller to produce patterns on the sueded fabric [9]. The action of the single-roller machine can thus be employed to create a wide range of surface effects. The ability to exert mechanical action on the fabric at a precisely-adjustable grinding depth eliminates all differences in fabric thickness [4,5]. Problems can arise, however, if there are natural differences in the fabric thickness – that is, through tight threads or differences in shrinkage, because these will be intensified on the single-roller machine. Single-roller machines also incorporate a self-cleaning dust exhaust and collection system.

4.6.3 Technology of emerising

On multi-roller machines, it is normal practice to have the first roller run in the counter direction to the fabric passage [5]. This exerts mechanical action against the weft threads, lifting the surface. The second roller operates in the same direction as the fabric passage, which emerises the weft thread. The third roller runs in the opposite direction to intensify the process and the following rollers run in the same direction as the cloth to produce the nap. There are many variations in operating procedure depending on the fabric structure, the number of emerising rollers and the effect required [5–9,11,12].

Because of the abrasive action on the fabric, care is required to ensure that the loss in fabric strength is not excessive. In addition, the deterioration of the abrasive surfaces of the emery-paper-covered rollers must be allowed for over the operating life of the roller (that is, about 100 hours of operation) [12]. As the emery surface wears, a larger surface contact area is required to achieve the same moment of friction as emery in a finer state. The emery-paper-covered rollers may be replaced easily – one at a time, if required – to minimise the change in the mechanical action on the cloth.

4.6.4 Fabric construction

Yarn selection and fabric construction are important factors in sueding and emerising [4,5]. With woven fabrics, it has been observed that, as in raising, the weft yarns contribute the most towards surface fibre development. Thus, a tight fabric construction in a plain weave will be much more difficult to suede or emerise than a $2/1$ or $3/1$ twill, where the long weft floats can be utilised to enhance surface fibre development [4]. Finer fibres, such as microfilament fabrics, produce a greater degree of surface cover and because the fibre resilience is lower, the handle is softer after emerising.

4.6.5 Abrasives and emery grades

The use of a relatively coarse grade (grain or grit size) of 80–100 allows the weft threads to be caught and lifted by the emery-paper-covered rollers. This coarse grain generally produces a dense, long pile [5]. However, light-weight ladies' outerwear fabrics of $100\text{--}180\text{ g m}^{-2}$ are sueded with a grain size of 280–320 to produce a short, dense nap. With the finer microfibres of polyester and nylon, the grain size is increased to 400–600 for emerising [5]. Higher grain sizes of around 600–800 are rarely used because they exert a polishing action rather than an emerising action on the fabric. If the abrasive is too fine, then enough heat may be generated in synthetic fibre fabrics to induce fusing and harshening of the fabric, while too coarse an abrasive grade could tear or rip a fabric unevenly [6].

Emerising rollers on multi-roller machines may be of cylindrical or of slatted design [5]. Rollers of the latter type exert extreme mechanical action on the fabric surface to lift, emerise and nap the weft. A grain size of 80–120 is used on the slats, which are used to advantage on smooth cotton, cellulosic fibre or woollen blends to give them a more wool-like character.

However, slatted rollers can lead to high noise levels and in some cases the rollers are enclosed in a soundproofed chamber to keep the noise generated to an acceptable level.

Silk, jacquard and more delicate fabrics are only treated using cylindrical rollers, which run quietly and are easily changed [5]. Where microfibre fabrics are emerised, the action of the cylindrical rollers can be carefully controlled by using uniform fabric tension and ensuring that the fabric is in tangential contact with the abrasive rollers, minimising the surface contact area [9]. The use of slats or battens held in a segmented roller can generate a beating action on the cloth to aid the removal of dust. On cylindrical roller machines, dust may be forced into the fabric and must be removed using brushes or suction devices.

4.6.6 Fabric tension

As stressed previously, the tension must be adjusted to suit the particular fabric being emerised or sueded. The tension should be controlled at a pre-set level and any changes in fabric length should not lead to tension changes on the machine [5]. This is particularly important in relation to the emerising of knitted fabrics which are generally more dimensionally unstable compared with woven fabrics when placed under tension.

4.6.7 Emerising of polyester microfabrics

Typical processing sequences for woven polyester microfabrics (composed of polyester microfilament yarns) are illustrated in Table 4.6 [6].

Polyester fibres are tough and will cause greater wear of abrading surfaces than many other fibres. The hydrophilic nature of polyester fibres also allows static electricity to accumulate on the fabric. To help avoid this problem, static eliminators may be fitted to the emerising machine. However, before emerising is carried out, it is essential to treat the fabric with a non-permanent

Table 4.6 Processing woven polyester microfabrics

Loomstate fabric		
Route 1	Route 2	Route 3
Desizing and washing Boil-off, open width, tensionless	Desizing and washing Boil-off, open width, tensionless	Desizing and washing Boil-off, open width, tensionless
Apply sueding lubricant and stenter dry	Dye or print	Denier reduction
Sueding (emerising) and stenter dry	Apply sueding lubricant	Dye or print
Pre-heat set	Sueding (emerising)	Finish and heat set
Dye or print	Finish and heat set	
Finish and heat set		

softener (or sueding lubricant) [6–9]. This is carried out on fully-scoured and relaxed fabric to ensure that close control over the emerising treatment, and a better visual appearance, is obtained after dyeing. Products, such as a formulation containing a fatty acid condensate combined with an antistatic, are normally padded onto the fabric, which is then dried to about 7% moisture content [9]. Over-drying the fabric at this stage can result in emerising being excessively severe.

The majority of polyester microfibres are emerised before dyeing as this gives more uniform results. Emerising after dyeing and finishing using a standard softener can lead to a shade change and a frosty appearance, especially in medium/heavy depths of shade [9]. The function of the lubricant is to lower the inter-fibre and fibre–metal friction and minimise static build-up. This promotes uniform emerising and eliminates problems of fabric control due to static accumulation.

The factors that are important in emerising are [9]:

- (1) choice of the emerising machine;
- (2) emery grit grade;
- (3) roller speed;
- (4) roller direction (with or against the fabric passage);
- (5) fabric tension control;
- (6) fabric processing speed.

If excessive dust and lint are generated, these may be washed out of the fabric at 85 °C prior to post-stentering/dyeing. Peach-skin and suede effects can be produced by emerising micropile and micro-loop fabrics, respectively, composed of yarns of differential shrinkage characteristics [9]. Medium differential shrinkage yarns produce a micropile fabric during relaxation/shrinkage which forms the basis for light emerising to yield a peach-skin finish. Very high differential shrinkage yarns form micro-loop fabrics, the basis for suede-like effects.

4.6.8 Surface emerising for the stone-washed effect

The Biancalani Petra machine has been developed to provide a stone-washed effect on woven fabrics, the intensity of which can be varied reproducibly [14,15]. In this machine, one side of the fabric is given a uniform surface treatment that removes any loose dyestuff and imparts a slightly lighter colour. Fabric is wound under a uniform tension from one roller to another, both rollers being driven. In between the rollers, the fabric is subjected on one side to the action of a number of hinged transversal beams to which an abrasive ceramic material (for example, natural pumice stone) is fastened [14]. These stone-supporting bars are adjustable in angle and pressure against the fabric and abrade the fabric as it passes from roll to roll. After abrasion, any loose dyestuff or fibre may be subsequently rinsed off the fabric by a directed jet of water, and the fabric then dried.

This surface treatment may be applied to light-weight silk fabrics, heavy cotton denim, bleached fabrics and purely synthetic fabrics because of the precise buffing action that the

machine imparts. The swinging, reciprocal action of the stone-supporting bars creates an intensive and uniform effect over the whole surface of the fabric. Apart from exhibiting a polished surface effect, the fabric usually acquires a soft handle and good drape without any fabric deformation. The use of the Biancalani Petra machine may be linked to the Biancalani Airo machine in which the fabric is further mechanically softened by an intensive mechanical action in hot air to provide novel appearance and handle properties [15].

4.7 RAISING

4.7.1 Types of raised fabrics

Raised fabrics are of two main types. The first is produced from staple-fibre spun yarn fabrics, such as woollens, worsteds or cotton winceyettes and velours; the second is made from continuous filament synthetic yarns. The raising process, especially as it is applied to wool fabrics, is described more fully in Section 12.6.

The process for staple fibre constructions consists of pulling out a layer of fibres from the structure of a fabric to form a pile. This results in a lofty handle, and may also subdue the weave or pattern of the cloth in addition to blending the various colours.

In the case of filament yarns, loops in the fabric structure are stretched by the raising action but are not usually broken. Raised loop fabrics are used for nightwear or bed sheets.

4.7.2 Raising machinery

Double-acting machines

Most modern machines are double-acting – that is, they have both pile and counter-pile rollers. Cotton is almost always raised on double-acting machines.

A diagram of a modern raising machine is shown in Figure 4.9. It consists of a drum or cylinder, round the surface of which are mounted a number of wire-covered rollers. The fabric is transported over the wire points, which penetrate the cloth surface to a depth depending on the relative speeds of cloth and rollers. The rollers can be of two types; pile and counterpile, depending on the direction of the points of the bent wires. A typical raising machine is fitted with twenty-four rollers, twelve pile and twelve counterpile, mounted alternately. Each set of rollers is independently driven; their relative speeds, together with that of the cloth, govern the raising effect.

Fabric may require several passes through the machine, or be processed through a line consisting of several machines, in order to obtain the desired effect.

Modern machines are equipped with seam detectors, which interrupt the raising process while a seam passes through the machine, and computers to store raising conditions for various fabrics, so that these can be reset for future runs of the same fabric structure.

The type of nap is controlled by varying the ratio between pile and counterpile energies. With high counterpile energy, a shorter, thicker nap is produced. High pile energy produces a longer, loftier nap.

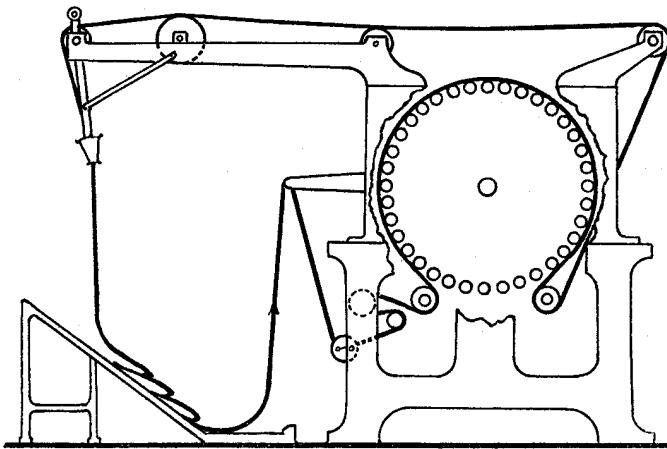


Figure 4.9 Raising machine

If the roller peripheral speed is equal to the cloth speed, no raising takes place, and this is the ‘no-raise’ condition.

Single-acting machines

Single-acting machines are called felting or napping machines. A single-acting machine with pile rollers may be used at the end of the line for felting. If the rollers are set to counterpile only a sueding effect is obtained [16].

4.7.3 Problems in raising

A good account of the causes of faults in raised knitted fabrics is given by Pehl [17].

- (1) Variations in temperature and humidity conditions can affect the raising effect. Cotton is usually processed in a warm, dry condition, although if it is badly creased it may be pre-wetted and re-dried.
- (2) If the pile action is much greater than the counterpile, the cloth may tend to cling to the pile rollers. The cloth on the feed side then becomes very tight and on the backside very slack. This may result in creasing. The machine should be reset to a more balanced action.
- (3) Bad setting of the cleaning brushes ('fancies') can do a lot of damage, but in general uneven raising should be corrected by re-grinding or replacing the wire.
- (4) Changing the fabric width may produce lines due to wire damage at the selvedge of the previous cloth.
- (5) Lateral striping can be caused by yarn variation, which may not show up before raising.
- (6) Streaky or patchy raising may be due to traces of finishing agents.

4.7.4 Raising knitted fabrics

The construction of knitted fabrics has an important bearing on the effectiveness of the raising process. Velour fabrics are knitted with a loop pile on the face, and the choice of yarn for the pile is important. The loops should stand erect without twisting, so twist factor (English) must not be higher than about 3.8. Loop height should be 3.0–3.8 mm, unlike normal terry, which customarily has a loop height of less than 2.5 mm.

Usually raising is carried out after dyeing and drying.

It has been suggested that the fabric should be sheared before dyeing, as the loops are more erect and can therefore be cut more uniformly. This can result in less weight loss and a longer pile.

4.7.5 Testing raised fabrics

The raising effect is assessed by its influence on properties such as:

- (1) tensile strength;
- (2) abrasion resistance;
- (3) air permeability;
- (4) thickness;
- (5) thermal insulation;
- (6) flammability and surface flash (cellulosics).

4.8 COMPRESSIVE SHRINKAGE

For many years relaxation drying was the only way in which fabric shrinkage could be reduced in final processing. In the method known as ‘London shrinking’, the fabric is placed in contact with a dampened wrapping material and allowed to stand under tensionless conditions for some time – usually a few days – and then hung on a frame to dry.

The use of overfeeding mechanisms on a pin stenter, mentioned in Section 2.3.2, was pioneered by Krantz, and this is still a very widely employed method for controlling length shrinkage.

For the production of finished fabrics with the virtual elimination of length shrinkage, however, it is necessary to resort to the technique usually described as ‘compressive shrinkage’.

Two very similar methods were developed at almost the same time: the ‘Sanforizing’ process [18], and the technique devised by Wrigley and Melville, which led to what was later known as the ‘Rigmel’ process [19].

Both depend on the cloth being held in contact with an elastic surface that is changing from an extended state to a contracted form under the action of a compressive force, so that the cloth is also subjected to the same compression.

In the original Sanforizing machine the elastic surface was a thick felt blanket, the thickness varying between 0.275 and 0.45 inches depending on the material to be treated.

The Rigmel system used a thick rubber belt to achieve a similar effect.

The present version of the Sanfor range uses a rubber belt [20]. The fabric is first humidified and steamed. A short stenter is then employed to achieve the desired finished cloth width. The cloth is then processed through the rubber belt shrinking unit to apply the required length shrinkage, and dried on a drum dryer, on which it is held by means of a felt blanket.

With careful control, residual length shrinkage of woven fabrics can be limited to one per cent or less. At the delivery stage, and during inspection and making-up, it is of course important that the fabric is not subjected to re-stretching. Contact rollers are now usually employed for tensionless batching.

For knitgoods stabilisation, modern machines, such as the Sperotto-Rimar TS 150 (for tubular fabric) and TS 240 (for open-width goods), employ a combination of overfeed and tensionless drying/calendering, while compressive shrinkage machines, such as the Tube-Tex 'Compactor', have been developed specifically for knitted fabrics.

A variant of the compressive shrinkage technique, known as the 'confining passage' method, was developed specifically for knitgoods. An example of this is the 'Bestan' machine produced by Hunt and Moscrop.

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CHAPTER 5

Water-repellency and waterproofing

I Holme

5.1 INTRODUCTION

Many terms have been used to describe the water-repellency of textile materials, particularly fabrics, but these terms are often imprecise and do not provide the basis for a clear definition. Marketing terms such as the following have all been used in the past [1]:

- (1) showerproof;
- (2) showerproofed;
- (3) rainproof;
- (4) waterproof;
- (5) rain-resistant;
- (6) shower-resistant;
- (7) rain-repellent;
- (8) shower-repellent;
- (9) stainproof;
- (10) siliconised.

The literature on water-repellency and waterproofing is therefore confusing, firstly because the repellency effect observed depends upon the test method and the test conditions used [2,3], and secondly because in much of the earlier-published literature the term ‘waterproofing’ was universally used [4].

The term ‘water-repellent’ is actually a relative term because there is always some attraction between a liquid and a solid with which the liquid is in contact [5]. Although this force of attraction may be small, it is considered that no solid surface actually exerts a repulsive force upon a liquid. Thus, water-repellency is taken to be ‘the relative degree of resistance of a fabric to surface wetting, water penetration, water absorption or any combination of these properties’ [6] but its assessment is dependent upon objective and/or subjective factors appertaining to the test conditions used.

The term ‘waterproof’ is normally taken to represent the conditions where a textile material (treated or untreated) can prevent the absorption of water and also the penetration of water

into its structure [6–8]. Thus, a waterproof surface provides a barrier to water under all practical end-use conditions. In absolute terms, a waterproof fabric is fully resistant to penetration by water, implying that the fabric water penetration resistance is equivalent to its hydraulic bursting strength [7]. However, in practice a minimum performance of no penetration by water below a hydrostatic pressure of 100 cm (10 kPa) is taken to represent a waterproof fabric [2]. The major differences between water-repellent and waterproof fabrics are illustrated in Table 5.1 [7].

Table 5.1 Water-repellent and waterproof fabrics [7]

	Water-repellent fabric	Waterproof fabric
Pores	Open	Filled
Water vapour permeability	Small to large	Zero to very small
Air permeability	Usually large	Zero to small
Resistance to water penetration	Resistant to wetting by rain drops and spreading and wicking of water. Permits water passage under external hydrostatic pressure	Highly resistant even under external hydrostatic pressure

The most widely used method of producing a waterproof fabric is by coating the fabric with a solid polymeric coating – for example, neoprene (synthetic rubber), polyvinyl chloride or polyurethanes [9]. Such coatings are not porous and therefore provide a continuous solid barrier to liquid water and other liquids, such as oils. However, such solid non-porous continuous coatings are impermeable both to the passage of air and of water vapour. Such coated fabrics are therefore classed as waterproof but are not water vapour permeable – that is, they are not ‘breathable’ [10,11].

For many non-apparel end-uses – such as technical textiles, industrial fabrics, and textiles destined for outdoor use, such as tarpaulins or awnings – this does not create any problem. However, for high levels of comfort in apparel, a fabric in garment form must allow air, and especially the moisture (water vapour) generated by the exudation of perspiration from the skin during physical activity, to pass through the fabric. This maintains the wearer of the garment in warm, dry conditions with high levels of thermophysical and thermophysiological comfort [12,13].

This chapter will discuss the theory of repellency as it applies to textile materials, and the various methods by which both water-repellent and waterproof fabrics may be produced. The extended performance required for the production of textile materials with enhanced easy-care properties – for example, soil- and stain-resistance – and treatments to promote breathability are also described. In addition, the evaluation of water-repellent and waterproof fabrics using standardised test methods is briefly reviewed.

5.2 THEORY OF WETTING AND REPELLENCY

5.2.1 Wetting

Wetting is a most important phenomenon and many treatments in textile wet processing rely fundamentally upon complete wetting out of a textile structure to achieve satisfactory performance [8,14]. The wetting of plane surfaces by liquids can be considered relatively simply in scientific terms. However, the heterogeneous nature of fibre surfaces and the complexities introduced through the nature of the fibre composition and the actual construction of the textile material create difficulties in attempting to predict what the wettability of a particular textile material will be in practice. Another important variable is the temperature of the liquid, because the surface tension of a liquid decreases with increase in temperature [15]. The surface tension of water is also markedly decreased by the presence of relatively small concentrations of surfactants [14,15]. Both these factors can increase the wettability of fibres by water and are of importance in textile wet processing.

Thus, the wettability of a fabric is important from two points of view. Firstly, good wettability is usually associated with good textile wet processing; equally, the ability of the finished fabric to exhibit repellency (zero or low wettability) properties in the presence of water, oil and stains is essential if high standards of water-repellency, oil-repellency and stain-repellency are to be achieved under end-use conditions [8].

In classical thermodynamic theory, the wetting of a solid by a liquid occurs if there is a decrease in the free energy of the system [5,8,14,15]. If the sum of the interfacial energies, F , decreases, then spontaneous wetting will occur as a result of the liquid–solid contact. This may be expressed by the equation:

$$F = A_S\gamma_{SV} + A_L\gamma_{LV} + A_{SL}\gamma_{SL} = \Sigma A\gamma \quad (5.1)$$

where A denotes the area and the subscripts S, L and V represent the solid, the liquid, and the vapour of the liquid respectively. γ is the surface tension – that is, the surface energy per unit area.

Thus, spontaneous wetting occurs when the change in the free surface energy of a system (ΔF) is negative, when the surface energy F_1 changes to F_2 , whence:

$$\Delta F = F_2 - F_1 = \Sigma(\Delta\gamma)_2 - \Sigma(\Delta\gamma)_1 \quad (5.2)$$

Where a liquid contacts a solid, as in immersion or in capillary sorption, the solid–vapour interface disappears to be replaced by a solid–liquid interface. The work of immersion (W_I) or the work of penetration (W_P) under these two conditions respectively are normally defined in terms of the free energy change that takes place when the liquid and solid in contact are separated (that is, the reversal of the wetting condition) [5,8,14].

To obtain spontaneous penetration and a positive capillary rise, the work of penetration must

be positive. This is achieved where the interfacial energy of the solid in contact with vapour (γ_{SV}) is greater than the interfacial tension between the solid and the liquid (γ_{SL}):

$$W_I = W_P = \gamma_{SV} - \gamma_{SL} \quad (5.3)$$

In the case of a solid and liquid in contact, the work of adhesion, W_A , represents the attraction between the two surfaces in contact [8,15]. This work of adhesion is equal to the change in surface free energy of the system when the contact between the liquid and the solid is broken. The loss of the solid–liquid interface and accompanying loss in interfacial surface tension, γ_{SL} , leads to the formation of two new surfaces, namely between the solid–vapour and the liquid–vapour interfaces with associated surface tensions γ_{SV} and γ_{LV} respectively.

The work of adhesion, W_A , is given by the change in free surface energy through the Dupré equation [8,15,16]:

$$W_A = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \quad (5.4)$$

In the case of a liquid, the work of cohesion, W_C , may be expressed in terms of the reversible work required to pull apart a liquid column to create two separate liquid surfaces, each of which will have an interfacial tension γ_{LV} . Thus, the work of cohesion, W_C , per unit area of the interfaces using the Dupré equation yields:

$$W_C = 2\gamma_{LV} \quad (5.5)$$

These idealised equations are, however, only valid for ideal, smooth, homogeneous, impermeable and non-deformable surfaces, but these conditions are not applicable with textile fibres, yarns and fabrics, for which wetting is a much more complex phenomenon [8,14].

Spreading of a liquid over the surface of a solid involves the flow of liquid at least two molecular layers thick. The work of spreading, W_S , similar to the work of cohesion, W_C , is given by the reversible work done, which is equal to the free energy change occurring on the separation of the liquid from the solid. During spreading, both the solid–liquid and liquid–vapour interfaces increase, but the solid–vapour interface decreases. Thus, the work of spreading, W_S (sometimes referred to as the ‘spreading coefficient’), is given by the change in free surface energy per unit area of interface, viz:

$$W_S = \gamma_{SV} - \gamma_{LV} - \gamma_{SL} \quad (5.6)$$

Spontaneous spreading thus occurs when W_S is positive. In practice a drop of liquid placed on a solid is observed to flatten when it spreads, which decreases the liquid–vapour interface because of the decreased curvature of the drop. This decrease is, however, relatively small and is usually considered to be negligible [8].

5.2.2 The equilibrium contact angle

A major problem in the use of these idealised equations in practice is that there is no direct method available for measuring γ_{SV} and hence wettability is normally evaluated using the forces in balance at a three-phase boundary. This is typified by the equilibrium contact angle of a drop of liquid that does not spread over a solid surface, the three phases being the solid, liquid and vapour phases respectively. This is illustrated in Figure 5.1.

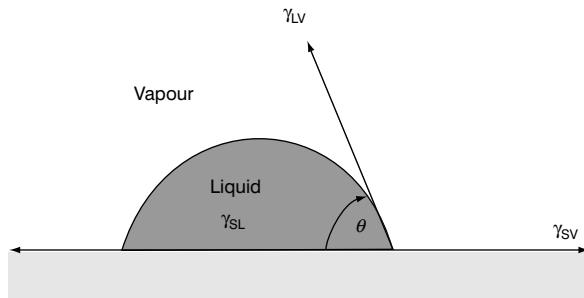


Figure 5.1 Equilibrium contact angle [8]

Where a drop of liquid is placed upon a solid surface and does not spread, the drop shape appears to be constant and the contact angle is given by the value of θ [5,8,14,15]. The equilibrium contact angle θ is generally considered to be indicative of the wettability of the solid by the liquid. High values of contact angle θ indicate poor wettability (for example, $\theta > 110^\circ$) while low contact angles indicate good wettability. Theoretically, the equilibrium contact angle of a completely non-wetting liquid on a perfectly smooth, homogeneous, impermeable and non-deformable surface should be 180° , but in practice none of these conditions are obtained, and indeed the action of gravity can deform the shape of the drop. Thus, values less than 180° are always observed.

The equilibrium of forces on a liquid drop on a plane solid surface as shown in Figure 5.1 is given by the Young equation [17]:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta \quad (5.7)$$

where θ is the contact angle in the liquid at the solid–liquid–vapour boundary. This can be combined with the Dupré equation (Eqn 5.4) [16], substituting for γ_{SV} using the Young equation:

$$W_A = (\gamma_{SL} + \gamma_{LV}\cos\theta) + \gamma_{LV} - \gamma_{SL}$$

$$\text{whence } W_A = \gamma_{LV}(1 + \cos\theta) \quad (5.8)$$

Eqn 5.8 is more useful in practice because the value of γ_{LV} , the surface tension of the liquid, and the value of the contact angle θ are both measurable [5,8]. In addition, the adhesion is related to the cohesion of the liquid because Eqn 5.5 can be rearranged to give:

$$\gamma_{LV} = \frac{W_C}{2} \quad (5.9)$$

Thus, the relative wettability, or otherwise, of a liquid on a surface such as a textile fibre is often indicated by the value of the measured contact angle. Smaller measured contact angles are exhibited by liquids that wet a solid surface, and higher measured contact angles ($> 90\text{--}180^\circ$) indicate a lack of wettability and increased repellency [5,8,14,15].

It should be noted, however, that all the theoretical equations derived so far apply to an ideal system and to the equilibrium contact angle, which differs from the measured contact angle in a real system – that is, water or oil on a textile fibre. An important difference is that in practice in real systems the contact angle measured after the liquid front has advanced on a dry surface is generally greater than the receding contact angle after the liquid has receded from a surface that previously has been wetted [5,8,14].

Thus, there is a real difference between the advancing and the receding contact angles, which is expressed in terms of the contact angle hysteresis [8]. This hysteresis may arise from the surface energy of the solid being changed because of adsorption of the liquid, giving a lower receding contact angle. Other factors that may affect the contact angle hysteresis are the surface heterogeneity or surface roughness. In the latter case, the surface roughness of the solid may be considered in terms of a roughness factor, r , as follows [8,14,18,19]:

$$r = \frac{A_o}{A_r} = \frac{\cos \theta'}{\cos \theta} \quad (5.10)$$

where A_o = observed (microscopic) surface area

A_r = real surface area

θ' = measured contact angle

θ = true contact angle (on a smooth surface)

Thus, if the surface roughness is increased when $\theta = 90^\circ$ an increase in the contact angle is expected, whereas where the contact angle is $< 90^\circ$ an increase in surface roughness should decrease the contact angle [8].

From the viewpoint of textile finish application, it is clearly important that the fibre surfaces in the textile material are uniformly (that is, homogeneously) covered with the finish to ensure uniform treatment and uniform performance. So, for example, the removal of surface contaminants from fibres and fabrics prior to the application of a water-repellent finish is essential to ensure that uniform repellency properties are obtained over the whole surface of the fabric. In practice this is difficult to achieve and the inhomogeneity of the treated fabric surface can give rise to variable repellency performance.

5.2.3 Critical surface tension of a solid

From Eqns 5.3, 5.4, 5.6 and 5.7 given above, it is clear that wetting depends upon the surface free energies of the solid and the liquid. Thus, if the surface free energy of a solid is known, the likelihood of that solid being wetted by a liquid could be predicted [5,8,14,15].

Pioneering work by Zisman and his coworkers [20] established that when the advancing contact angles of a series of homologous liquids on low-energy surfaces (for example, fluorocarbons and hydrocarbons) were measured, a plot of the $\cos\theta$ values against the surface tension of the liquids extrapolated approximately to the same value of γ_{LV} at $\cos\theta = 1$. This surface tension value was termed the ‘critical surface tension of the solid’, γ_C . It was further proposed that only liquids with surface tension values lower than γ_C would spread on the surface, whereas liquids with surface tension values greater than γ_C would form a finite contact angle on the solid. While the critical surface tension concept has been criticised because it is empirical rather than thermodynamically-based, and the concept has some limitations, nevertheless, it has proved to be a very useful approach for use in research and development work on water- and oil-repellent treatments for textile fabrics [21].

Water has a hydrogen-bonded liquid structure with a high surface tension, γ_{LV} (72.75 mN m^{-1} at 20°C) [22]. It has been established that repellent finishes that contain either a hydrocarbon base with a γ_C value of about 30 mN m^{-1} or polysiloxane (silicone) finishes with a γ_C value of around 24 mN m^{-1} can give very good water-repellency [8,20]. However, the surface tension values of hydrocarbon-based oils are much lower than water, and generally within the range $20\text{--}31 \text{ mN m}^{-1}$. Under such circumstances, it is not surprising that the hydrocarbon and the polysiloxane water-repellent finishes do not provide oil-repellency, because in this case the surface tension of the oil may be low enough to wet the surface of the finish. Therefore, to repel hydrocarbon-based oils with surface tension values (γ_{LV}) of around $20\text{--}31 \text{ mN m}^{-1}$ it is necessary to use finishes with even lower critical surface tension values (γ_C). Fluorocarbon (fluorochemical) finishes are available with critical surface tension values below 15 mN m^{-1} and these provide satisfactory water- and oil-repellency depending upon the nature of the pendant fluorocarbon chains (Table 5.2) [8,20,23].

The surface tensions of selected liquids (γ_{LV}) at 20°C are given in Table 5.3 as well as the critical surface tension values (γ_C) at 20°C for various fibres [24,25]. It is clear that the majority

Table 5.2 Surface tension values of surfaces composed of various chemical groups

Surface constitution	Critical surface tension, γ_C , at 20°C (mN m^{-1})
$-\text{CF}_3$	6
$-\text{CF}_2\text{H}$	15
$-\text{CF}_3$ and $-\text{CF}_2$	17
$-\text{CF}_2-$	18
$-\text{CF}_2-\text{CFH}$	20
$-\text{CH}_3$	22
$-\text{CH}_2$	31
$-\text{CCl}_2-\text{CH}_2-$	43

of the liquids have lower surface tension values than the critical surface tension values of the fibres and hence will wet and spread on the fibre (and fabric) surface. The incorporation of a wetting agent (that is, surfactant) into water lowers the surface tension below that of most textile fibres [14,15], promoting wettability and penetration within the structure of the textile material. The presence of impurities in water also lowers the surface tension, and increasing the temperature from 20 °C to 100 °C decreases the surface tension of water from 72.75 mN m⁻¹ down to 58.9 mN m⁻¹ [25].

Table 5.3 Surface tension values (γ_{LV}) of a range of liquids and surface energies (γ_C) of a range of textile fibres, at 20 °C

Liquids	γ_{LV} (mN m ⁻¹)	Textile fibres	γ_C (mN m ⁻¹)
Water	72.75	Polyamide 6.6	46
Peanut oil	40	Wool	45
Olive oil	32	Bleached cotton	44
Paraffin oil	31	Polyester	43
Petrol	26	Polypropylene	29
<i>n</i> -octane	22		
<i>n</i> -heptane	20		
Water with wetting agent	25–35		

5.2.4 The critical surface tension of cotton fibres

The surface of the raw cotton fibre is covered with a thin coating of natural waxes, which makes raw cotton inherently water-repellent. Typical critical surface tension values for four varieties of raw cotton have been determined by the sink–float method and are given in Table 5.4 [26]. While the chemical composition of the waxes present may vary between the four cotton cultivars, the critical surface tension values are very similar and in the range 25.2–26.1 mN m⁻¹.

Table 5.4 Critical surface tension values for four varieties of raw cotton [26]

Raw cotton cultivar	Critical surface tension (mN m ⁻¹)
Ranji	26.1
Deltapine	25.2
Coker	26.1
Lambert	26.1

In practice, nearly all cotton fabrics are subjected to chemical pretreatments that remove impurities – for example, desizing, scouring and bleaching. In addition, fibre swelling/relaxation treatments, such as mercerisation or anhydrous liquid ammonia treatments, may also be given to the fabric. Chemical pretreatments such as alkalis and oxidising agents all modify the surface of

the cotton fibre by removing the natural waxes [27,28]. The underlying cellulose fibre surface may then be further chemically attacked by oxidative treatments, which lead to chain breakage and to the introduction of aldehyde (keto) groups and carboxyl groups, in addition to the normal cellulose hydroxyl groups in the fibre surface [27,29]. Carboxyl groups are more polar and more hydrophilic than hydroxyl groups, and therefore the critical surface tension values for cotton that has been scoured or bleached, or mercerised or anhydrous-liquid-ammonia-treated are increased. In the case of mercerisation and anhydrous liquid ammonia treatment, the critical surface tension value is also dependent upon the cellulose fibre structure [26,28]. Raw cotton is cellulose I, mercerised cotton is cellulose II, and anhydrous-liquid-ammonia-treated cotton is either cellulose I or cellulose III depending upon the conditions during the removal of the ammonia from the fibre [30].

The critical surface tension values of cotton fibres taken from the same woven cotton fabric, which had been commercially pretreated by different preparation routes, are illustrated in Table 5.5 [28,31,32]. Scouring treatments give rise to a marked increase in fibre critical surface tension because these remove the waxes from the fibre surface, and there is a strong interrelationship between increase in fibre critical surface tension and decrease in fibre wax content. Increasing the number of oxidative chemical pretreatments, or fibre swelling/relaxation treatments, further modify the nature of the fibre surface and lead to an increase in fibre critical surface tension.

Table 5.5 The effect of cotton fabric pretreatment upon fibre critical surface tension [28]

Cotton fabric pretreatment sequence	Mean cotton fibre critical surface tension (mN m^{-1}) ^a
Raw cotton fibre	26
Two pretreatments, no scour:	
Standard mercerise, peroxide bleach	27.6
Standard mercerise, hypochlorite bleach	26
Two pretreatments, scour included:	
Vaporloc scour, peroxide bleach	44
Vaporloc scour, hypochlorite bleach	36
Three pretreatments, scour included:	
Vaporloc scour, standard mercerise, peroxide bleach	38
Vaporloc scour, standard mercerise, hypochlorite bleach	36.6
Four pretreatments, scour included:	
Vaporloc scour, standard mercerise, Erba peroxide, anhydrous liquid ammonia	55.8

a Determined by the sink-float method using ethanol/water at 20 °C

It is interesting to note that a good chemical pretreatment, which leads to high fibre critical surface tension, gives rise to a fabric that exhibits rapid wetting and wicking characteristics [28,31,32]. Such fabrics also give rise to improved water-repellency when treated with a water-

repellent finish [33]. This at first seems a surprising and unexpected result, but because the fabric surface is wettable, the application and distribution of the water-repellent finish are more uniform and are greatly enhanced, and this is the reason why improved water-repellency is observed.

5.2.5 Repellency of textile fabrics

The repellency of a textile fabric depends upon the resistance to wetting and penetration by a liquid. Water and oil are the most important liquids for normal textile fabric end-uses [8,23,24]. The main parameters that determine the resistance of a fabric to wetting are [8,9,20,32]:

- (1) the chemical nature of the fibre surfaces (for example, presence of polar or non-polar groups);
- (2) the geometry and roughness of the fibre surfaces (for example, longitudinal striations, fissures, crenulations and so on, and modified cross-sections that promote wicking);
- (3) the nature of the capillary spacings in the fabric (for example, inter-fibre and inter-yarn capillary spaces).

The resistance to penetration of a liquid into a porous solid like a textile fabric is normally expressed [8,19,34] in terms of the pressure difference between the two sides of a curved liquid surface of surface tension γ_{LV} . The pressure difference, ΔP , is the hydrostatic pressure that is required to force the liquid through the fabric.

For a capillary of circular cross-section, the value of ΔP is given by the Laplace equation:

$$\Delta P = \gamma_{LV} \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (5.11)$$

where R_1 and R_2 are the principal radii of curvature of the liquid surface (that is, the maximum and minimum radii of curvature). Where the liquid surface forms part of a sphere, R_1 and R_2 are very small and are equal, so that:

$$\Delta P = \frac{2\gamma_{LV}}{R} \quad (5.12)$$

The value of ΔP is positive on the concave side of the surface when wetting takes place. This equation thus applies to a wetting liquid where the contact angle θ approaches zero (that is, no definite contact angle is observed) and $\cos\theta$ approaches 1 [8,34].

Where the contact angle θ is not zero, the equation becomes:

$$\Delta P = \frac{2\gamma_{LV}\cos\theta}{R} \quad (5.13)$$

By rearranging Eqn 5.7, the following can then be expressed according to Eqn 5.13:

$$\gamma_{LV} \cos \theta = (\gamma_{SV} - \gamma_{SL})$$

$$\text{whence } \Delta P = \frac{2(\gamma_{SV} - \gamma_{SL})}{R} \quad (5.14)$$

For a fabric to be repellent to a liquid (that is, resist the penetration of the liquid into the textile material) ΔP must be negative and large in value. Hence the value of $(\gamma_{SV} - \gamma_{SL})$ must be negative and the value of R (which can be considered to be the largest opening into the textile structure) must be very small [8].

Clearly, if the fabric structure is chosen to consist of fine yarns arranged in a close-packed structure (for example, high sett weave), the value of R will be small. In addition, the surface energy of the fibre surface can be decreased by deposition of low-surface-energy finishes. Therefore, the surface energy (that is, the critical surface tension) of the solid surface becomes lower than that of the liquid, so that $(\gamma_{SV} - \gamma_{SL})$ will become negative and high repellency will be obtained. By ensuring that there is a large difference in surface energy (that is, surface tension) between γ_{SL} and γ_{SV} , and that $\gamma_{SL} > \gamma_{SV}$, high levels of repellency can be obtained [8,14,34]. Thus the high surface tension of water at 20 °C ($\gamma_{LV} = 72.75 \text{ mN m}^{-1}$) means that water is unable to wet and penetrate into fabrics that have been uniformly treated with a hydrocarbon ($\gamma_C = 30 \text{ mN m}^{-1}$), silicone ($\gamma_C = 24 \text{ mN m}^{-1}$) or a fluorochemical ($\gamma_C \sim 15 \text{ mN m}^{-1}$) water-repellent finish. But hydrocarbon oils ($\gamma_{SL} \sim 20\text{--}31 \text{ mN m}^{-1}$) require oil-repellent finishes with much lower values of γ_{SV} (measured as γ_C) and hence fluorochemical finishes ($\gamma_C \sim 15 \text{ mN m}^{-1}$) are required in order to obtain satisfactory oil-repellency [8,14,23,24].

Thus, there are three different types of behaviour of a liquid (such as water) on a solid surface [34,35]:

- | | | |
|----------------|--|---|
| (1) region I | $(\gamma_{SV} - \gamma_{SL}) \geq \gamma_{LV}$ | the drop spreads right out – wetting occurs; |
| (2) region II | $\gamma_{LV} > (\gamma_{SV} - \gamma_{SL}) > -\gamma_{LV}$ | a non-spherical drop with a finite contact angle is formed; |
| (3) region III | $(\gamma_{SV} - \gamma_{SL}) \geq -\gamma_{LV}$ | a completely spherical drop is formed. |

These conditions are illustrated in Figure 5.2.

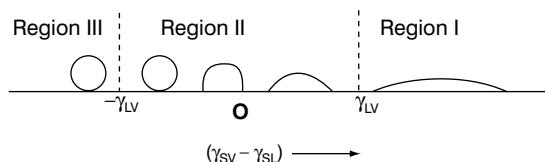


Figure 5.2 Shape of a drop on a solid surface for different values of $(\gamma_{SV} - \gamma_{SL})$ [34,35]

5.2.6 Liquid penetration into a yarn (inter-fibre capillary spaces)

In the case of penetration of liquids between the fibres of a yarn, the hydrostatic pressure required is determined by the fibre diameter, the fibre separation and the fibre–liquid advancing contact angle [8,14,34]. The relation between the pressure difference, ΔP , across a cylindrical liquid surface of radius R and surface tension γ_{LV} is given by [8,14,34]:

$$\Delta P = \gamma_{LV} / R \quad (5.15)$$

In order to determine whether the liquid can pass between two parallel cylinders (for example, fibres) when the advancing contact angle is maintained, the minimum value of R must be calculated.

In Figure 5.3 the cross-sections of three cylinders of radius r , separated by a distance $2d$, are shown whose respective axes are at L, M and N, the positions of L and N being in the periphery of the yarn, and M inside the yarn [8,34]. Hence the centre of the curved liquid surface must, by symmetry, lie on the line OA. The position of A is taken to be a distance x from the point O.

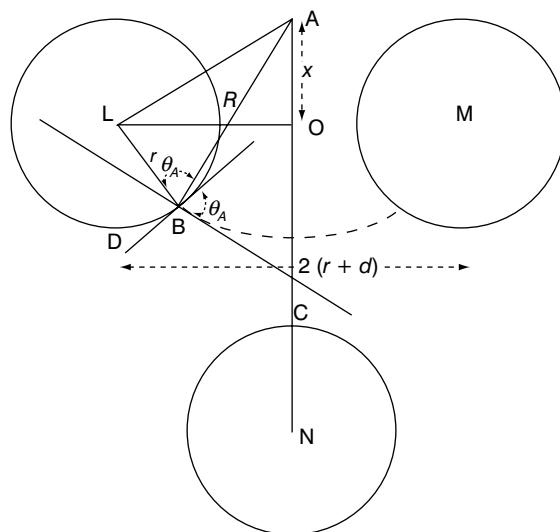


Figure 5.3 Penetration of water between cylinders [34]

If the liquid surface intersects the cylinder whose centre is L at point B, then the tangents of the two circles make an angle θ_A – the advancing fibre–liquid contact angle – with one another, and the radii joining their centres to B must also make this angle with one another. The angle θ_A is thus represented by the angle LBA. The distance R is given by the length AB. It can be shown [34] that:

$$R = AB = r \cos \theta_A + \left[LA^2 - r^2 \sin^2 \theta_A \right]^{\frac{1}{2}} \quad (5.16)$$

Differentiating with respect to x yields:

$$\frac{dR}{dx} = \frac{LA}{[LA^2 - r^2 \sin^2 \theta_A]^{\frac{1}{2}}} \cdot \frac{d(LA)}{dx} \quad (5.17)$$

Now dR/dx is zero when $d(LA)/dx$ is zero, which represents the condition when point A lies at point 0. At this point the value of R is then at a minimum, R_{\min} , and because the distance $LA = (r + d)$ it follows that:

$$R_{\min} = r \cos \theta_A + \left[(r + d)^2 - r^2 \sin^2 \theta_A \right]^{\frac{1}{2}} \quad (5.18)$$

Hence the minimum pressure for the liquid to penetrate in between the fibres [34] is given by:

$$\Delta P = \frac{\gamma_{LV}}{\left[(r + d)^2 + r^2 \sin^2 \theta_A \right]^{\frac{1}{2}}} \quad (5.19)$$

5.2.7 Liquid penetration into a woven textile fabric (inter-yarn capillary spaces)

In the case of a woven textile fabric, a liquid will pass through the pores between the warp and weft yarns only when the pressure is high enough. Taking the case of a woven fabric with warp and weft yarns of the same yarn radius a , with the advancing yarn–liquid contact angle as θ_D , and the distance apart of the yarns as $2b$, then the distance apart of the warp and weft yarn centres is $2(a + b)$. The pressure required to force a spherical liquid surface through the inter-yarn pores will be given [34] by the Laplace equation (see Eqn 5.12), in which R is the minimum radius of curvature of the liquid surfaces. It is to be noted that this formula relates to a spherical liquid surface and hence the pressure required is double that for the cylindrical surface given in Eqn 5.15. Thus:

$$R = a \cos \theta_D + \left[(a + b)^2 - a^2 \sin^2 \theta_D \right]^{\frac{1}{2}} \quad (5.20)$$

$$\text{Hence } \Delta P = \frac{2\gamma_{LV}}{\left(a \cos \theta_D + \left[(a + b)^2 - a^2 \sin^2 \theta_D \right]^{\frac{1}{2}} \right)} \quad (5.21)$$

Thus wetting and penetration of the liquid into the fabric pores are promoted if γ_{LV} and/or θ_D decrease, and repellency is promoted if γ_{LV} and/or θ_D increase [8,34].

Eqn 5.21 indicates that the pressure needed for penetration increases with decreased inter-yarn spacing if the advancing yarn–liquid contact angle is greater than 90°. A tight weave structure and high yarn bulk density also enhance repellency. However, this behaviour may be modified in its effect because it has been established that the apparent yarn–liquid contact angle observed in practice increases with a decrease in yarn bulk density [34].

5.2.8 Conditions for high fabric repellency

In summary, therefore, the conditions for high levels of fabric repellency depend upon the use of:

- (1) fine yarns and a close-packed textile structure (for example, high sett weave);
- (2) a thoroughly prepared fabric surface free from impurities (for example, sizes, lubricants and especially surfactants with a rewetting action);
- (3) uniform application of a chemical finish to provide a low-energy surface that has a lower critical surface tension (γ_C) than the surface tension values of the liquids (γ_{LV}) likely to be encountered.

Traces of surfactants with a rewetting action – used in aqueous scouring, for example – must be removed by extended thorough rinsing. Alternatively, some textile finishers use solvent scouring in perchloroethylene to avoid the problem that arises with aqueous scouring.

5.3 FABRIC CONSTRUCTION AND PREPARATION FOR WATER-REPELLENT FINISHING

5.3.1 Fabric construction for water-repellency

The vast majority of water-repellent fabrics are based upon woven fabrics because these can be tightly woven to decrease the inter-yarn capillary spaces (or pores) [8,19,34,36]. The openness of the weft knitted and warp knitted constructions leads to large inter-yarn spaces that can allow water to penetrate readily through the structure unless this is given an impermeable coating, such as polyurethane, polyvinyl chloride or neoprene. Application of a water-repellent finish cannot usually prevent the penetration of water into such knitted structures because of the large inter-yarn pores. Non-woven fabrics of many different types can be treated with water-repellent finishes, provided that the underlying fabric structure has a smooth surface and small inter-fibre or inter-yarn pores. The felting of wool fibres that occurs during the milling of woven wool fabrics and in the production of pressed wool felts can lead to a thicker and denser fabric structure with an improved inherent fabric water-repellency.

Not all fabric constructions are suitable for the production of high water-repellency, and the fabric must be carefully engineered to obtain the best results in the intended end-use [19,34,36].

For staple fibre-based fabrics, both singles yarn and folded yarns can be used, but it is important that the fibres are bound tightly within the body of the yarn to ensure that free fibre ends do not project from the fabric surface because this can impair the water-repellency. Folded yarns may also provide a higher yarn strength allowing the use of a higher tension during weaving that results in a tighter woven fabric. Another possible advantage of folded yarns is that their profile is less regular than that of singles yarns and it has been considered that this may contribute to closer yarn packing and greater blocking of the inter-yarn spaces in a woven fabric by virtue of the folded yarns fitting more tightly together [37].

For rainwear, the yarn count used should be sufficient to provide a suitable defence against the penetration of water, and hence the fabric thickness becomes important. Thin fabrics generally provide poor water-repellency even when treated with water-repellent finishes, unless the inter-yarn pores become blocked – for example, as can occur in coating or with high-chemical add-on of a water-repellent finish [34].

Woven cotton poplin fabric (a plain weave fabric with weftway ribs and high warp sett) has often been used as the base for water-repellent finishing. The fabric should be tightly woven and finished as narrow as possible followed by compressive shrinking to obtain satisfactory dimensional stability to wet treatments [37].

Where synthetic filament yarns are used, the thermoplastic nature of the filaments can be utilised during finishing to promote thermal shrinkage, altering the fabric construction and decreasing the mean inter-yarn pore size [36]. In addition, the use of synthetic microfibres and microfilament yarns in a closely woven fabric can serve as an excellent base for application of water-repellent finishes [38]. Microfibres or microfilaments of linear density 1.0 dtex or less (for example, 0.1–0.3 dtex f⁻¹) can thus enhance water-repellency but these finer fibres possess a decreased resistance to abrasion and wear.

5.3.2 Fabric preparation for water-repellent finishing

Fabric preparation for water-repellent finishing is of prime importance, because without thorough preparation, inferior water-repellency may be obtained [37,39]. Woven fabrics must be thoroughly desized and scoured to remove impurities and to render the fabric highly absorbent. It is equally important to ensure that the fabric absorbency is not due to the presence of wetting agents, and all traces of wetting agents and emulsifiers must be removed by rinsing treatments with hot water. The presence of wetting agents and emulsifiers in a fabric finished with a water-repellent can be deleterious to obtaining a high degree of water-repellency [39].

Research work has demonstrated that thorough scouring of woven cotton fabric is essential to remove the fatty lubricants used in sizing and the natural cotton waxes from the fibre surface [28,31–33]. If this is accomplished then the water-repellent can wet and spread to form continuous films over the fibre surfaces, which contribute to a highly water-repellent effect. The presence of impurities, particularly of waxy substances, can greatly interfere with efficient wetting and spreading. This can lead to disruption of the continuous film of water-repellent finish on the fibre surface and hence to a decrease in the effectiveness of the water-repellent treatment [37].

Some textile finishers have avoided the use of the wetting agents and assistants used in conventional aqueous fabric scouring treatments by scouring the fabric in an organic solvent, such as perchloroethylene (also known as tetrachloroethylene or tetrachloroethene). Batchwise treatment in a rotary cage solvent scouring machine, or continuous open-width solvent scouring machinery, may be used but such treatments are now much less common because of the environmental and ecotoxicological considerations surrounding the use of the organic solvent [40]. The high initial cost of the solvent, the necessity to recover and recycle the solvent to a very high level of efficiency, the need to monitor and control the machine environment to comply with atmospheric pollution legislation, and the high cost of continuous open-width solvent scouring machinery have all contributed to a decline in interest in solvent preparation.

In addition, desizing is usually carried out using aqueous methods, because solvent desizing complicates the efficiency of the solvent recovery process [40]. If the solvent scouring route is used, it is essential that pure solvent is used without any additives that incorporate wetting agents or emulsifiers, and the removal of solvent from the fabric should preferably be 99.9% or greater. In this way, the solvent recovery is maximised, the atmospheric pollution generated by residual solvent evaporating from the fabric is minimised, and compliance with environmental legislation on solvent emissions is achievable.

Most fabrics intended for water-repellent finishing or coating are singed at open-width – by direct (or flame) singeing, or by passage through an infrared singeing machine – in order to remove protruding surface fibres that could impair the uniform application of the chemical finish or coating [41]. Such fibres could subsequently provide a means by which water could wet and wick into the fabric structure and impair the performance of the water-repellent finish or coating. Singeing may be carried out prior to desizing and scouring, but may also be carried out prior to the application of the water-repellent finish or coating.

5.4 WATER-REPELLENT FINISHES OTHER THAN FLUOROCHEMICALS

5.4.1 Metal salt finishes

In the period from 1880 onwards, when water-repellent finishing became more important, it was normal practice to impart water-repellency to tightly woven cotton canvas by lengthy impregnation (24–48 h) in an aluminium acetate solution (5–9 °Tw.). (Degrees Twaddell, °Tw., is a measure of the specific gravity, SG, of the liquor and is defined from ${}^{\circ}\text{Tw.} = 200(\text{SG} - 1)$.) Alternatively, water-repellency was achieved by jig or pad application of such an aluminium acetate solution followed by careful drying in festoon form or on a stenter [4,42–44]. To avoid precipitation of insoluble basic acetates, the impregnation liquor temperature was maintained below 38 °C. During drying, the removal of water was accompanied by removal of some acetic acid, which then converted the water-soluble monobasic salt into an insoluble dibasic compound. The latter was precipitated onto the fibres to give a water-repellent finish with a harsh handle, and with very limited durability to washing. Aluminium formate could also be applied in a similar manner and was often preferred because, in contrast to aluminium acetate,

it did not leave a disagreeable odour on the fabric. One problem with aluminium salt finishes was that the water-repellent finish tended to dust off the fabric and improvement in this respect was obtained by the use of aluminium soap finishes based upon aluminium stearate, oleate or palmitate [44].

5.4.2 Soap/metal salt finishes

One method of improving the water-repellency obtained through the use of aluminium salts is by combining the aluminium salt treatment with treatment in a soap in order to deposit an insoluble hydrophobic aluminium soap within the fabric [39,42–44]. Alternative procedures were developed to achieve satisfactory results. In one treatment [39], cotton fabric was first impregnated in 5–9 °Tw. aluminium acetate, squeezed and dried, or partially dried. It was then passed through a weak aluminium sulphate solution. This latter stage ensured that the maximum water-repellency was developed because any soluble sodium soap remaining in the fabric was then converted into the water-insoluble aluminium soap. The fabric could then be rinsed in soft or hard water and dried. Alternatively, 2–5% soap solution at 60 °C was padded onto the fabric, which was then partially dried [39]



Scheme 5.1

The aluminium acetate treatment was then carried out in a winch or jig at 25–30 °C, giving sufficient time to ensure complete conversion of the soluble sodium soap into the insoluble aluminium soap. Winch or jig treatment was much more effective than padding in this respect because of the longer immersion time. The use of aluminium salts is advantageous for apparel fabrics because the treatment does not colour the fabric. Other water-soluble metal salts, such as copper, in the form of the acetate, formate or sulphate, can also be applied by a similar two-bath technique to give a water-repellent effect [39]. However, copper treatments impart a green colour to the textile, which greatly restricts their universal application. The fabric handle is also somewhat greasy and thus the major outlet for this type of finish was in cotton tentage and awning fabrics where the presence of at least 0.5% copper as a fungicide on the dried fabric conferred a valuable degree of protection against attack by micro-organisms. Thus, a combined water-repellent and rotproof finish was imparted to the fabric.

Optimum water-repellency from such treatments is clearly dependent upon complete conversion of all the water-soluble sodium soap in the fabric into the water-insoluble aluminium soap form. The presence of any sodium soap leaves a detergent/wetting agent in the fabric, which detracts from the optimum water-repellent effect.

Woollen fabrics, after milling in soap, could conveniently be immediately impregnated in

aluminium acetate solution without any intermediate rinsing and drying. However, with heavy-weight fabrics, such as duffle cloths, the padding conditions had to be adjusted to ensure complete penetration and complexing of the metal salt with the soap. Any excess sodium soap expressed from the milled fabric into the pad bath containing the aluminium acetate can lead to the formation of white deposits, which can subsequently be taken up by the fabric and give rise to a blotchy surface appearance.

Two-stage treatment procedures are generally time-consuming, less convenient and less economic to operate, and more difficult to control in practice. For this reason, one-bath treatment procedures were developed by application from stable aqueous dispersions or by application of the aluminium soap from an organic solvent [44]. Protective colloids such as proteins (gelatin or glue) or polyvinyl alcohol have been used to stabilise aluminium dispersions. Protective colloids may be incompatible with resin finishes and proteins left on the fabric can act as nutrients for micro-organisms, giving rise to microbial attack.

The wash fastness of aluminium soap treatments is poor in alkaline detergent solution, because the aluminium soap dissolves. In contrast, their durability to water, in which they are insoluble, is far greater. Some other techniques developed have included the use of aluminium acetate combined with soap and wax emulsions and also wax/aluminium salt products [39]. Some improvement in durability to alkaline washing treatments can be obtained by the use of zirconium soaps, using zirconium acetate or zirconium oxychloride. In the case of zirconium oxychloride, hydrolysis leads to the formation of HCl and hence it must be buffered using sodium acetate [39,44,45].

However, because of the increasing standards of fastness to domestic washing and commercial laundering now demanded, the use of aluminium, zirconium and copper soaps is rare for water-repellent finishing except for a few temporary finishes, because superior durability to wash treatments is available from other more advanced chemical finishes.

5.4.3 Wax finishes

A popular form of water-repellent treatment over the twentieth century, and still used today, is the application of wax treatments to fabrics at open-width. Many patents have been issued on the application of fats and waxes; typically wax formulations contain paraffin wax (melting point 52–56 °C) either by itself or in combination with one or more waxes based upon esters of higher fatty acids and higher monohydric alcohols [44]. Beeswax (mainly myricyl palmitate, $C_{15}H_{31}COOC_{30}H_{61}$, m.p. up to 62–65 °C), carnauba wax (myricyl cerotate) $C_{25}H_{51}COOC_{30}H_{61}$, m.p. 83–86 °C) and Vaseline (C_{18} – C_{22} alkane, m.p. up to 60 °C) have also been used according to the finisher's requirements [4,39,44].

In the past, a common method was by application of 4–6% of paraffin wax dissolved in an organic solvent, such as benzene, using a lick-roller application method, followed by drying over steam-heated cylinders, or in a stenter or drying chamber [4]. This method is now clearly highly undesirable from the ecotoxicological point of view. Another method involved passing the fabric

at open-width through a steam box before it was rubbed against a number of thick wax bars. The treated cloth was then subjected to a warm calendering process, which melted the applied wax and ensured a more uniform distribution over the fabric [4,44].

An alternative method was to spray molten wax onto the moving fabric from a series of high-pressure steam jet sprays that covered the width of the fabric. Again the wax was melted and distributed more evenly over the fabric by passage over heated drying cylinders.

The most common method of application now, however, is to pad an aqueous wax emulsion onto the fabric followed by melting and redistributing the wax by some form of heating under pressure – for example, by hot calendering [4,9,34]. Fabric is often calendered first to close up the inter-yarn pores, and this process is followed by impregnation in hot molten wax (high melting point wax, 80–90 °C). Excess wax is removed by doctor blades, the fabric is skyed to allow the wax to cool and re-solidify, and the waxed fabric is then wound onto a roller. Such treatments have been widely applied to the fabrics used for the waxed jackets often favoured by farmers and others exposed to foul weather conditions in a rural environment.

5.4.4 Pyridinium-based water-repellent finishes

In 1931, research work by Deutsche Hydrierwerke led to patents on the manufacture of quaternary ammonium salts with the objective of giving an increased dyeing effect on cotton and cellulosic fibres [8,44,46,47]. Typically halogen ethers of the general formula shown in Structure 5.1 were reacted with tertiary bases to yield water-soluble quaternary ammonium compounds. (R = alkyl radical (at least C_8), X = halogen radical, R' = hydrogen or a hydrocarbon radical (at least C_8)).

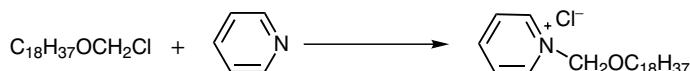


5.1

Thus the reaction of octadecanol, formaldehyde and dry HCl could yield a substituted methyl chloride via the reaction in Scheme 5.2. This could then be further reacted with tertiary bases such as triethylamine or pyridine to generate quaternary ammonium compounds with good aqueous solubility, and strong wetting out and foaming properties (Scheme 5.3)



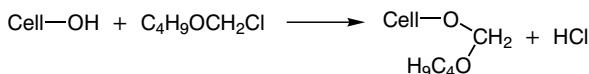
Scheme 5.2



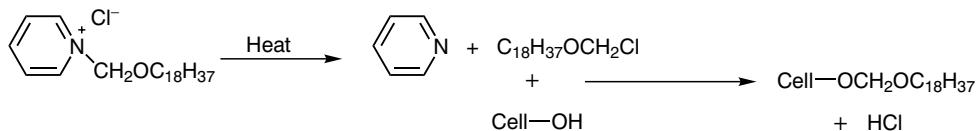
Scheme 5.3

It was noted that the pretreatment of cotton with such quaternary ammonium compounds did give an increased dyeing effect on cotton and cellulosic fibres, but in addition, it was

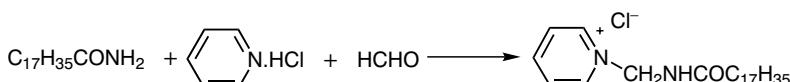
advisable to wet out such pretreated cotton prior to dyeing because of its water-repellent properties [44,47]. It was considered, where butyl chloromethyl ether and pyridine were used to form the quaternary ammonium compound, that chemical reaction with cellulosic hydroxyl groups took place via the butyl chloromethyl ether with the formation of an acetal [8,44]

**Scheme 5.4**

In an important further development, it was discovered that impregnating cotton fabrics with aqueous solutions of quaternary ammonium compounds such as octadecyloxymethyl pyridinium chloride (Structure 5.2) could give rise to a durable water-repellent finish after drying and heating [8,44,48]. It was considered that during the heating stage thermal decomposition of the pyridinium salt took place, which was then followed by the reaction of the liberated chloralkyl ether with the cellulosic hydroxyl groups (Scheme 5.5).

**Scheme 5.5**

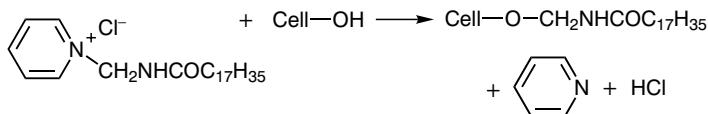
As a result of this work, further patents appeared, of which one in particular led to the commercialisation of Velan PF (ICI) in 1937 as a durable water-repellent for cellulosic fabrics [49]. This product was considered to be stearamidomethyl pyridinium chloride, which was formed by the reaction of stearamide, pyridine hydrochloride, pyridine and paraformaldehyde (Scheme 5.6) [8,44,46].



Stearamidomethyl pyridinium chloride

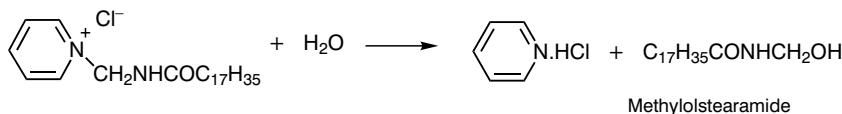
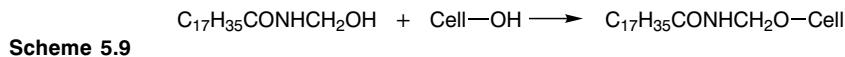
Scheme 5.6

Stearamidomethyl pyridinium chloride (Velan PF, ICI) was padded onto cotton fabric followed by drying and curing. Initially, it was considered that chemical reaction with cellulosic hydroxyl groups occurred with the formation of a strong covalent bond that imparted a durable effect to the water-repellent treatment [8,50]. The proposed reaction is shown in Scheme 5.7.

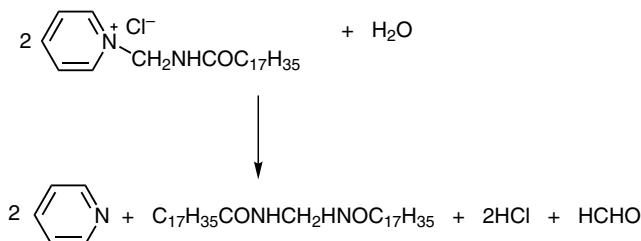
**Scheme 5.7**

This reaction only takes place in the absence of water, and the pyridine and hydrogen chloride liberated must be rapidly removed. Normally this was accomplished by scouring the fabric followed by drying.

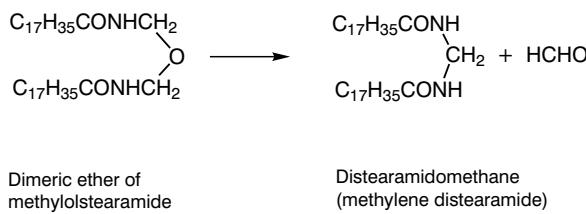
Velan PF – which consisted of 62% stearamidomethyl pyridinium chloride and 38% sodium chloride – should, therefore, after reacting with the cellulose to form a covalent bond, provide durable water-repellency [50]. However, analysis demonstrated that the actual situation is more complex, and that much of the water-repellent applied is removed by solvent extraction in boiling benzene-methanol or chloroform. However, some water-repellency remains after this solvent extraction treatment, and this is considered to arise from that part of the stearamidomethyl pyridinium chloride that reacts with the cellulose to form a covalent bond through the ether linkage (Scheme 5.7) [50]. It has been shown that stearamidomethyl pyridinium chloride breaks down on hydrolysis to form methylolstearamide and pyridine hydrochloride (Scheme 5.8). Part of the methylolstearamide can then condense with the cellulose to form a $>\text{CHOCH}_2-$ linkage [50] (Scheme 5.9).

**Scheme 5.8****Scheme 5.9**

In addition to breakdown to the methylolstearamide, when more than 2% owf (on weight of fibre) stearamidomethyl pyridinium chloride is present, self-condensation occurs to form the dimeric ether via the reaction in Scheme 5.10.

**Scheme 5.10**

Part of the methylolstearamide then loses formaldehyde to yield distearamidomethane, which is a hard insoluble wax and water-repellent but is non-permanent, being deposited on the fibres [50] (Scheme 5.11).



Scheme 5.11

The water-repellent effect obtained would thus seem to be derived in part from the hydrolysis reaction products, which are considered to penetrate inside the fibre and impart water-repellency. However, in dry-cleaning, these compounds, which are not covalently bound to the fibre but only held through strong physical forces, can be removed. Nevertheless exhaustive solvent extraction does not completely remove the water-repellency, nor does acid attack short of degradation of the cellulose. This has been taken as evidence that some covalent reaction with cellulosic hydroxyl groups does take place, imparting durability to part of the water-repellent agent originally applied to the fabric [50]. Certainly research studies confirm that stearamidomethyl pyridinium chloride reacts with cellulose to the extent of 1–2% owf, suggesting that the reaction is restricted to the fibre surface, hence contributing very effectively to the water-repellency [50,51].

In the practical application of Velan PF it was necessary to avoid degradation of the cellulose by the HCl liberated during heating, and hence sodium acetate was incorporated into the pad liquor. A typical formulation for 1 litre of pad liquor would contain [39]:

- (1) 60 g Velan PF (pasted with 60 g ethanol and 250 ml water at 45 °C);
 - (2) 20 g sodium acetate crystals (dissolved in 250 ml water at 40 °C and added to the Velan PF dispersion);
 - (3) the total volume made up to 1 litre with water at 40 °C.

Cotton fabric is then padded at 40 °C with Velan PF pad liquor to give a wet pick-up of 70%. The padded fabric is then stenter dried at temperatures up to 100 °C with good air circulation. After drying, the treated cloth is then cured (baked) for 3 min at 150 °C. After curing, an afterwash is given in 2 g l⁻¹ soap and 2 g l⁻¹ sodium carbonate at 50 °C in order to remove pyridine odours, sodium chloride and excess sodium acetate. It is essential to rinse off thoroughly, followed by drying. Thorough wash-off and rinsing to remove any residual products from the chemical treatment and any residual soap (which is a wetting agent) from the afterwash in the treated fabric are essential to develop the full water-repellency. It is also possible to combine Velan PF treatment with the application of resin precondensates in order to provide good easy-care performance, but it is essential to ensure that the finishes are chemically compatible so that good pad bath stability is obtained [39].

Zelan A (Du Pont) was similar to Velan PF (ICI) and based upon stearamidomethyl pyridinium chloride [44], but was later modified to give a product Zelan AP (Du Pont) which was less sensitive to adverse drying conditions that could promote hydrolysis [39]. Zelan AP was particularly used in the USA on high-speed continuous processing. Cerol WB (Sandoz) was also introduced and applied in a similar manner to Velan PF (ICI). Zelan B (Du Pont) was considered to be based upon stearoxymethyl pyridinium chloride.

One commercial preparation used in the USA was a paste containing stearamidomethyl pyridinium chloride, distearamidomethane, a nitrogenous resin, together with pyridine and isopropanol [51].

The major problem with this type of water-repellent finish is the liberation of pyridine, which has an unpleasant odour and pyridine is also a chemisterilant. Any pyridine liberated during curing is clearly undesirable and afterwashing is essential to remove any unpleasant odour on the fabric. For these reasons, and for toxicological considerations, the production of pyridinium-based water-repellents has been curtailed, and the use of this type of water-repellent treatment is limited to end-uses for which it is specifically required, such as certain military end-uses.

Laundering tests on cotton treated with distearamidomethane showed that the water-repellency was destroyed after 4–6 launderings, while treatment with stearamidomethyl pyridinium chloride was more permanent [51]. However, the distearamidomethane-treated sample demonstrated no water-repellency after one laundering cycle unless the treated fabric was subjected to reheating. Presumably during laundering the distearamidomethane was removed from the fibre surface, impairing the water-repellency. This was restored by migration of the finish from inside the fibres to the fibre surface during the reheating treatment. In this work, it was also shown that when sodium acetate is present in a stearamidomethyl pyridinium chloride emulsion some stearamidomethyl acetate was formed.

This compound was also shown to be capable of reacting chemically with cellulose, but only to a slight extent compared with stearamidomethyl pyridinium chloride, which formed 1–1.5% by weight of stearamidomethyl cellulose, substituting about one stearamidomethyl group per 150 anhydro glucose units. The water-repellency of the treated cloth was thus dependent not only upon stearamidomethyl groups covalently bound to the cotton but also on deposited stearamidomethyl compounds that were not chemically bound to the fibre. The latter were removed during successive launderings of the fabric and a further problem was the retention of residual soaps, formed during laundering and dry-cleaning, that could mask the physical properties of the water-repellent.

Pyridinium-based water-repellents co-applied with fluorocchemical repellents were used in the past in the USA in the QUARPEL finish [52]. This combination of chemical finishes led to a synergistic improvement in fabric performance that resulted in superior protection against rain and good durability to laundering and was devised particularly for military clothing.

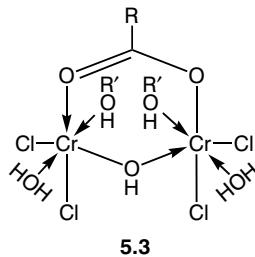
5.4.5 Organo-metallic complexes

Both chromium and aluminium organo-metallic complexes have been used to impart a semi-

durable water-repellency to textiles composed of either natural or synthetic fibres [45,46]. Quilon (Du Pont) was marketed as a concentrated solution of a Werner type chromium compound in isopropanol and applied by a pad-dry-cure method [8,45,46]. The Quilon chrome complexes produced fabrics with a soft handle and with a high initial water-repellency, but their more widespread application was greatly restricted because of the blue-green coloration that was imparted to the fabric [53]. The main textile end-uses were therefore restricted to tents, awnings, boat covers, and surgical drapes and gowns made from non-woven materials. Similar products were marketed by a number of manufacturers – for example, Phobotex CR (Ciba), Quintolan W (ICI) and Ombrophob C (Sandoz) [45]. While Quilon chrome complexes are still manufactured, their main applications now lie in materials other than textiles, such as paper, packaging, release films and leather.

The aluminium analogue, initially marketed as Aluminium Complex 101, was a coordination complex of aluminium and myristic acid dissolved in isopropanol [45]. This product was more difficult to use than the chromium complexes, because dilute aqueous solutions were less stable – at a concentration above 3%, the aluminium/myristic acid complex had poor stability and its use was not recommended. However, the application method was simple; the aqueous solution was padded onto the fabric at room temperature, followed by stenter or festoon drying, without any need for a subsequent curing treatment. The aluminium/myristic acid complex could be applied to most fibres, but was generally less effective on fabrics composed of cellulosic fibres, compared with those containing wool or synthetic fibres [45].

Quilon chrome complexes have not been isolated from solution and therefore their structure has been inferred, rather than confirmed. The likely structure [54,55] is shown in Structure 5.3, where R represents a fatty acid radical of chain length C₁₃–C₁₇ and R' represents the C₃ alkyl group of isopropanol (propan-2-ol).



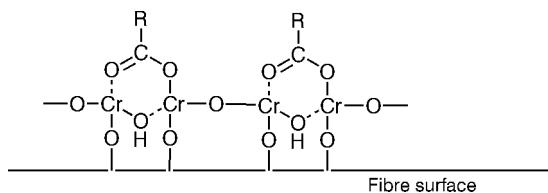
If the Quilon solution in isopropanol is diluted with water, this replaces the coordinated alcohol groups and some of the chlorine atoms. The chlorine atoms enter the solution as chloride ions and hence the molecules of the Quilon chromium complex become positively charged. Thus dilution with water, raising the pH value of the solution by neutralisation with a weak base, or heating, causes the complex to hydrolyse. The water molecules within the complex then lose protons (H⁺) and the molecules can then polymerise through the formation of hydroxyl bridges to yield linkages of the –Cr–O–Cr– type [8].

It is important, during the application of the chromium solution to fabrics, that this

polymerisation is restricted, otherwise the polymer generated may precipitate out of solution. The stability of Quilon solutions is thus dependent upon the concentration, temperature, amount of neutralisation and the time that the solution is left standing [55]. The solution becomes more acidic because of the greater number of protons released during the polymerisation process. With careful control, precipitation can be prevented, and in the colloidal or sub-colloidal state prior to precipitation the best water-repellency results are achieved, because this avoids particle formation.

Fabric is normally padded through an aqueous solution of Quilon C, a chrome–stearic acid/chrome–myristic acid complex, which is buffered with hexamethylene tetramine or NaOH to a pH of 4.5 [55]. Quilon S, a stearic acid complex, and Quilon M, a myristic acid complex, are buffered to pH 3.5, the pH adjustment being necessary when Quilon chrome complexes are applied to acid-sensitive materials. In a typical application, the pad liquor containing 30 g l⁻¹ Quilon (30% stearato chromic chloride) is buffered with 4 g l⁻¹ hexamethylene tetramine. It is prepared from a 10% Quilon solution, which has been preheated for 5 minutes at 95 °C to effect limited polymerisation without the product becoming insoluble in water and precipitating. The liquor is cooled to 30 °C, diluted and buffered with hexamethylene tetramine, padded and the treated fabric dried at 100 °C or higher. Curing can be effected at temperatures of 150–170 °C, whence further polymerisation of the chromium complex occurs.

Textile fibres that contain hydroxyl (–OH), carboxyl (–COOH), amide (–CONH₂) or sulphonic acid groups (–SO₃H) in the fibre surface generate a negative surface charge when placed in water. The high positive charge on the chromium atoms in the Quilon polymer causes these to strongly bond to the negatively charged fibre surface [8,45,55]. Thus, as the chromium atoms are bonded to the fibre surface, the organic fatty acid groups, which are hydrophobic, are caused to be oriented perpendicularly away from the fibre surface (Scheme 5.12). Drying and curing irreversibly eliminate water molecules and the chromium complex becomes strongly bonded to the fibre surface, the hydrophobic fatty acid groups giving rise to the water-repellent effect.



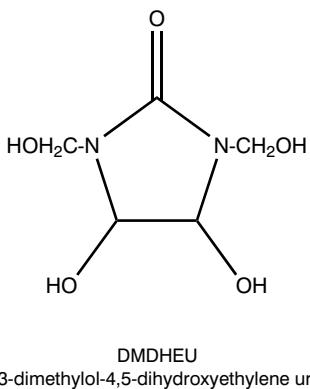
Scheme 5.12

5.4.6 N-Methylol derivatives

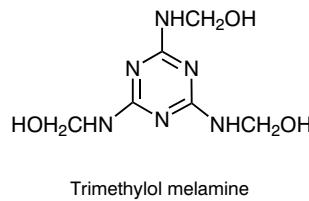
The introduction of N-methylol (N-hydroxymethyl) compounds as self-crosslinking resins, and of cyclic reactants that can form crosslinks with functional groups in fibres, gave rise to a new method of water-repellent finishing, namely the use of resin-wax emulsions or dispersions [46]. A large number of patents have been issued in this field since the 1930s largely because this

route opened up the possibility of producing wax-based water-repellent finishes that were durable to high temperature washing [8]. As a result, a large number of waxy and long-chain fatty acid type compounds have been reacted with various N-methylol-based derivatives in order to produce water-repellent finishes with greater durability that may also be incorporated as extenders for fluorocarbon finishing.

N-Methylol compounds normally react preferentially with the primary C₆ hydroxyl groups of cellulose to form a methylene ether linkage [56]. Compounds such as 1,3-dimethylol-4,5-dihydroxyethylene urea (DMDHEU) (Structure 5.4) are considered to act as crosslinking agents reacting primarily with the fibre hydroxyl groups rather than by self-crosslinking, which is predominantly the case with urea formaldehyde resins. Melamine formaldehyde derivatives, such as trimethylol melamine (Structure 5.5), are particularly valuable because each melamine ring contains three amino groups, each of which can react with one or two moles of formaldehyde (methanal). Thus melamine can be used to provide resin precursors with up to six N-methylol functional groups, each of which may be capable of reacting either with a hydrophobe (that is, a long-chain alcohol, amine or fatty acid) or with the C₆ hydroxyl groups of cellulose, or with amino or carboxyl groups in other fibres [8,46,57].



5.4



5.5

It is clear that any covalent linkages formed between the fibre and the melamine formaldehyde resin, and similarly between the hydrophobe (or wax) and the melamine formaldehyde resin (Structure 5.5), should provide a durable fibre–melamine–wax linkage. In addition, melamine formaldehyde with three or more N-methylol functional groups can self-crosslink (or condense) in three directions leading to the formation of a stable thermosetting resin of high molecular weight trapped within the fibre structure and to which the hydrophobe (or wax) is attached by strong covalent bonds [8,46]. Both these situations may occur in practice depending upon the specific treatment conditions, and both reaction sequences will produce a water-repellent finish that is much more durable to hot washing treatments.

The early patents stressed the formation of the water-repellent finish within the fibre by reaction of the N-methylol compound and the hydrophobe in situ [8]. However, since the 1970s,

increasing use has been made of prior reaction of the N-methylol-based melamine derivative with the long-chain waxy compound to form the water-repellent melamine-based derivative, which is then co-applied with a wax to increase the water-repellent effect obtained. In one patent, methylolmelamine is reacted with methanol to form the methyl ether derivative [58]. This is more stable chemically and can be reacted with a long-chain fatty acid such as stearic acid, $C_{17}H_{35}COOH$. The resultant ester that is formed is then mixed with molten paraffin, a non-ionic surfactant, dimethylethanolamine, polyvinyl alcohol or hydroxyethyl-cellulose and water.

Fat-modified melamine resins such as Phobotex FTC New (Ciba) cannot be dissolved or emulsified directly but are melted with hot water and then emulsified with acetic acid or Catalyser RB [59]. Phobotex FTC New forms a cationic emulsion that is compatible with cationic or non-ionic products, although preliminary trials are always advisable to ensure chemical compatibility in the pad bath. Catalyser RB gives very finely dispersed emulsions of good stability and moreover avoids the presence of offensive odours in processing or on the finished goods.

In general, 2–5% owf Phobotex FTC New is required for good water-repellency [59]. Typical conditions for a 4% add-on are 50 g l^{-1} Phobotex FTC New either with 12.5 g l^{-1} Catalyser RB or with 6.25 g l^{-1} acetic acid (80%) and 2.5 g l^{-1} aluminium sulphate ($Al_2(SO_4)_3 \cdot 18H_2O$).

The liquor is padded at room temperature to 80% wet pick-up on woven cotton fabric using a two- or three-bowl mangle (medium hardness). The padded fabric is then dried on a stenter at $150\text{ }^{\circ}\text{C}$ or for shorter times at higher temperature. The curing units used must be well-ventilated because small amounts of volatiles are removed during curing. Curing can be accomplished on cylinder dryers, tensionless nozzle-type hot flues or in hot-air chambers (vertical, horizontal or festoon systems). If superheated steam is used for curing the time required will generally be shorter.

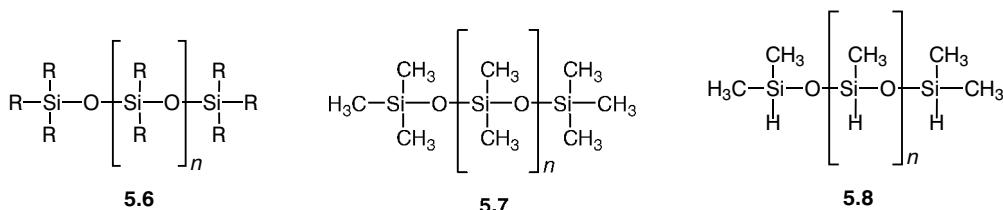
Fat-modified melamine finishes like Phobotex FTC New may be combined with other easy-care agents, according to the degree of performance required, provided that there is no chemical incompatibility in the pad bath [59]. Outstanding water-repellency and impermeability to water can be obtained, with very good wash fastness and freedom from odour even though washing-off after curing is not required. The good handle is combined with good sewability and the finish is fast to repeated washing on cotton even at the boil. However, it is essential to remove all traces of surfactants before padding, drying and curing and the wash fastness varies according to the fibre type. In addition, because the finish is soluble in dry-cleaning solvents it is normally found that dry-cleaning appreciably decreases the water-repellent effect and the permeability to water. While Phobotex FTC New does not prevent grease or oil stains it does offer some protection against water-borne or mineral stains and can be used as an extender with fluorochemical finishes to improve the durability of the total finish to washing treatments [59].

5.4.7 Silicone finishes

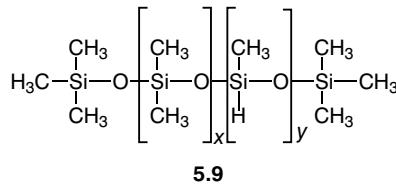
It was fifty years after the discovery of tetra-substituted asymmetric silicon compounds by Kipping and his coworkers in 1901 that silicones, based upon polysiloxanes, were first used as

textile water-repellents in the UK [60]. The hydrophobicity of silicones was first discovered by Patnode who noted that paper treated with chloromethylsilanes was water-repellent after exposure to moist air [61]. Water hydrolyses chloromethylsilanes to silanols, which then condense spontaneously to form siloxanes.

Polysiloxanes are based upon Structure 5.6, with an $-O-Si-O-Si-$ backbone, where R may be a hydrogen, hydroxyl, alkyl, aryl or alkoxy group [8,60,62]. Polysiloxanes for use as water-repellent agents for textiles are usually mixtures of linear polydimethylsiloxanes (Structure 5.7) and polymethylhydrogen siloxanes (Structure 5.8).



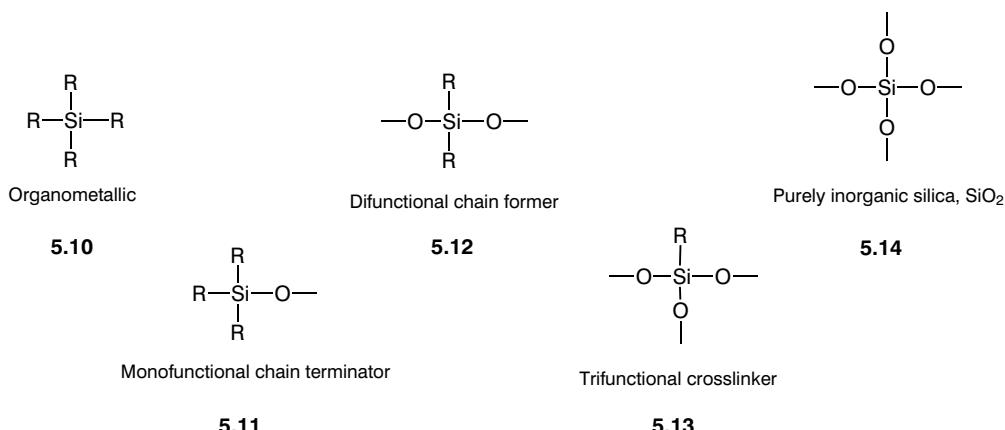
Commercial water-repellents for textiles are thus based [60,62] upon block copolymers of the form shown in Structure 5.9.



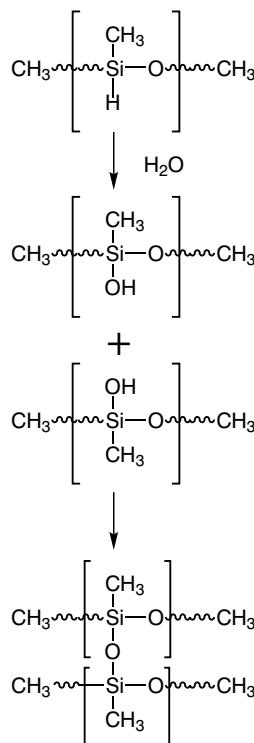
The introduction of the reactive hydrogen atoms in the polymethylhydrogen siloxane lowers the temperature and time required to cure the silicone water-repellent finish down to acceptable commercial application conditions, namely 120–150 °C for several minutes, whereas the fully methylated siloxane would require several hours at 200–250 °C to obtain satisfactory water-repellency [60].

Polydimethylsiloxanes form a flexible surface film over textile fibres, which imparts a soft handle whereas polymethylhydrogen siloxanes polymerise to leave a hard brittle surface film with a harsh handle [8]. The incorporation of the polydimethylsiloxane thus acts as a plasticiser and provides good water-repellency with a soft handle.

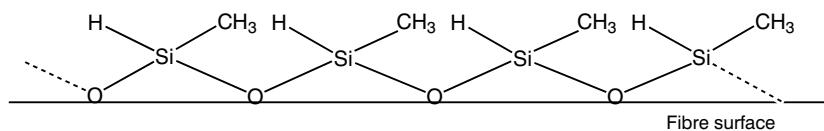
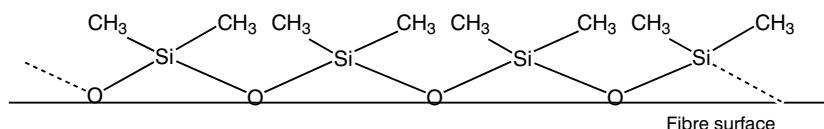
Silicones are intermediate in character between inorganic and organic materials, and possess hybrid properties [60]. This can be seen in the following structures: organometallic (Structure 5.10), monofunctional chain terminator (Structure 5.11), difunctional chain former (Structure 5.12), trifunctional crosslinker (Structure 5.13), and purely inorganic silica SiO_2 (Structure 5.14).



Thus the chemical manufacturer of silicones can use chain terminating, chain forming, and/or crosslinking functional groups to modify the chemical composition of the polysiloxane and the molecular weight distribution of the silicone polymers generated, and thereby modify the performance and properties of the water-repellent finish [60,62–64]. The $\equiv\text{Si}-\text{H}$ bond is hydrolysed by water to form a silanol group ($\equiv\text{Si}-\text{OH}$), which can then condense with another silanol group or a silane group ($\equiv\text{Si}-\text{H}$) to form crosslinks [8,60,62–65] (Schemes 5.13 to 5.15).



Scheme 5.13

**Scheme 5.14****Scheme 5.15**

The $\equiv\text{Si}-\text{H}$ bond in polymethylhydrogen siloxanes can be rapidly hydrolysed in alkali, or in strongly acidic conditions, and is therefore normally buffered at pH 3–4 and stabilised with certain organic compounds [8]. This prevents the slow release and build-up of hydrogen that can create fire hazards on storage, which should therefore preferably be under relatively cool conditions to minimise this possibility. The silane group, $\equiv\text{Si}-\text{H}$, can also be oxidised by the oxygen in the atmosphere or by oxidising agents to form silanol groups, $\equiv\text{Si}-\text{OH}$, which then can contribute to the crosslinking process [8].

It is well known that a fabric that has been padded with silicone, dried and heat-cured, if tested immediately after heat-curing, does not always give the optimum water-repellency value [65]. The reason for this is that during heat-curing the crosslinking process is not fully completed, and upon storage of the treated fabric under normal ambient conditions for about 24 hours, crosslinking is fully completed by hydrolysis and/or oxidative attack on the silane groups, $\equiv\text{Si}-\text{H}$, to form the fully crosslinked silicone polymer film on the fibre surfaces. This imparts the maximum water-repellency and durability of the finish to subsequent washing and dry-cleaning treatments.

The effectiveness of the polysiloxane water-repellent finish is greatly enhanced by the use of auxiliary compounds, often termed catalysts, which function by improving the adhesion of the polysiloxane chain to the fibre surface, and orient the low-surface-energy hydrophobic methyl groups on the polysiloxane backbone away from the fibre surface [8,60]. Thus the oxygen atoms in the polysiloxane are oriented towards the fibre surface and the hydrocarbon layer formed by the methyl groups is oriented away from the fibre surface [8,66].

The action of the so-called catalysts is not therefore a true catalytic action, but rather that of a compound that promotes the correct alignment of the polysiloxane chains on the fibre surfaces [8,60,62–65] (Schemes 5.14 and 5.15). Zirconium oxychloride, and zirconium acetate used as catalysts with polysiloxane emulsions are considered to function in a similar manner to tetrabutyl zirconate and tetrabutyl titanate, which are usually used with solvent-based polydimethylsiloxanes [8,62,67]. Hydrolysis introduces an insoluble layer of metal oxide on the fibre surface through which the oxygen atoms in the polysiloxane chain are attracted by chemical coordination. This

contributes to the sorption and orientation of the polysiloxane water-repellent. Other catalysts such as divalent carboxylates – for example, stannous octoate, zinc octoate and zinc naphthenate – have been considered to function as phase-transfer agents [65], while organic peroxides may operate as catalysts via a free-radical crosslinking mechanism [68].

Application of polysiloxane water-repellent finishes

Polysiloxanes are normally applied to textiles by padding the material through an aqueous polysiloxane emulsion followed by drying and curing for several minutes at 120–150 °C [8,60,62–64]. Alternatively the polysiloxane emulsion is applied by exhaust procedures, using a cationic surfactant to overcome the negative surface potential of most fibre surfaces in water. Normally the treatment is designed to leave 1–2% silicone water-repellent on the fibre surfaces, but where zirconium or titanium may be co-applied, the application level may be less than this because of the improved orientation of the methyl-rich surface layer away from the fibre surface.

Improved water-repellency and durability of the finish after heat-curing is normally observed by ‘ageing’ for 24 hours before testing the finish performance. Durability can be enhanced by co-applying suitable easy-care or durable press finishes in the pad bath followed by drying and curing under appropriate conditions [8].

Polysiloxanes are soluble and stable in xylene and chlorinated organic solvents such as perchloroethylene (tetrachloroethylene) so that it is also possible to apply water-repellent finishes to textile materials using exhaust procedures in special solvent finishing machines, which are normally reserved for this purpose. This solvent application can give rise to an enhanced water-repellent effect compared with that obtained via the aqueous emulsion application method, because the presence of residual surfactants from the aqueous method can give some impairment of the water-repellency.

The durability of modern silicone finishes on synthetic fibres like polyester and polyamide remains fairly resistant to normal laundering and dry-cleaning treatments. However, some decrease in performance is normally observed after dry-cleaning which may be attributed to the absorption of hydrophobic impurities deposited on the fibre surface from the dry-cleaning solvent and also to some dissolution of the polysiloxane in the organic solvent [63,64]. Where silicone finishes on natural fibre fabrics are laundered under aqueous conditions, the polysiloxane film may be ruptured by the swelling of the fibres [8,66,69]. Even during subsequent heating treatments, such as tumble-drying or hot ironing, the polysiloxane film cannot be melted, nor can it flow together, to seal the cracks in the film surface. As a result some deterioration in performance after laundering is normally observed with fibres that swell considerably in water, such as cotton, viscose, and other cellulosic fibres.

Polysiloxane finishes were widely used in the period 1970–1990 because of their wide applicability to many textile materials, their ease of application and ability to be combined with other chemical finishes to provide multifunctional finishes, the relatively low add-on and soft handle compared with other available water-repellents, and their lower cost compared with

fluorochemicals [8,63]. Over the last decade of the twentieth century, however, there was considerable growth in the use of the more expensive fluorochemical finishes, which can be applied at a lower add-on – for example, 0.15–0.3% o/wf. This came about as a result of the increasing market demands for water-repellency and oil-repellency.

The critical surface tension of a fully oriented polysiloxane finish is only $\sim 24 \text{ mN m}^{-1}$, which is not low enough to prevent hydrocarbon-based oils – for example, *n*-heptane ($\gamma_{\text{LV}} = 20 \text{ mN m}^{-1}$) and *n*-octane ($\gamma_{\text{LV}} = 22 \text{ mN m}^{-1}$) – from wetting, spreading and wicking into the structure of the silicone-treated textile material [8,20,23]. Fluorochemicals, which exhibit a lower surface energy ($\gamma_c \sim 15 \text{ mN m}^{-1}$) than silicones, do however enable the textile finisher to provide both water- and oil-repellency.

Thus the market in fluorochemicals has advanced considerably in comparison with all other methods of water-repellent finishing, particularly in markets in which the highest standards of durability and performance are required. The increasing consumer demand for easy-care properties, such as soil- and stain-repellency and soil- and stain-release properties, may be met by modification of the fluorochemical structure and the use of extenders. Hence, fluorochemical finishes are likely to dominate the textile market for repellent finishes over the early part of the twenty-first century [38].

5.5 FLUOROCHEMICAL REPELLENT FINISHES

5.5.1 Fluorochemical finishes

Fluorochemical finishes (also termed fluorocarbon finishes) were first applied to textiles in the 1960s [35,39,70] and their growth, particularly during the 1990s, has been greatly stimulated by the consumer demands for easy-care properties such as water- and oil-repellency, stain-repellency, and soil- and stain-release properties. Unlike silicone- and wax-based finishes, which confer water-repellency but not oil-repellency on textile fibre and fabric surfaces, fluorochemical finishes can combine outstanding water-repellency with oil-repellency [24,35,71,72]. This provides a level of protection to textile fibre surfaces against both aqueous and oily liquids, which confers upon fluorochemical-treated textiles both stain- and soil-repellent properties. The relative advantages and disadvantages of water-repellent finishes based upon paraffin waxes, silicones and fluorochemicals are compared in Table 5.6 [73].

Fluorochemicals (fluorocarbons) are a class of synthetically produced organic chemicals that contain a perfluoroalkyl residue in which all the hydrogen atoms have been replaced by fluorine [8,24,35,39,71–73]. Fluorochemicals exhibit outstanding chemical and thermal stability, low reactivity through their incompatibility with water and oil, and considerable reduction in surface tension [8,23,24,71–73]. It is this latter property which is of particular importance in the context of water- and oil-repellency, while their chemical and thermal stability contribute towards the durability of the surface finish to fabric care treatments such as laundering, dry-cleaning and tumble-drying.

Fluorine, first isolated by Moissan in 1886, is the most strongly electronegative element in

Table 5.6 Repellent finishing of textiles [73]

	Advantages	Disadvantages
Paraffin waxes	Good water-repellency Resistant to water pressure Low price	Little breathability No oil-repellency Not wash fast
Silicones	Good water-repellency Water-vapour-permeable Soft handle Good price/performance ratio	No oil-repellency No soil-repellency
Fluorocarbons	Good oil- and water-repellency Resistant to washing and dry-cleaning Soil-repellency Good price/performance ratio	High price level

nature and is extremely chemically reactive [72]. In the fluorine atom the electrons are held close to the atomic nucleus. The interaction of fluorine atoms with carbon atoms to form strong carbon–fluorine bonds leads to the carbon atoms in fluorocarbons being closely surrounded by fluorine atoms [71,72]. Thus the basis for the low reactivity of fluorochemical finishes is the high degree of protection provided by the fluorine atoms to the shielded carbon scaffold. In addition, the extremely low critical surface tension and high surface activity associated with fluorochemicals are also a consequence of this unique molecular topography [8,35,38,71–73].

Fluorochemicals are used in many fields, for example, as durable lubricants, corrosion-protection coatings for metals, flame-retardant polymers, fluorine elastomers used in the rubber industry and heat transfer fluids in refrigeration technology [72]. They are widely used as protective agents against water and oil, stains and soiling in the textile, paper and leather industries. Some fluorochemicals are used for specialist wetting applications in the textile field, others are used in firefighting, and in the electroplating and electronics industries [71].

5.5.2 Synthesis of fluorochemicals

Fluorine occurs widely in nature principally in the form of fluorspar (CaF_2), cryolite (Na_3AlF_6) and fluoroapatite ($\text{CaF}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2$) and is, in fact, more abundant than chlorine in the Earth's crust [72]. Fluorspar may be treated with sulphuric acid to provide hydrogen fluoride via the following reaction (Scheme 5.16).

Hydrogen fluoride is then used in various reactions to synthesise fluorochemicals.

**Scheme 5.16**

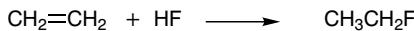
The current techniques available for the formation of fluorochemicals depend upon [24,35,71–73]:

- (1) telomerisation;
- (2) electrochemical fluorination;
- (3) direct fluorination.

However, the first two techniques have been the most widely used to manufacture fluorochemicals for repellent finishes [35], but finishes based on electrochemical fluorination were discontinued by 3M (Minnesota Mining and Manufacturing Company) in 2001 on ecotoxicological grounds concerning the type of fluorochemicals produced [74,75].

Telomerisation

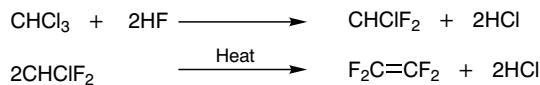
Addition of hydrogen fluoride to unsaturated organic compounds such as ethylene (ethene) can be used to form an organofluorine compound, ethyl fluoride (Scheme 5.17).



Scheme 5.17

Alternatively, organofluorine compounds can be generated through halogen exchange reactions (Scheme 5.18). Tetrafluoroethylene (the telogen) is then subjected to a free-radical polymerisation process as shown in Scheme 5.19 [35,76]. This gives rise to linear polymers of the general formula $\text{C}_n\text{F}_{2n+1}\text{C}_2\text{H}_4\text{I}$ with a chain length distribution n ranging from 4 to 14 or 6 to 12 [73].

On average, the telomer chain length found in commercial fluorochemical finish formulations is around 8–10 [35]. The telomerisation production method (Scheme 5.19) is used

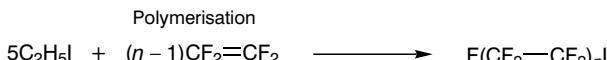


Scheme 5.18

Tetrafluoroethylene



Telogen



Polymerisation



Scheme 5.19

Termination

for a range of fluorochemicals based upon a large number of perfluorinated raw materials, intermediates and end-products supplied by Du Pont (Teflon) in cooperation with Ciba Specialty Chemicals (Oleophobol range) [77].

Telomerisation is also used in the production of the Nuva range of Clariant [73] and the Foraperle range of Elf-Atochem [24]. The telomerisation synthesis is utilised to provide subsequent high yields of perfluoroalkyl mercaptans and alcohols with the general formula $C_nF_{2n+1}CH_2CH_2XH$ where $X = S$ or O , and $n = 6–14$. The general effects of the linear chain length distribution on the repellency properties obtained are illustrated in Figure 5.4 [78].

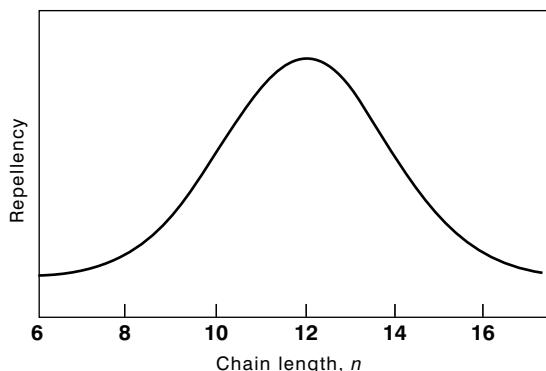
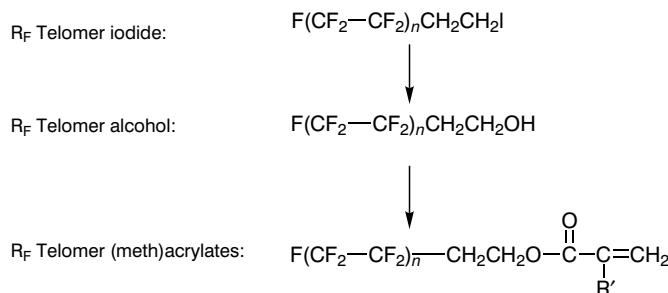


Figure 5.4 Effect of linear fluorocarbon chain length on repellency [78]

Telomerisation yields only linear chains, which in the Clariant process [73] due to the radical nature of the reaction, exhibit a certain distribution from C_6F_{13} up to $C_{12}F_{25}$ at C_2F_4 intervals. The precise distribution may be altered within certain limits by varying the reaction conditions or by distillation and can therefore be engineered towards specific performance requirements. For classic fluorochemical applications in textiles for water-repellency, a high content of C_8F_{17} is advantageous, whereas for surface-active properties a high C_6H_{13} content is generally preferred [73].

The synthesis of fluorochemical building blocks using telomerisation as the starting route is summarised in Scheme 5.20 [35], whereby telomer alcohols and telomer (meth)acrylates can be

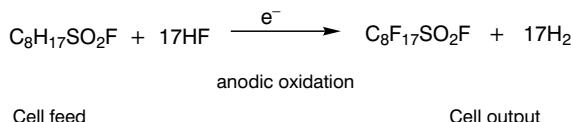


Scheme 5.20 where $R' = —H$ or $—CH_3$

produced, which can then be utilised to manufacture the final active components that can impart repellency properties to textile materials.

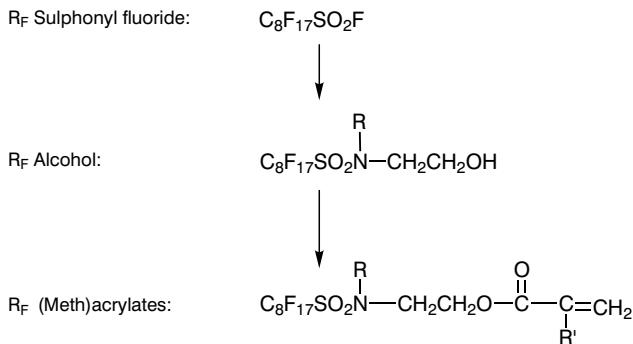
Electrochemical fluorination

Professor Joseph Simons of Pennsylvania State University discovered that a fluorocarbon could be produced by passing a direct electric current through an organic hydrocarbon dissolved in anhydrous hydrogen fluoride [79,80]. Replacement of hydrogen atoms by fluorine atoms takes place in the hydrocarbon when the electric current is passed through the solution, generating a fluorocarbon that is used as a functional intermediate for subsequent reactions. Research workers in 3M advanced the technique of electrofluorination to produce novel fluorochemical finishes [35]. A typical reaction is given in Scheme 5.21.



Scheme 5.21

The octanesulphonyl fluoride is thus converted into perfluorooctane sulphonyl fluoride, which then forms the basis for the synthesis of perfluorinated alcohols and perfluorinated (meth)acrylates (Scheme 5.22) [35,76].



where R = —H, —CH₃, —CH₂CH₃ etc.

R' = —H or —CH₃

Scheme 5.22

The conversion of the sulphonyl fluoride into an alcohol group can be utilised in the synthesis of polyurethane derivatives, esters and (meth)acrylic polymers shown in Scheme 5.22, which ensures that the solubility and melting characteristics can be modified according to whether the

R-group in the alcohol is methyl, ethyl, butyl and so on [35]. By suitable selection of the appropriate R-group and acrylic backbone (for example, acrylic or methacrylic) the thermal, melt and mechanical properties of the final polymer can be controlled.

Electrofluorination technology is highly flexible and versatile and has formed the basis for the manufacture of the Scotchgard Protector range of products from 3M. It is important to realise that the fluorochemicals derived from electrofluorination are uniquely different to those produced by the telomerisation route [72,77]. The electrofluorination technology produces both linear and branched chain fluorochemical polymers with an average chain length of eight carbon atoms. This gives rise to a greater number of $-CF_3$ end groups compared with the products produced via telomerisation, which are solely linear chain polymers with a wider variety in chain length distribution.

However, electrofluorination of hydrocarbons and the use of perfluorooctanyl sulphonate was phased out by 3M, the major manufacturer using this production route, in March 2001 [74,75]. Thus, in future, the major route to fluorochemical manufacture will be via telomerisation.

Synthesis of active compounds used in fluorochemical finishes

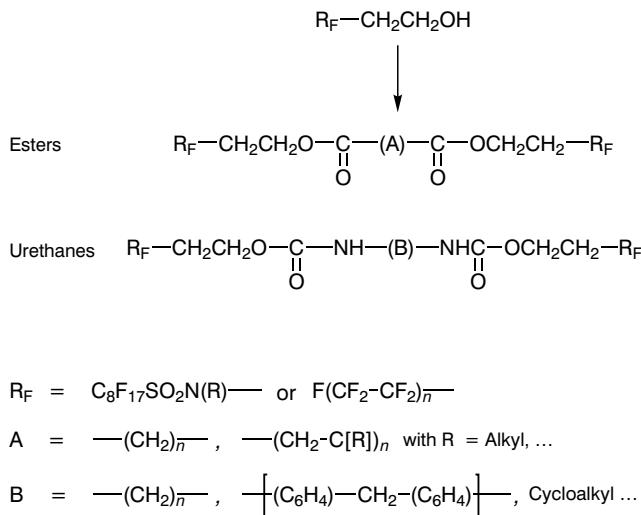
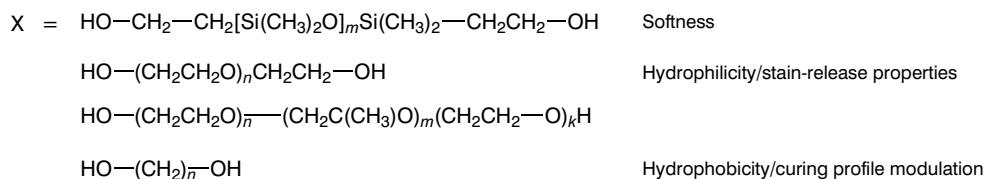
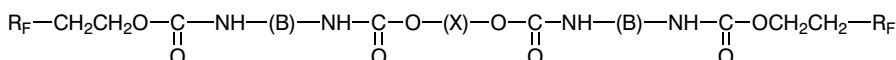
Fluorochemical building blocks manufactured via the telomerisation or electrofluorination technologies can be utilised to manufacture the final active components of fluorochemical finishes, which, when correctly applied to textile materials, impart repellency to water, oil, stains and soils. Three major categories of fluorochemicals are manufactured based upon esters, polyurethanes and acrylic polymers [35,73]. The wide variety of components that can be combined in the final active product formulation gives great scope to the chemical manufacturer to chemically engineer the fluorochemical finish. In this way the performance profile of the fluorochemical finish can be optimised for each specific application area. This versatility and flexibility of performance that is possible by modification of the building blocks for fluorochemical manufacture is a major reason for the continuing commercial success of fluorochemical finishes [35,71–73,77,78]. Fluorochemical finishes thus produce durable surface finishes for textiles with repellency properties that contribute greatly to the high standards of easy-care performance desired by the consumer in both apparel and household textiles.

Formation of fluorochemical block copolymers

In Scheme 5.23, it can be seen that depending upon the use of ester or urethane chemicals there is a wide variety of carboxylic acids – for example, dicarboxylic, tricarboxylic, and poly-acids – and isocyanates based upon aliphatic and aromatic structures with different degrees of functionality that can be used to modify the performance profile of the active components used in the fluorochemical finish [35].

Fluorochemical copolymers with specific properties

The production of fluorochemical copolymers of the general formula illustrated in Scheme 5.24

**Scheme 5.23****Scheme 5.24**

can be subtly modified in order to impart specific performance characteristics [35]. The introduction of poly(dimethyl siloxane) units can promote softness of handle while the introduction of ethylene oxide (oxirane) moieties confers hydrophilicity and release properties. The introduction of hydrocarbon chains can confer hydrophobicity and be utilised to modify the curing profile.

The nature of the chain extender X incorporated in the polyurethane structure can be further modified to alter the performance profile of the end-products [35]. It is noteworthy that polydimethylsiloxane units yield fluoropolymer urethanes with improved softness together with the additional advantage of improved compatibility with other silicone emulsions.

Polymerisation of polyfluoro (meth)acrylates

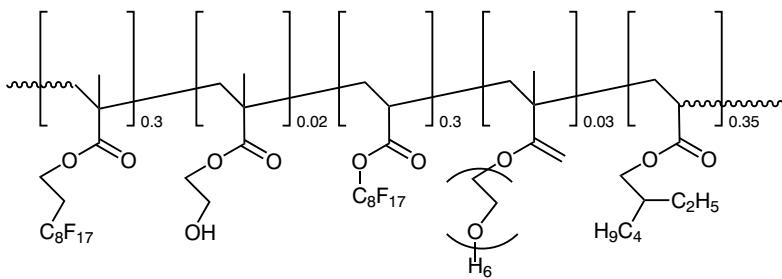
Polyacrylates are widely used as components in fluorochemical finishes [35,71–73]. These are

used in combination with fluorochemical (meth)acrylates and hydrocarbon monomers to influence the performance profile of the final polymer [35]. Thus, performance characteristics such as:

- (1) curing profile;
- (2) dynamic repellency (spray rating, Bundesmann performance);
- (3) static repellency (oil- and water-repellency);
- (4) durability to domestic laundering;
- (5) durability to dry-cleaning;

can all be modified to optimise the performance profile of the fluorochemical finish for a specific application or end-use.

The very wide range of active components used in fluorochemical finish formulations include, amongst others, fluorochemicals based upon (meth)acrylates, alcohols, esters, urethanes, and carbodiimides [35,71–73]. The Scotchgard Protector range of fluorochemicals are polymerised and formulated in organic solution and then pre-mixed with water and carefully selected emulsifiers, which may be cationic, non-ionic or anionic, according to final performance requirements [35]. Other monomers may be polymerised and emulsified in water directly. High shear homogenisation is then utilised to decrease the particle size of the polymer emulsion and then the solvent is removed. This gives rise to a carefully engineered range of fluorochemical finishes that are tailor-made for a particular application method and end-use. Thus environmentally friendly solvent-free dispersions can be simply applied by exhaust or pad-dry-cure procedures. However, for some applications it is not possible to remove all the organic solvent and the fluorochemical finish may be supplied with the minimum of solvent commensurate with satisfactory application and performance properties [35,72].



The structure of fluorinated acrylic latices can be chemically engineered to produce specific performance characteristics. One example of a water- and oil-repellent fluorinated acrylic coating has been described [81] and an example is shown in Structure 5.15.

Clearly, by varying the type of functionality – for example, hydrophobic/oleophobic groups or hydrophilic groups within the side-chains, and their amount, position and sequence along the

polymer backbone (main chain) – a very wide spread of functional performance can be obtained, and specific performance properties can be engineered into the finish [24,35,38, 71–73,78,81].

5.5.3 Fluorochemical finish formulations

Fluorochemical finishes are based upon fluorocarbon dispersions and are mainly acrylate polymers containing a perfluorinated acrylate as the major component [24,35,71–73]. However, practically none of the commercial fluorochemicals consist of pure perfluoroacrylate homopolymer and normally there are various comonomers present.

The main components that may be present in a typical fluorochemical dispersion are illustrated in Figure 5.5 [73]. Oil-repellency and water-repellency depend crucially upon the perfluoroacrylate component but the presence of long-chain fatty alcohol acrylates, such as lauryl and stearyl acrylate, has been shown to produce synergistic improvement in water-repellency with the perfluoroacrylate without adverse impairment of the oil-repellency. Vinyl chloride, vinylidene chloride, methyl methacrylate and acrylonitrile are also frequently incorporated as comonomers where special performance characteristics are required, such as soil-repellency or resistance to organic solvents and white spirit.

Fastness of the fluorochemical finish to domestic washing, laundering and dry-cleaning can be achieved using reactive monomers such as acrylates containing methylol- or epoxy- functional groups [73]. Such reactive functional groups may self-crosslink or alternatively react with functional groups such as hydroxyl, amino or carboxyl groups in the fibre surface. The net result is

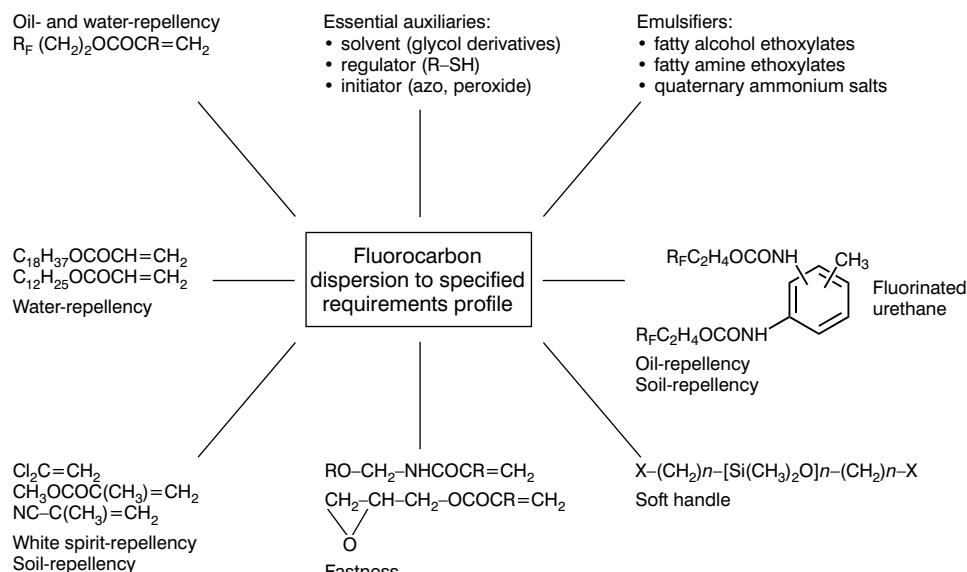


Figure 5.5 Major components of a fluorocarbon dispersion [73]

that the fluorochemical polymer becomes crosslinked and is covalently bound to the fibre surface, greatly increasing the durability to domestic washing, laundering and dry-cleaning.

A softer handle can be attained by the incorporation of high molecular weight polydimethylsiloxanes [73]. The oil-repellency can be enhanced by the use of fluorinated urethane structures, and the precise structure of the urethane components used can be varied within wide limits in order to optimise the performance capabilities of the fluorochemical finish to suit the end-use requirements.

The aqueous fluorochemical emulsion or dispersion must be stabilised using an appropriate emulsifier. Fatty alcohol ethoxylates are used as non-ionic emulsifiers, and quaternary ammonium salts used as cationic emulsifiers [73]. Anionic surfactants are also used but in practice it has been found that combinations of several surfactants provide more stable emulsions, and hence this approach is widely utilised.

The choice of emulsifier is critical because it has a considerable impact on the overall performance of the fluorochemical formulation [35]. In processing, the emulsifier system used must provide a formulation that exhibits acceptable manufacturing characteristics allied with satisfactory shelf-life and transportation properties. In terms of the application of fluorochemical formulations to textile materials, the diluted emulsion must be stable under the application conditions. This means that the diluted emulsion must be robust to changes in pH, temperature, pad speed, shear resistance and pumping conditions. Equally important is the stability in the end-use formulation applied to the textile in which the fluorochemical may be co-applied in combination with other additives such as extenders, flame-retardants, resin or crosslinking finishes, and also fabric impurities. Of decisive importance is the nature of the emulsifier in terms of its chemical composition – for example, hydrophobic and hydrophilic segments – and the amount of emulsifier present. If the emulsifier is not selected with care, the performance of the fluorochemical finish on the textile material may be adversely affected by the presence of emulsifier [24,35,71–73]. Thus careful matching of the fluorochemical formulation to the application conditions (for example, exhaust, padding, spraying, coating, and so on) and to the performance criteria required are essential.

Other auxiliaries used along with fluorochemical finish formulations include solvents, regulators (or chain transfer agents) and initiators [73]. The solvent is essential for synthesising the emulsion and also assists in the film-forming process. Regulators are used to decrease the molecular weight obtained from free-radical acrylate polymerisation, which itself is catalysed by initiators based upon azo or peroxide compounds.

In order to optimise specific performance criteria, usually based upon standardised test methods, the necessary components required for the fluorochemical finish are selected in appropriate ratios and the fluorochemical dispersion produced from these components by emulsion polymerisation [24,35,73]. This ultimately yields a commercial fluorochemical finish with a typical solids content of 15–30% and a fluorine content between 5 and 15% [73].

The general product-related properties of importance for fluorochemicals for use in textile finishing are summarised in Table 5.7 [82].

Table 5.7 Properties of fluorochemicals for use in textile finishing [82]

Product related	
Appearance:	Watery dispersion or emulsion
Viscosity:	Highly liquid
Dilutability:	With cold water
Flash point:	Without solvent (>100 °C)
Storage stability:	At least 12 months, longer as a rule
Thermostability:	Up to +40 °C
Cold-resistance:	Down to -10 °C
Combinability:	With crosslinking agents, catalysts, extenders, flameproofing agents, fillers, softening agents, antistatic agents, antimicrobial agents

5.5.4 Fabric preparation for fluorochemical application

In accordance with good practice in textile dyeing and finishing, fabrics should be clean and free from other processing agents [77,83]. Problems can arise from the following:

- (1) silicone-containing defoamers must be avoided because they normally impair the oil-repellency performance;
- (2) a typical fabric pH of 5–7 is desirable – any residual alkali may destabilise the fluorochemical dispersion and/or may impair the curing of applied crosslinking agents;
- (3) presence of residual surfactants, which exert a rewetting action, can increase the interfacial tension and also decrease both the rating of the hydrophobic properties and the bath stability;
- (4) presence of spin finishes and/or residues of lubricants may impair uniform fabric wetting and the formation of a cohesive fluorochemical film.

Fibre composition and fabric construction can both affect the final performance obtained. The correct choice of fluorochemical must be made for a particular fibre/fabric combination and fibre-blended fabrics can sometimes lead to difficulties in selection of the appropriate fluorochemical. Extenders are required in many cases to provide greater durability to fabric care treatment – for example, domestic laundering and dry-cleaning treatments [77]. Velvets and pile fabrics, because of the nature of their surface structures, may require different fluorochemicals compared with those used on flat fabrics, in order to achieve a uniform distribution throughout the pile structure. Much consolidated information is available from the manufacturers of fluorochemicals upon the best product formulation for a specific fibre substrate/fabric construction and the necessary performance requirements for the intended end-use [24,35,71–73,77,82].

5.5.5 Application methods for fluorochemical finishes

The method of application of the fluorochemical finish to the textile depends upon the form of the material – for example, flat woven, weft knitted fabric, velvet or pile fabric or carpet – and

whether the fluorochemical finish is required to penetrate the structure and provide a film covering all the fibres uniformly, or whether a topical (or surface) application is all that is required [24,35,71–73,77,82]. Light- and medium-weight fabrics (linings, apparel, and home furnishing fabrics) may be saturated by immersion in a pad bath containing the fluorochemical and any appropriate auxiliaries followed by squeezing in a two-bowl or three-bowl nip [24,77,82]. The fibre content and fabric construction normally dictate the wet pick-up range that is possible, and the wet pick-up is controlled by the nip bowl pressure. The chemical add-on of fluorochemical deposited on the fabric is typically around 0.15–0.3% on the weight of the fabric. The chemical add-on is controlled principally by regulating the fluorochemical finish concentration in the pad bath, rather than by regulation of the wet pick-up. As an alternative to padding, other methods of minimum application may be used such as lick-roll or nip padding or vacuum extraction. In the latter case, excess removal may be recycled back to the pad bath.

The vast majority of the fluorochemical finishes used in the treatment of textiles are cationic in nature and the recommended pH of the finishing bath should therefore preferably be around pH 5, which can be attained usually by addition of a small amount of acetic or formic acid [24,35,71,73,83]. This ensures that any residual alkalinity in the fabric is neutralised and also that the finish bath is stabilised because the cationic emulsifiers used are much more effective at this pH level.

Heavier weight fabrics, as used in upholstery, awnings and blinds, may be foam-coated or sprayed with the fluorochemical finish [24]. Foam-coating involves coating the fabric with a stable foam, produced from a diluted solution of the fluorinated treatment, using a squeegee or a roller. For carpet applications recourse is made to foam-coating or to spraying across the carpet width using a series of atomised spray jets, the area sprayed by each jet ensuring that uniform application and penetration of the fluorochemical solution is achieved without overlap or missing areas due to jet blockage. Regular maintenance of the jet spray devices is essential to prevent clogging and spraying is normally conducted with the carpet passing at open-width through a chamber to contain the atomised spray. The chemical add-on and wet pick-up are controlled by the bath concentration and by adjusting the spray pressure in accord with the processing line speed. Foam-coating of carpets is generally carried out on the Autofoam II carpet applicator [84].

After impregnation, the fabric is dried at temperatures of about 110–130 °C followed by heat-curing at a temperature normally in the range 150–170 °C [77]. This may be carried out in separate stages in circulating hot air ovens or more usually in a single-pass treatment on a stenter. The higher the curing temperature, the shorter is the curing time to avoid yellowing of the textile material. Thus, heat-curing treatments at 150 °C for 3–4 min, or 160–180°C for 30–45 s, are typical of the conditions to be encountered in practice [83]. However, carpet products may be heat-cured at a minimum temperature of 110 °C while other products may be treated for 2 min at 170 °C, or for as little as 30 s at 190 °C. The heat-curing conditions used must provide optimal film formation and are dependent upon the chemical nature of the fluorochemical, the presence of extenders used to boost the fluorochemical performance and the durability performance required. Fibres that are heat-sensitive, such as wool or polypropylene, are cured at lower temperatures [77]. Where multifunctional finishes are used – for example, fluorochemical combined with an easy-care finish

– the heat-curing conditions selected must ensure that both the fluorochemical and the easy-care finish are satisfactorily crosslinked to achieve the optimum fabric performance.

Pad bath additives

Depending upon the nature of the fibre substrate, the fabric construction and the performance requirements of the finished fabric, various additives may be mixed into the pad liquor [24,35,77,78].

Wetting agents

Where thorough wetting of the substrate is necessary to achieve a uniform repellent treatment the use of a fugitive wetting agent is normally preferred to avoid problems arising from the presence of residual surfactant. Isopropanol (propan-2-ol) used at 1–3% has been successful in this respect. However, in cases where extreme hydrophobicity is experienced the use of a thermally degradable surfactant, or one with a low residual wetting effect is normally satisfactory [24,35,77].

Thermosetting resins

Thermosetting resins and catalysts are used to improve fabric dimensional stability and resistance to laundering as well as imparting stiffness [8,35,73,77]. Melamine resins are used to improve the handle of nylon taffeta while glyoxal-based products provide wrinkle resistance on cotton/polyester fabrics.

Extenders

Hydrocarbon-based water-repellents and resin-wax dispersions may be used as extenders to boost the repellency performance of the fluorochemical and aid durability [8,35,73,77]. Their addition to the pad bath frequently improves the pad bath stability. Silicone-based products must be avoided because these impair the oil-repellency of the fluorochemical through chemical incompatibility and phase separation problems. Melamine resins, modified by fatty acids, blends of waxes with zirconium salts, or polyurethane resins, have been quite widely used to improve the final performance of the fluorochemical finish [35,73,77].

Other products

Chemical additives, such as softeners, antistatic agents, builders, flame-retardants, or fungicidal or anti-bacterial agents, may also be incorporated into the pad bath to obtain multifunctional finishes [35,77]. Their effects upon the pad bath stability, or problems due to chemical incompatibility that may impair the final finished fabric performance, must be evaluated to optimise both the process and product performance.

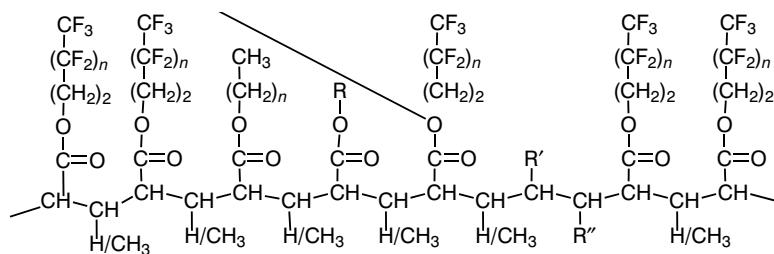
Antistatic agents are generally applied to synthetic microfibres, such as polyester or polyamide microfibres, because of their greater propensity to develop static charges through their considerably greater surface area per unit volume [35,77]. Antistatic agents are normally hygroscopic and can adversely affect the hydrophobic nature of the fluorochemical. Thus careful selection for chemical compatibility and optimum finish performance must be practised.

5.5.6 Fluorochemical structure in relation to performance

The chemical structure of a fluorochemical is based upon a polyacrylate (Structure 5.16). The perfluorinated side-chains of the polyacrylate are oriented away from the fibre surface towards the air and hence the $-CF_3$ terminal groups form a low-energy repellent surface [8,23,71,73,78,83]. For physical reasons the optimum orientation only takes place if the length of the perfluorinated side-chain is at least seven atoms. This maximises the $-CF_3$ group density projecting away from the fibre surface. The exact nature of the comonomers designated R¹, R² and R³ in the structure may be varied in order to regulate the properties of the fluorochemical film [71,73]. Methylol- and epoxy-functional groups can introduce chemical crosslinks that increase the durability to washing. The functional groups must be matched to the fibre surface, and cotton that is rich in hydroxyl groups can react strongly with methylol groups. However, hydrophobic fibres such as polyester with relatively few functional groups require other functional groups in the fluorochemical to obtain greater durability to washing [73].

Some fluorochemicals contain relatively small amounts of polar monomers, which can be of advantage even if these are hydrophilic in nature. Polar monomers are used to create a sustainability of the fluorochemical polymer for the fibre surface, thereby assisting the orientation of the film as well as improving the dispersion stability [73].

The effect of the fluorochemical chain length upon the critical surface tension (γ_C) is illustrated in Figure 5.6 [35]. It can be clearly seen that the critical surface tension decreases fairly rapidly as the chain length (n) increases from 1 to 8, after which little further decrease in critical surface tension is noted [24,35]. As the critical surface tension of the fluorochemical film on the fibre surface is decreased, the water- and oil-repellency rise, reaching their



where R, R', R'' = functional or polar groups, responsible for film formation and hardness, crosslinking to increase fastness to washing, emulsification, and affinity for the textile surface [73]

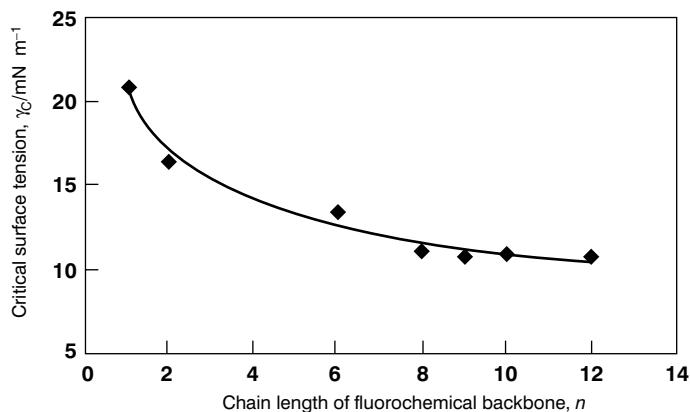


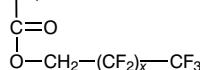
Figure 5.6 Effect of the fluoroochemical chain length on surface tension [35]

Table 5.8 Oil- and water-repellency of fabrics treated with acrylic polymers^a [24]

Perfluorinated groups	Measurement of oil-repellency (AATCC 118)	Spray test (ISO 4920)
-CF ₃	0	50
-CF ₂ -CF ₃	3-4	70
-(CF ₂) ₂ -CF ₃	6-7	70
-(CF ₂) ₄ -CF ₃	7-8	70
-(CF ₂) ₆ -CF ₃	7-8	70
-(CF ₂) ₈ -CF ₃	8	80

Support: printed cotton 1% polymer applied onto fabric

a Acrylic polymers: —(CH₂—CH)—



maximum protective value around a chain length of $n = 9$. This dramatic improvement in repellency performance is illustrated in Table 5.8 in which the oil-repellency (as measured according to AATCC Test Method 118) rises from 0 with a $-CF_3$ terminal group to 8 with a $-(CF_2)_8-CF_3$ side-chain [24]. In addition, the water-repellency (as determined by the spray test ISO 4920) also rises from 50 up to 80. Thus an increase in the perfluorinated chain length from CF_3 to C_9F_{19} (that is, $-(CF_2)_8-CF_3$) gradually enhances the oil-repellency and, to a lesser extent, the water-repellency.

Most fluorocchemical products on the market retain surface energies (or critical surface tension) values in the range 10–15 mN m⁻¹. Their application to textile fibres therefore lowers the critical surface tension (γ_C) of the fibre surface and imparts oil- and water-repellent properties [24,35,73]. Thus the stain-repellency performance is greatly enhanced compared with silicone-based finishes, which merely act as water-repellents because their surface energy values

at around 24 mN m^{-1} are low enough to repel water (surface tension γ_L 72.75 mN m^{-1}) but not low enough to repel oils and hydrocarbons such as *n*-octane (γ_{LV} , 22 mN m^{-1}) and *n*-heptane (γ_{LV} , 20 mN m^{-1}) [8,23,24,35,73].

The fluorinated finishes form low-energy films that sheath the fibres in a textile substrate. Although the textile material may retain its porosity after fluorochemical treatment, the penetration of oil or water into the fabric pores (or capillaries) depends upon the capillary pressure, ΔP (Eqn 5.21) [34].

Because the advancing contact angle (θ_D) of water and oils on a fluorochemically-finished textile fabric is high and the pore radius is very small, it follows that the capillary pressure required to drive the water or the oil into the pore is also high. It is for this reason that the water- and oil-repellency performance values are enhanced after fluorochemical treatment. Only if a high external pressure is applied to the water or oil will the value of ΔP be exceeded, in which case some penetration of water or oil may take place within the pores of the textile material [34]. However, the effects of penetration and soiling by oil may be ameliorated if soil-release properties are imparted to the fluorochemical film, enhancing the removal of oil and soil during domestic laundering [23,24,35].

5.5.7 Improvement of the durability of fluorochemical finishes

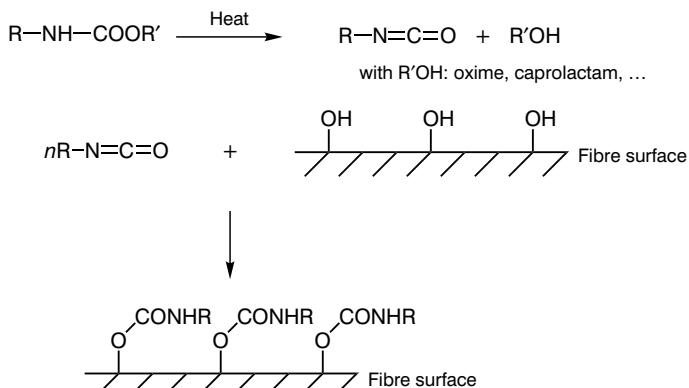
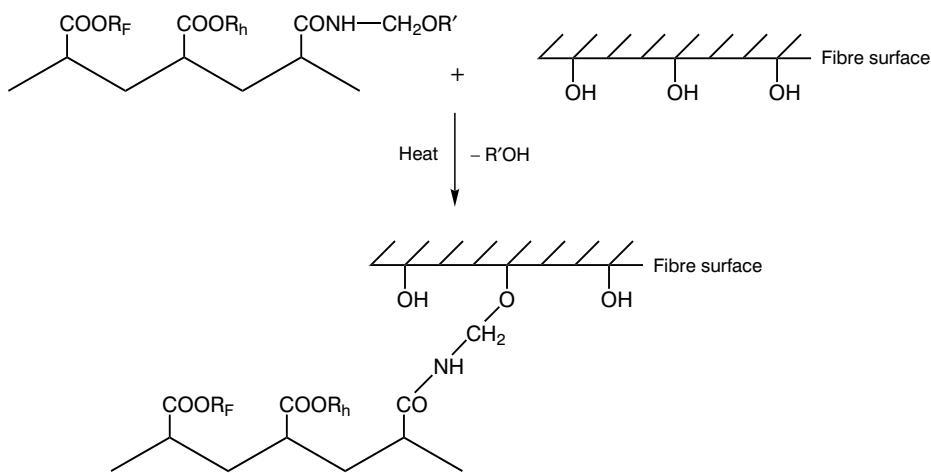
The durability of fluorochemical finishes can be improved by crosslinking systems that modify the structure of the film formed on the fibre surface. Three approaches have been used [35]:

- (1) masked polyurethanes;
- (2) crosslinkable monomers;
- (3) polycarbodiimides.

Masked polyurethanes

Whereas many urethanes prepared from the reaction of isocyanates with alcohols are thermally stable under normal textile curing conditions, it is possible to modify the urethane to impart thermo-labile properties. Thus the reaction of isocyanates with specific blocking agents derived from oximes, imidazoles, sodium bisulphite and caprolactam can be utilised to provide urethanes with a thermo-labile functionality [35].

Typically the textile material is padded or applied via a foam application method, followed by drying and curing at $150\text{--}170^\circ\text{C}$ for the appropriate time. At the curing temperature a certain fraction of the blocked isocyanate functions decompose, generating isocyanate and also a blocking group that is normally volatilised to exhaust. Formation of the isocyanate within the fluorochemical structure facilitates instantaneous reaction with hydroxyl, amino or acid groups present on the fibre surface (Scheme 5.25). This results in the formation of strong covalent bonds between the fluorochemical and the textile fibres, greatly increasing the durability of the finish to wear, domestic washing, and dry-cleaning [35].

**Scheme 5.25**

R_F = fluorocarbon chain

R_h = hydrophilic group

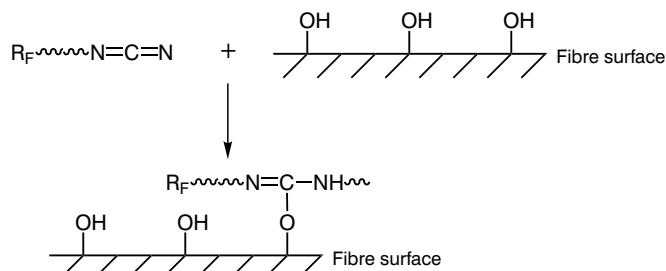
Scheme 5.26

Crosslinkable monomers

Where acrylate-based fluorochemical finishes are applied to textile materials, efficient crosslinking of the fluorochemical with the textile fibres can be achieved using selected crosslinkable comonomers, such as glycidyl methacrylate, 2-chloro-3-hydroxypropyl methacrylate, N-hydroxymethyl acrylamide, N-isobutoxymethyl acrylamide or 2-chloroethyl methacrylate [35]. Incorporation of a crosslinkable monomer into the fluorochemical backbone structure enables the reactive comonomer to react with functional groups in the fibre, such as hydroxyl groups, during the curing step in finishing (Scheme 5.26). The crosslinking of the fluorochemical finish with the fibres thus ensures greatly enhanced durability to wear, domestic washing, laundering and dry-cleaning.

Polycarbodiimides

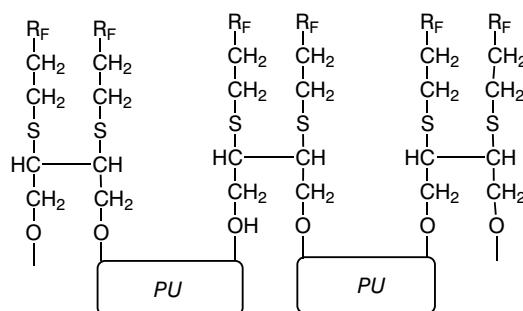
The use of polycarbodiimides can also be effective in improving the durability of the fluorochemical finish to wear, laundering and dry-cleaning. In this method the polycarbodiimide acts as a masked isocyanate, which can react with hydroxyl groups or other functional groups in the fibre at mild temperatures to improve the finish durability (Scheme 5.27) [35].



R_F = fluorocarbon chain

Scheme 5.27

The chemistry of fluorochemical finishes can thus be engineered to provide specific performance properties by simple alteration of the underlying molecular structure of the fluorochemical [23,24,35,71,73,77]. Extra chemicals can be introduced either by chemical reactions or by compounding. The options available can thus be manipulated by the chemical manufacturer to provide desirable properties such as a soft handle or finishes that are designed for application to specific textile substrates and end-products. As an example of this approach, the development of twin-tail chemistry, in which the fluorochemical finish contains spatially very closely adjacent perfluoroalkyl chains, has been demonstrated to provide outstanding repellent effects, particularly upon cotton and cotton-blend fabrics (Structure 5.17) [78].



where $R_F = C_6-C_{14}$ based fluorocarbon chain

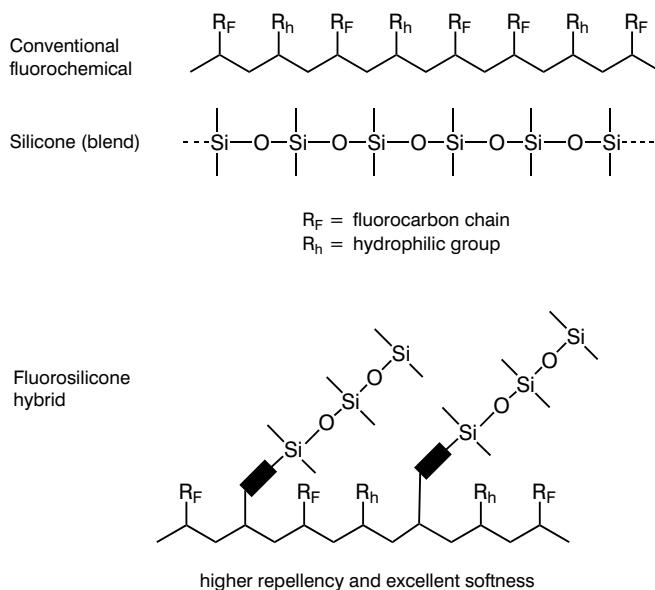
PU = polyurethane

5.5.8 Fluorosilicone hybrids

Although silicones are widely used in textile finishing as water-repellents and softeners, incorporation of silicones with fluorochemicals often leads to phase separation due to chemical incompatibility and to the formation of an inhomogeneous island structure on the coating surface [35]. Because of this, and the higher surface energy of the silicone, the repellency performance is impaired, particularly oil-repellency. To overcome this problem, 3M have developed several fluorosilicone hybrid technologies.

Fluorosilicone macromer copolymers

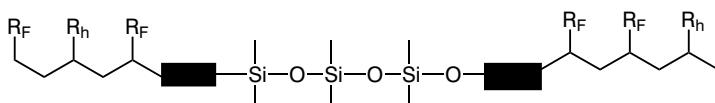
In this novel approach, hydrocarbon comonomers and silicone macromers are copolymerised with a fluorochemical monomer [35]. Silicone macromers are silicone polymers that possess a polymerisable functional group on one of the chain ends. This results in the silicone units being chemically linked to the polymer in the fluorosilicone macromer copolymer, thereby limiting the phase separation (Scheme 5.28).



Scheme 5.28

Fluorosilicone block copolymers

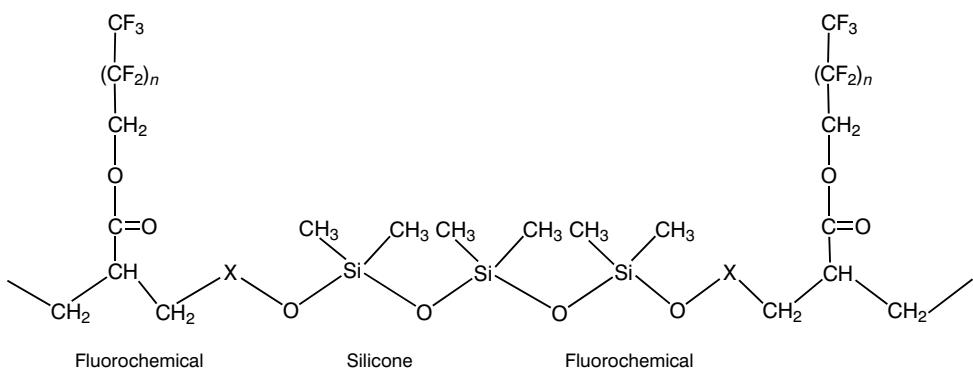
In an alternative approach, the linkage of reactive silicones with fluorochemical copolymer segments is accomplished via different condensation mechanisms [35]. Phase separation and silicone migration are prevented by the block copolymer structure so that there is no loss in fluorochemical repellency or of silicone softness (Scheme 5.29). The incorporation of flexible silicone segments within the block copolymer structure results in excellent low temperature cure properties, which is an additional advantage. A typical representation is given by Structure 5.18 [85].



higher repellency + excellent softness + low cure temperature properties

R_F = fluorocarbon chain
 R_h = hydrophilic group

Scheme 5.29



where X = the bridging group in the block copolymers

5.18

Modified silicone softeners for fluorochemical soil-release treatments

Fabrics treated with fluorochemical finishes in combination with durable press finishes become harsh and less comfortable to wear. Conventional softeners are not very effective in softening such fabrics and high performance silicone softeners improve the fabric handle substantially but impair the soil-release properties of the fluorochemical. Careful selection and blending of silicone softeners can impart a substantial and durable improvement in fabric softness with minimal effect on soil-release.

In one study, it has been reported that the blending of a silicone terpolymer modified with both pendant amino and polyalkylene oxide groups (Magnasoft HSSD) (OSi Specialties Inc.) (Structure 5.19) with a high performance aminosilicone softener (Magnasoft Plus) (Structure 5.20) achieves a satisfactory combination of fabric softness combined with high soil-release performance [86]. A novel $(AB)_n$ linear, polydimethylsiloxane aminopolyalkylene oxide block copolymer (Magnasoft SRS) (Structure 5.21) also provides similar performance.

The proposed orientation of the Magnasoft SRS $(AB)_n$ copolymers on polar fibres is depicted in Figure 5.7.

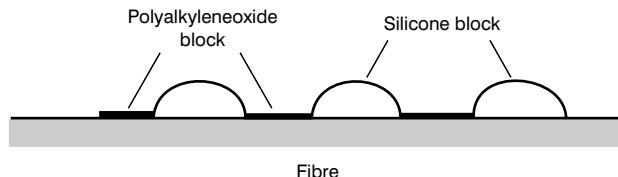
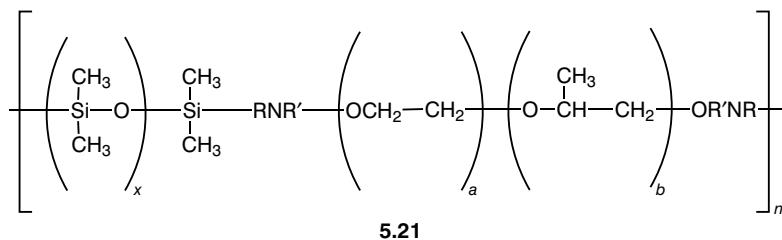
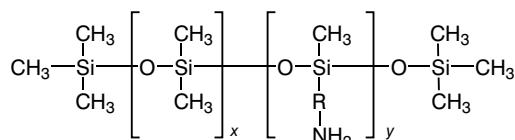
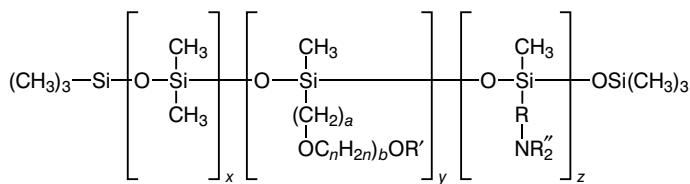


Figure 5.7 Proposed orientation of $(\text{AB})_n$ copolymers on polar fibres [86] (previously published as Figure 5 in 'Modified silicone softeners for fluorocarbon soil-release treatments' by A M Czech, J Pavlenyi and A J Sabia, in *Text. Chem. Colorist*, **29** (9) (1997) 29; reproduced by permission from AATCC)

5.6 REPELLENT FINISHES

5.6.1 European market for fluorochemical finishes

The outlets for fluorochemicals in Europe in 1991 are illustrated in Figure 5.8 [78]. The clothing sector accounts for 60%, the remaining 40% being divided almost equally between household

textiles (excluding textile floor coverings) and technical textiles. The market segmentation includes:

- (1) sportswear;
- (2) protective clothing;
- (3) curtains;
- (4) upholstery fabric;
- (5) table linen;
- (6) awnings;
- (7) pre- and post-impregnation;
- (8) others.

The different commercial markets (paper, leather, carpet, textile) are represented in Table 5.9, where it can be seen that fluorochemical dispersions have a wide variety of end-uses [35].

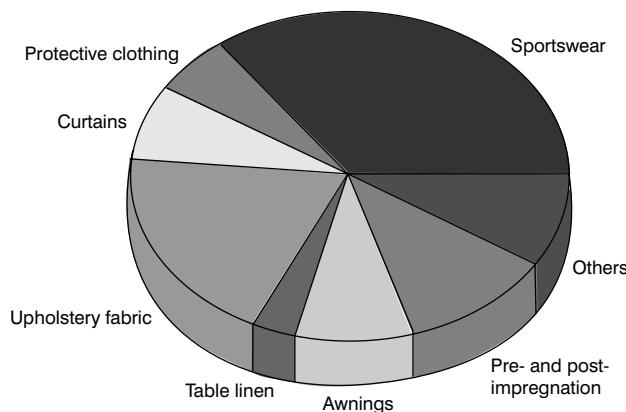


Figure 5.8 Market segmentation of European fluorochemicals (1991) [78]

Table 5.9 Application areas for fluorochemical dispersions [35]

Markets				
	Paper	Leather	Carpet	Textile
End-uses	Paper Board	Shoe Rainwear Upholstery	Floor covering Spin-finish	Rainwear Outerwear Upholstery Workwear Awnings and tents Medical Technical textiles Non-wovens

A more detailed breakdown of the market requirements by market sector and by fibre type has been provided by Lämmermann (Table 5.10) [71]. It is clear that fluorochemicals are very frequently applied to polyamide sportswear, leisurewear, carpets, cotton/polyester uniforms and workwear, acrylic awnings and curtaining fabrics, and cotton upholstery and automotive fabrics, bed and table linen [24,35,71,73,78,82,85,87]. Most of these areas are concerned with the protection of the textile material against staining and soiling.

Table 5.10 Fields of application for fluorochemical finishes [71]

	PA	AR	AC	PP	PE	PE/CO	CO	WO	PE/WO	CA	GL
Sportswear/ leisurewear	B				A	A	C				
Uniforms/workwear	C	C			C	B	A		A		
Upholstery/automotive fabrics	C		B		C		B	A			
Awnings/curtaining fabrics			B		A		A				
Bed and table linen						A		B			
Coated fabrics	C				A	A	A				
Technical textiles	C	C			C		C			C	C
Carpets	B			A	C						

PA	Polyamide	CO	Cotton	A	frequently used
AR	Aramid	WO	Wool	B	very frequently used
AC	Acrylic	CA	Carbon	C	less frequently used
PP	Polypropylene	GL	Glass		
PE	Polyester				

5.6.2 Fluorochemical requirements profile

The market requirements demanded of fluorochemical finishes depend greatly upon the textile material and the performance expected in end-use [24,35,71,73]. Properties such as stain-repellency depend upon [71]:

- (1) water-repellency;
- (2) oil-repellency;
- (3) dry soil-repellency;
- (4) soil-release;
- (5) antistatic performance;
- (6) resistance to rubbing;
- (7) durability;
- (8) handle.

However, the requirements differ according to the end-use. Some indispensable market requirements for various types of textile materials are shown in Table 5.11 [71].

It is clear that, depending upon the field of application, the requirements demanded of a fluorochemical finish can be completely different, and in some cases even conflicting [24,35,71,73,77,78,85,87]. Thus it is unlikely that a universal fluorochemical finish will emerge

Table 5.11 Market requirements for various types of textile materials [71]

Sports and leisurewear	Workwear and uniforms
Water-repellency Handle	Water- and oil-repellency Durability Soil-release
Upholstery and automotive fabrics	Awnings and curtains
Oil-repellency Resistance to rubbing Antistatic performance	Water-repellency Soil-repellency
Bed and table linen	Carpets
Oil-repellency Soil-release Durability	Soil-repellency Stain-blocking action
Technical textiles	
Water- and oil-repellency Resistance to rubbing	

to satisfy all the market requirements and be suitable for application to all fibres by different application methods. Requirements spectra of the type illustrated by Lämmermann [71] are helpful in the design of new finishes and in the selection of fluorochemicals for use (Figure 5.9). In general, it may be noted that there are two main types of fluorochemicals that are developed – those for natural fibres and others for synthetic fibres – because of the differing chemical compositions of these types of fibres [24,35,71,87].

5.6.3 Dual action hybrid fluorochemical finishes

With conventional fluorochemical finishes, oily stains can be introduced by pressure into the treated fabric. Such oily stains can normally be easily removed by dry-cleaning or solvent spotting. However, because the fluorochemical film is hydrophobic in nature this often makes for poor removal of oily stains in domestic washing or laundering [8,23]. The non-polar fluorochemical film that remains in place and presents the same surface to the oil in water as it does in air thus favours the retention of oil through the washing process.

It is well known that superior oil-release in washing results when fabrics have a high surface affinity for water and a high oil-repellency, but this can also result in a low resistance to staining from water-based stains [23]. A major step forward in this field was the introduction of dual action or total action fluorochemical finishes, which are classed as hybrid fluorochemicals

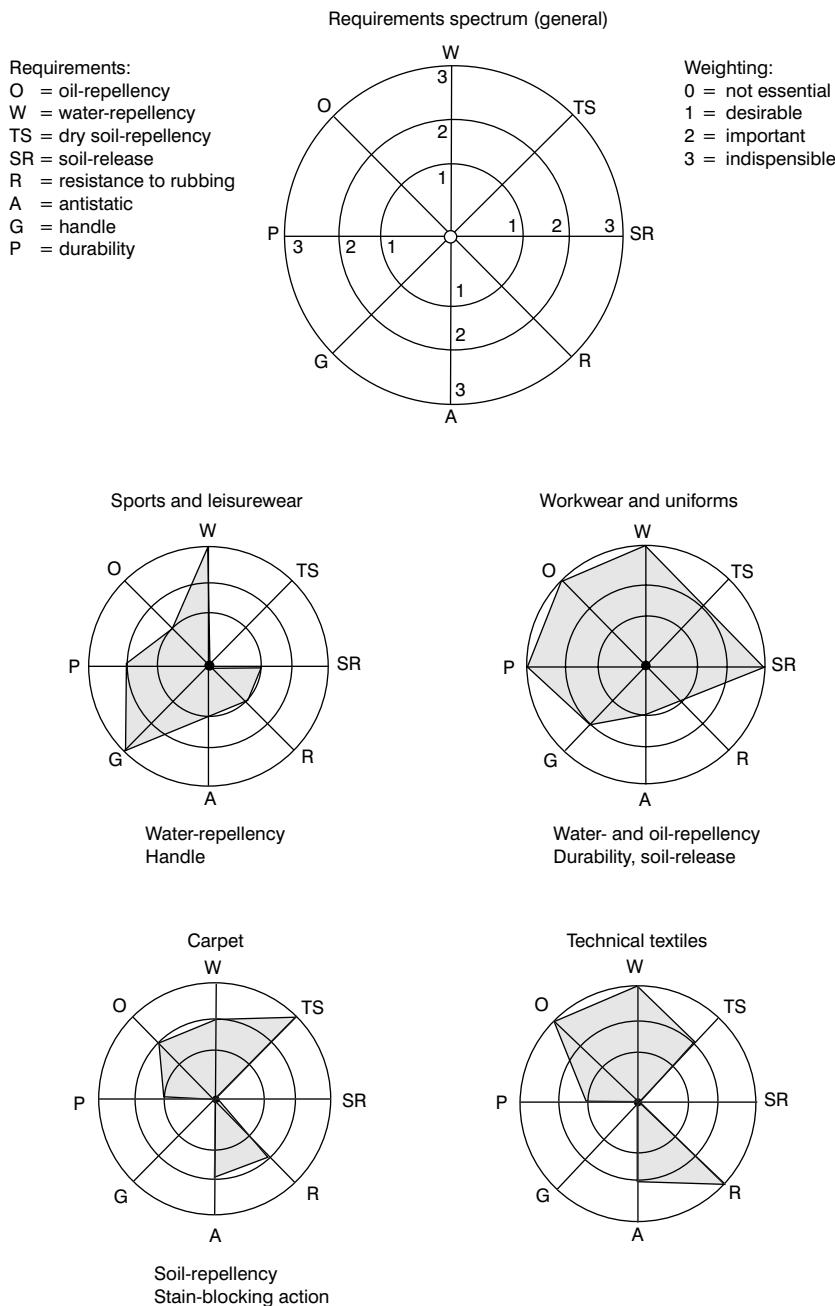


Figure 5.9 Fluorochemical requirements profiles [71]

[23,89]. Hybrid fluorochemicals have a unique molecular structure that incorporates both highly hydrophilic polymer segments (that is, high surface energy) and highly fluorinated polymer segments (that is, hydrophobic and low surface energy). By manufacturing a block

copolymer containing both highly fluorinated and highly hydrophilic polymer segments within a single chain molecule, the desired surface energy in air or in an aqueous environment (for example, washing) can be attained. Thus the hybrid fluorochemical functions effectively as a stain-repellent in air and also as an effective oily soil-release finish in washing [8,23,24,73,87].

The polarity of the environment thus determines the surface configuration of the polymer, and the surface state in air is dominated by the closely packed perfluoroalkyl chains while the hydrophilic groups lie below the surface (Figure 5.10) [23,72,88]. However, on immersing the treated fibres in water, the hydrophilic groups orient toward the polar aqueous environment with the accompanying collapse of the fluorochemical groups below the surface. The net result is therefore that the release of oily stains is strongly promoted [8,23,24,35,88].

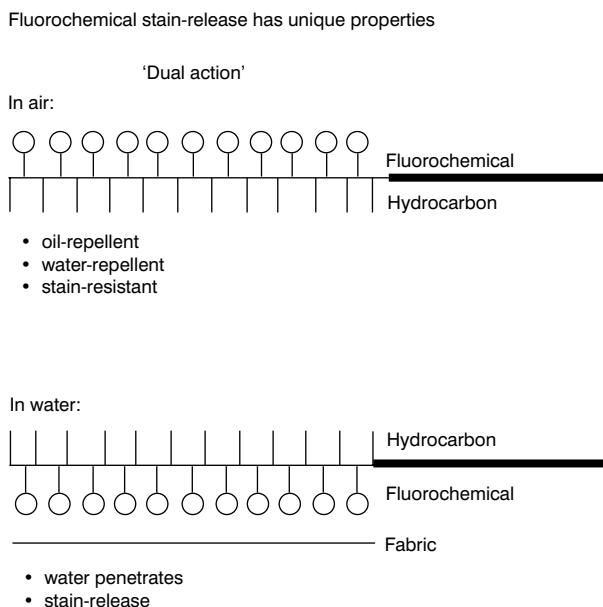


Figure 5.10 Dual action fluorochemical: in air, close-packed fluorochemical groups dominate; in water, they flip to leave the hydrocarbon oriented towards the surface

On completion of the aqueous washing cycle and during the drying of the fabric re-orientation of the hybrid copolymer occurs again, allowing the stain-repellent perfluoroalkyl residues to reassert dominance at the air interface [35,38,72]. This process of molecular re-orientation, however, can be incomplete if the fabric is allowed to be line-dried – that is, dried at low temperature in air. With some hybrid fluorochemicals, it has been recommended that the washed fabric be tumble-dried or hot-ironed in order that the high temperature imparted to the fabric structure activates the molecular re-orientation of the perfluoroalkyl residues.

5.6.4 Laundry tumble-dry (LTD) and laundry air-dry (LAD) performance

Recent market requirements for rainwear and for sportswear have been for air-dry performance.

This means that after home laundering the excellent resistance to water- and oil-based spills and stains may be retained purely by a room temperature air-dry treatment [35,72,73]. No additional heating, tumble-drying or ironing is needed to reactivate the protective finish. The necessity for this performance requirement has arisen because of the widespread use of breathable water-repellent garments. These may be produced by lamination techniques – for example, Gore-Tex (WL Gore) and Sympatex (Akzo) – or coated with a breathable polyurethane coating, as in Breathe (UCB), or with a hydrophilic coating as in Witcoflex (Baxenden).

Garments produced in this way may be dry-cleaned or laundered but in many cases the application of a hot iron is not possible without damaging the garment and impairing its performance. 3M introduced FX-3575 as part of their Scotchgard Protector range; this novel product regains its performance after only a tumble-drying treatment (that is, laundry tumble-dry performance) [35,72]. The necessity for laundry air-dry performance led to the introduction by 3M of FC-5102, a fluorochemical that regenerates its performance by activating molecular re-orientation at ambient temperature [35].

Much consolidated research and development work has resulted in the development of novel fluorochemical finishes such as Nuva V3080 (Clariant), which retains its effectiveness over ten washes with superior performance compared with the first generation (older type) and the standard types of fluorochemicals currently in use [73]. It can be seen from Figure 5.11 that severe impairment of the water- and oil-repellency performance commences after two washes (older type) and after four washes (standard type) whereas the performance of Nuva V3080 is clearly greatly superior even after ten washes. In parallel with this superior performance, the effectiveness of the new product Nuva V3080 (Clariant) is retained even when it is cured at low temperatures, whereas the older and standard types of fluorochemicals require much higher curing temperatures [73] (Figure 5.12). Clearly the future objective is to attain full performance effectiveness by molecular re-orientation at room temperature, with considerable savings in energy and an improved easy-care performance.

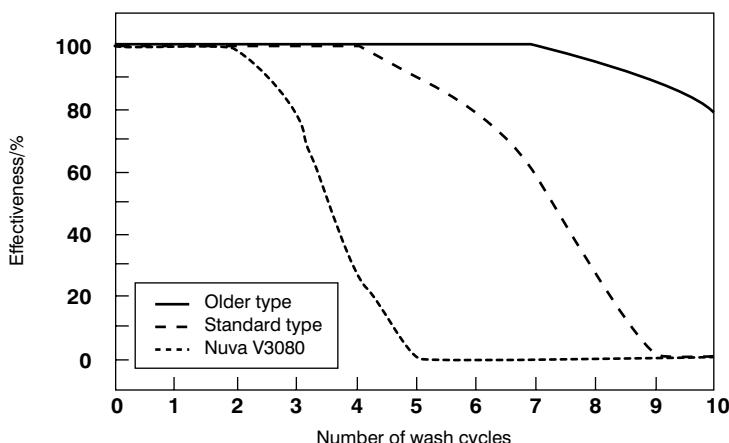


Figure 5.11 Effect of number of washes on water- and oil-repellency of a fluorochemical finished textile [73]

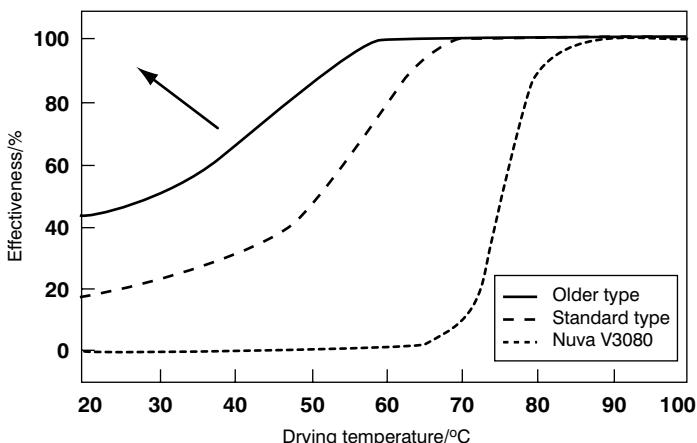


Figure 5.12 Effectiveness of water- and oil-repellency of a fluorochemical-finished textile washed and dried at different temperatures [73]

5.6.5 Stain-repellent and stain-release finishes

Many fabrics require treatment to improve stain-repellency, stain-release and soil-repellent properties, according to their end-use [8,23,24,35,38]. Typical performance requirements are shown in Table 5.12.

Table 5.12 Typical performance requirements of fabrics according to their end-use [8,23,24,35,38]

Stain-repellency	Stain-release	Soil-repellency
Rainwear	Washable apparel	Carpets
Outerwear	Sheeting	Upholstery
Upholstery	Tablecloths	Drapery
Drapery	Washable drapery	
Bedspreads		
Dual purpose		
Mattress ticking		

Stain-repellency is promoted by hydrophobic finishing, and various approaches have been adopted over the last four decades [8,23,24,35,38,71,73]. A comparison of the available stain-repellent products applied to textile fabrics is given in Table 5.13 [90]. It can be seen that the paraffin derivatives and melamine-modified fatty acids are economic, but are not durable and give rise to emission problems during production. These are mainly used as extenders with fluorochemical finishes. Silicone products give more soft and permanent effects but can cause problems in subsequent coating and can attract dirt. Silicones are not normally used as

extenders for fluorochemicals because their more open chemical structure and higher surface energy decrease the oil-repellency and the overall repellency performance [35,63]. This is considered to arise as a result of polymer phase separation due to chemical incompatibility. This gives rise to the formation of an inhomogeneous ‘islands-in-the-sea’ structure in the coating surface [35].

Table 5.13 Comparison of available stain-repellent products [90]

Parameter	I	II	III	IV
Chemical nature	Zr, Al salts of paraffin waxes	Fatty acid melamine condensation products	H-siloxane polymers	Fluorocarbons (FC) (acrylate, urethane)
Advantages	Water-repellent, hydrostatic pressure resistant, extender for fluorochemical	Water-repellent, hydrostatic pressure resistant, extender for fluorochemical	Water-repellent, soft feel, permanent	Water-, oil- and dirt-repellent, permanent
Fibres	Cotton, viscose	Viscose	Cotton, polyester/cotton	Universal
Cost	Low	Medium	High	Very high

5.6.6 Stain-blocking treatments for carpets

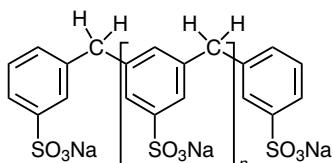
Carpets that contain polyamide or wool fibres must be protected against accidental staining due to spillages of coffee, tea, soft drinks and other liquids and foodstuffs containing substances that can act as colorants [91]. Some degree of protection is afforded by fluorochemical treatments that can be used to impart stain-resist and stain-release properties to the surfaces of the pile fibres. However, the carpet shearing process for cut pile carpets leaves many cut fibre ends relatively unprotected. Fluorochemical treatments can be used to increase both soil- and stain-resistance, particularly if the stains are mopped up and removed rapidly. However, some stains, which have structures similar to acid dyes and which are not treated rapidly, have time to chemisorb or ‘dye’ the fibres, particularly where nylon 6 and nylon 6.6 pile fibres are concerned, and the fluorochemical treatment alone cannot prevent this occurring [91].

The concept of stain-blocking was introduced to prevent chemisorption of stains containing colorants that function as acid dyes. Thus the co-application of a stain-blocker and a fluorochemical to the pile fibres of polyamide carpets can lead to substantial increase in soil- and stain-resistance [84]. Stain-blockers have been derived from syntans, which were first developed by Stiasny [92] to tan leather, but have been used increasingly since the 1960s as aftertreatments to improve the wet fastness of acid dyes on polyamide fibres.

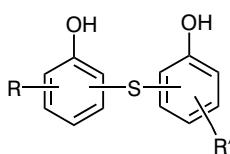
Syntans and stain-blockers are generally condensates of formaldehyde with phenolsulphonic acids, naphtholsulphonic acids and sulphonates of dihydroxydiphenylsulphone, or mixtures of

these [91]. Condensation products in which each repeat unit is monosulphonated are claimed to be more effective stain-blockers [93]. Cooke and Weigmann [91] have classified stain-blockers into the following categories.

- (Type 1) Phenolics: Systems consisting of aromatic rings with hydroxyl groups (Structure 5.22). These include phenol, cresol, naphthol and bisphenol. The products usually contain sulphonic acid groups and are applied in the form of metal salts [91].
- (Type 2) Thiophenolics: These are produced by reacting phenols with sulphur or sulphur mono- or dichloride. Monothiobisphenols or oligomeric thiophenols that are sulphonated and metallised are typical of this type of stain-blocker (Structure 5.23).
- (Type 3) Dihydroxydiphenylsulphones: These products are similar to the Type 1 phenolics. They contain hydroxyl and sulphonic acid groups and are applied in the form of their sodium, potassium or lithium salts (Structure 5.24).
- (Type 4) Non-aromatic: These products are based upon linear, branched chain or cycloaliphatic sulphonates [91].

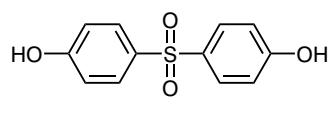


5.22



where R, R' = H, alkyl, halogen, etc.

5.23



5.24

The exact chemical composition, molecular size, degree of polymerisation and degree of sulphonation of most commercial stain-blockers are not generally known, and their effectiveness as a stain-blocker depends to some extent upon the method of application, the presence of other treatments (such as fluorocchemicals), and the effects of any heat treatments [84,91]. It has been suggested that subsequent heat treatment causes low M_r (relative molecular mass) stain-blocker moieties to preferentially diffuse into the fibre interior, while higher M_r components of the stain-blocker are transported into stain-blocking positions in peripheral fibre regions, improving the stain-blocking efficiency [91].

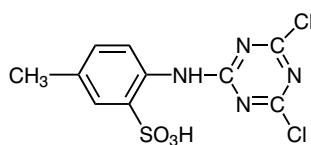
Thus the mode of action of different stain-blockers may vary, but three major factors may be involved [91]. Stain-blockers may be deposited in a ring-like manner on the fibre surface during the application treatment and partial diffusion into the fibre interior may occur during heating, or dyeing treatments if application is accomplished in conjunction with a dyeing process. The deposition of sulphonated stain-blockers on the fibre surface creates a high negative zeta potential (surface charge) on nylon fibres, which consequently should exert a strong repelling influence on the uptake of dye anions. High-affinity syntans exert the greatest resist effects upon dye anions of the lowest affinity (that is, polysulphonated dye anions) whereas the stain-

resist effect decreases for higher affinity (monosulphonated) dye anions. However, even some unsulphonated aromatic hydroxy compounds function as stain-blockers and it seems possible that their action depends upon their hydrophobic nature and their retention in the peripheral regions of the fibre, blocking adsorption of dye anions.

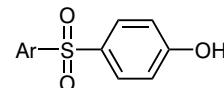
The low pH application level of pH 2–3 and the use of 2% magnesium sulphate in the application liquor for phenolic syntans precludes their application in dyeing. Foam application to the pile fibre on a continuous dyeing line followed by steaming, however, can be used [84].

Many stain-blockers do suffer from some disadvantages. Many stain-blockers give rise to fibre yellowing after application and the yellowing increases on exposure to ultraviolet radiation [91]. Approximately twice the application level is required for nylon 6 to achieve adequate stain-blocking protection compared with nylon 6.6. In addition, many stain-blockers adversely affect the colour fastness to light, and because the application method generally leaves the stain-blocker concentrated near the fibre surface the stain-resist effect can be decreased with wear and abrasion of the carpet pile fibres.

For wool carpet fibres, it has been found that the application of a fibre-reactive dichlorotriazine compound, Sandospace R (Clariant) (Structure 5.25), together with Thiotan CAS (Clariant) (Structure 5.26) – a complex mixture of condensation products of aryl sulphonate and formaldehyde – produces in combination a remarkable synergistic improvement in stain-blocking performance [96].



5.25

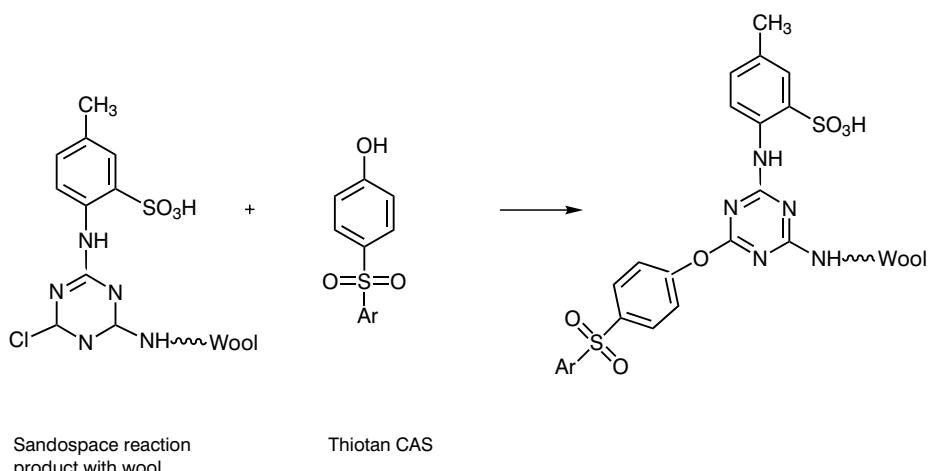


where Ar = aryl group

5.26

It was considered that the mechanism of action was based upon the Sandospace R being covalently bound to the wool and the Thiotan CAS being bound through the phenolic constituents to the second reactive group in the Sandospace R (Scheme 5.30). Thus the stain-blocker is covalently linked to the fibre reactive agent, which itself is covalently linked to the wool fibre substrate. Co-application of this patented system, the Wool Shield Process (Invicta Group Industries Ply Ltd.) can be carried out in continuous dyeing or from an exhaust bath when dyeing loose stock or yarn, and it can also be applied to polyamide fibres [96].

Another stain-release method introduced for wool carpets by 3M in collaboration with Wools of New Zealand, involved the co-application of a specially designed cationic fluorochemical FC-3606 and FC-369, an innovative sulphonated phenolic non-yellowing stain-blocker [94]. This Scotchgard Stain-release system (3M) could be applied during hank dyeing of wool with no need for additional baths. For cut pile carpet constructions, a light top spray of the fluorochemical and the stain-release agent could be applied to ensure that the cut fibre ends were fully treated to attain the highest level of protection.

**Scheme 5.30**

For nylon pile carpets, co-application of a stain-blocker and a fluorochemical finish may be carried out by foam application using a specially engineered carpet foam applicator (Autofoam Systems – Datacolor (UK)) that uses vacuum extraction to draw the foamed liquor deep within the pile yarn to achieve a uniform application level [84]. This 3M Scotchgard Protector system avoided the need for steam fixation and the risk of yellowing during subsequent heat treatments.

5.6.7 Environmental considerations: fluorochemical finishes

The two major manufacturing routes for fluorochemical finishes are telomerisation of tetrafluoroethylene (Teflon, Du Pont) and electrofluorination of hydrocarbons (Scotchgard, 3M) [24,35,73]. While production using the telomerisation route continues, it was announced in May 2000 that the production of Scotchgard Protector products based upon perfluorooctanyl compounds was to be phased out by March 2001 [74,75,97]. 3M voluntarily took the decision to phase out production based upon responsible environmental management and sound business reasons. The decision was not based upon any health or safety concern.

It has been reported that the major component of Scotchgard products (perfluorooctanyl sulphonate) had been detected at extremely low levels in human tissue, wildlife and the general environment [74,75]. The US government Environmental Protection Agency (EPA) commented that '3M data supplied to EPA indicated that these chemicals are very persistent in the environment, have a strong tendency to accumulate in human and animal tissues, and could potentially pose a risk to human health and the environment over the long term'. For these reasons, 3M took the responsible management decision to phase out production by electrofluorination of hydrocarbons and to introduce new chemical products into the Scotchgard Protector brand range.

The manufacture of Oleophobol (Ciba) using the telomerisation route utilises chemical engineering waste minimisation measures, including waste water and off-gas scrubbing technologies [98]. A three-step waste water treatment plant including mechanical, chemical and biological processes is used, in excess of regulatory requirements. Hydrocarbon residues in waste water from the application of Oleophobol completely biodegrade in the treatment process. Fluorinated organic components decompose to non-biodegradable perfluoro-carboxylic acids, which have low aquatic toxicity and pass through the waste treatment facility. Oleophobol is a solid, does not contain chlorofluorocarbons and cannot affect the atmospheric ozone layer.

Human exposure to typical fluorochemical formulation in the form of treated garments and home furnishings have given no sign of skin irritation or contact allergies. Textiles treated with Oleophobol C and Oleophobol S retain over 80% of the fluorine-containing component even after 10 launderings at 60 °C, while the amount initially applied to the fabric is very small, around 0.3% of the total weight of finished fabric [98]. Disposal of Oleophobol-treated textiles by incineration converts the small amounts of fluorine into hydrogen fluoride vapours, which are trapped in water and neutralised by an alkaline scrubber. This completely converts the organic fluorine into an inorganic salt, its natural state. Textile decomposition rates in landfill are little affected by the presence of Oleophobol, the amount of which present is extremely low – less than 1% of the total fluorine components in landfill..

Textile materials treated with Oleophobol contain only about 0.25 g fluorine m⁻², some 200 times less than a fabric laminated with polytetrafluoroethylene. The presence of the hydrogen components in Oleophobol donate enough energy to sustain safe incineration of Oleophobol-treated fabrics.

5.7 NOVEL TREATMENTS WITH POTENTIAL FOR WATER-, OIL-, SOIL- AND STAIN-REPELLENCY

5.7.1 The Lotus Effect: biomimetic ultraphobic surfaces

Biomimetics mimics naturally occurring biological mechanisms with modification, to produce useful imitative synthetic items using conventional methods available to science and technology [13]. The Lotus Effect has been named after the unusual properties of the leaf surfaces of the lotus plant, which are remarkably water-repellent and soil-repellent [99]. The surface of the lotus leaf is covered by a thin extracuticular membrane termed the cuticle, which is covered by waxes forming characteristic microstructures due to self-organisation [100]. On smooth wax layers (surface area contact 10%) the contact angle of water may reach 110°, but because of the surface roughness of the wax layer, whose dimensions can be measured in micrometres, a very pronounced superhydrophobicity is generated with contact angles up to 170° and surface area contact as low as 7%. (As an analogy, imagine a mercury droplet lying on a bed of nails or a pimple rubber mat.) As a result, the area for adhesion of water is markedly diminished and air is enclosed between the droplets and the wax crystals (Figure 5.13).

A similar situation holds true for particles that are located on the surface of the lotus plant

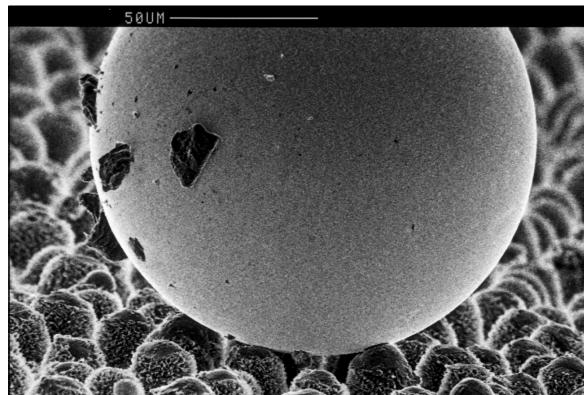


Figure 5.13 The Lotus Effect

leaf. The contact angle between the particle and the surface is minimised, which results in the adhesion of particles to the water surface. This is clearly illustrated in Figure 5.13. Thus, the pouring of water onto a leaf contaminated with soot and powdered Sudan Red B (FW-CI Solvent Red 25) causes the soot and dye particles to adhere to the water surface, and the water droplets roll off the leaf surface carrying the soot and dye particles on their surfaces, leaving the lotus leaf surface clean and dry [101]. Independent of their size and chemical nature, contaminants are removed from such optimised surfaces with only a small amount of water.

This remarkable self-cleaning effect is currently being harnessed to transfer the Lotus Effect into products with biomimetic self-cleaning surfaces. A façade paint suitable as an ‘anti-graffiti’ surface has already been devised and roof tiles and wood paints are currently under development [100]. It is conceivable that within the next decade the application of the Lotus Effect using nanotechnology, precision engineered polymers and suitable application methods could be used to provide a new generation of fabrics with ultraphobic surfaces. These would undoubtedly be expensive but would possess very high levels of water- and oil-repellency and outstanding soil- and stain-repellency properties. However, the adhesion of such polymers to the fibre surface and their durability to abrasion, wear, laundering and dry-cleaning would have to be appropriate for the end-use.

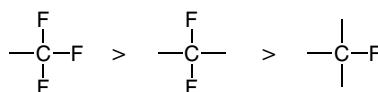
5.7.2 Pulsed plasma polymerisation of monomers

Conventional fluorochemical-based water-repellents are produced using combinations of resins, catalysts, homo- and copolymers, surfactants, pH adjusters, crosslinking agents, heat and solvents. It has been pointed out that such processes can consume large amounts of solvent, are costly, produce large amounts of waste and are highly substrate-dependent [102].

The method of pulsed plasma polymerisation of monomers containing long perfluoroalkyl chains linked to a polymerisable carbon–carbon double bond avoids the need for using solvents [102,103]. Deposited films can exhibit ‘super-repellency’ whereby liquid droplets just roll off the

surface. This phenomenon of super-repellency is, in part, dependent upon the length of the perfluoroalkyl chains.

The tightly bound non-bonding electron pairs that surround each fluorine atom core shell in fluorine–carbon bonds are not easily polarised [102]. This hinders the possibility of hydrogen bonding and dispersion interactions with polar and non-polar liquids. By increasing the degree of fluorine substitution at each carbon centre, this effect can be enhanced (Scheme 5.31).



Scheme 5.31

In addition, the effect can also be enhanced by increasing the length of the perfluoroalkyl group $\text{CF}_3(\text{CF}_2)_n-$ to $n = 7$, which leads to greater withdrawal of electron density from the terminal $-\text{CF}_3$ group.

The use of the pulsed plasma polymerisation technique has already been shown to be capable of producing a variety of surface functionality – for example, surfaces that are oleophobic when dry but become hydrophilic on exposure to water [104]. Clearly such a technique could produce interesting soil-release properties for easy-care treatments. The advantage of using a pulsed plasma method as opposed to conventional continuous discharge to induce initial excitation and fragmentation is that polymerisations appear to proceed much more cleanly by application of the electromagnetic field as pulses of sub-millisecond duration [102].

5.7.3 $\text{C}_2\text{F}_6/\text{C}_2\text{H}_4$ plasma treatments

Plasma treatment of textile fibres and other forms of textile material in fluorocarbon gases or gas mixtures have been studied in the research laboratory and by suitable adjustment of the process parameters non-wettable highly hydrophobic surfaces can be achieved on polyester textiles [105]. The chemical surface modification and the surface roughness have been demonstrated to be responsible for the non-wetting properties of the treated fibre surfaces, and the low-energy polymer surface treatment also acts as a diffusion barrier for protecting the bulk material against chemical attack.

5.7.4 Treatment with reactive fluorinated compounds in supercritical fluid carbon dioxide (SCFCO_2)

Research studies have shown that low molecular weight reactive fluorinated compounds can be made to react with fibres in a polymer-analogous way [106]. Thus it is possible to create a well-oriented very thin layer composed of $-\text{CF}_3$ groups. The close-packing of the $-\text{CF}_3$ groups ensures that there is a decreased tendency of re-orientation in the presence of polar interfaces. Therefore, the repellent effect persists under water.

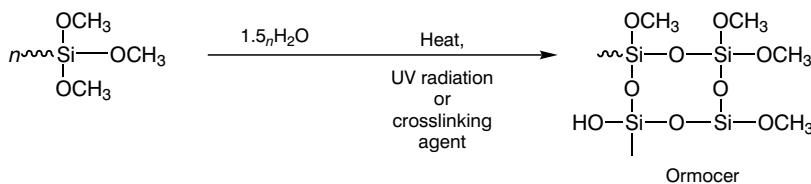
Coating is carried out in a solution of the fluorinated compound in supercritical fluid carbon dioxide, which has the added advantages of ensuring fibre swelling and avoiding the need for using an emulsion [106]. The fibre swelling that takes place facilitates the diffusion of the coating material into the fibre. Further research and development work is currently in hand with this novel approach, which is considered to be economically viable for some technical applications of textiles.

5.7.5 Coating textiles with organically modified ceramics (ormocers)

At present this technique is still in the development stage, but it is conceivable that it could prove to have potential within the textile industry. In this novel approach, the precursors (metal alkoxides and/or organically modified metal alkoxides) are converted into stable colloidal solutions (sols) by partial hydrolysis [107]. The coating of this colloidal solution onto the textile may be carried out by conventional techniques, such as dipping, spraying or padding. Treatment of the sol is then carried out using UV radiation, thermal treatment or by evaporation of the solvent, which leads to condensation reactions and agglomerations causing the sol to gelate and form transparent layers.

Ormocers combine properties known from ceramics together with those of organic polymers; the temperature resistance can be increased by decreasing the organic material component. The properties of the ormocer coating may be varied by the addition of nano-sized metal oxide particles, by organic substances or by the choice of the organic modification of the precursor. Clearly such a technique is capable of leading to the production of coatings with hydrophobic or hydrophilic properties, and hence their application for water-repellent, oleophobic finishes could be considered [107].

Work has already been carried out using 3-glycidyloxypropyltrimethoxysilane and *n*-propyltrimethoxysilane as precursors (Scheme 5.32) [107].



Scheme 5.32

Functionalised organic modification can be built into the network and coatings engineered in this way to contain 1–2% fluorination have been found to provide a high level of oil-repellency on polyester and polyamide fabrics.

5.8 WATERPROOFING OF TEXTILES

5.8.1 Origins of waterproofing

The earliest waterproofed fabrics within Europe were based upon the use of drying oils, specifically linseed oil (obtained from flax) rendered suitable for the purpose by refining to remove impurities [4,109]. Later, tar [109] and natural rubber [110] were also used for waterproofing. Successive coatings of linseed oil were applied to canvas or cotton duck fabric, each coating being allowed to dry before application of the next. Originally such treatments to produce the traditional oilskins worn by fishermen relied on individual garments being proofed in this way in the home on a craft basis, and could take 12–18 months to complete. The tacky nature of the final coating on the oiled fabric, even when dry, was overcome by various mixtures but when the oilproofing process became commercialised in the nineteenth century in the Forth and Clyde areas of Scotland a final coating with a varnish was applied to leave a smooth surface.

Linseed oil consists of the glycerides of unsaturated fatty acids and contains about 42.5% linoleic acid, 38% linolenic acid and 9.5% of oleic acid, together with small amounts of palmitic and stearic acids [4]. Boiling the oil leads to some polymerisation and thickening – that is, higher viscosity – while exposure to atmospheric oxygen leads to oxidation with the evolution of heat. This oxidation gives rise to a solid rubbery mass, which when applied to fabric to give thin layers leaves a clear hard film. The rate of oxidation must be carefully controlled by regulating the drying temperature and atmospheric conditions, and by the use of metallic salts termed ‘driers’ [4,108]. Lack of process control could lead to spontaneous combustion of the impregnated fabrics due to heat evolved. The presence of the metallic salts markedly decreases the drying time of the coating on the fabric to 7–8 hours. The varnishes applied to overcome the tacky nature of the fabric surface usually consisted of mixtures of boiled oils, gum resins (for example, rosin), and turpentine. In the earlier part of the twentieth century many lighter fabrics made from woven cotton, or silk (termed ‘oilsilk’), were produced, and detailed accounts of the production methods then in use have been given elsewhere [4,108].

Other treatments that have been used include the application of tar to fabric to provide tarpaulin for awnings [109] and the commercial application of natural rubber to fabrics from around 1824 was greatly stimulated by the work of Thomas Hancock [110]. It is interesting to note that the native Indians in South America produced water-repellent fabrics in the thirteenth century by coating fabric with natural rubber latex [111]. The coating of fabrics with natural rubber dissolved in organic solvents, and the production of Mackintosh fabric (produced by adhering two fabrics together with a layer of impermeable natural rubber) has been described in detail elsewhere [110–112]. Until the discovery of vulcanisation, which crosslinks natural rubber, the coated fabrics suffered from poor coating adhesion and poor mechanical properties [111–112].

For most industrial and technical fabrics, coating with an impermeable layer of synthetic rubber, plasticised polyvinyl chloride or polyurethane can meet most performance specifications

for waterproofing. For comfort in apparel end-uses, however, waterproof fabrics must be permeable to air and water vapour (that is, breathable) and hence for apparel fabrics breathable waterproof coatings are more important (Section 5.8.3) [10,11,13,113].

5.8.2 Fabric construction for waterproofing

Fabrics for waterproofing by application of coating materials must generally be prepared in a similar manner as for water-repellent finishing. It is important that the fabric surface is smooth and hence most fabrics are singed to remove protruding surface fibres that could either become detached by the action of the doctor knife in coating, or subsequently penetrate through the coating surface to give an uneven coated surface and/or provide sites in the fabric surface that could promote wicking of liquids.

The fabric construction for waterproofing is bound by the same considerations that apply to fabrics designed for water-repellent finishing [19,36,37]. Fabrics for coating must have a smooth fabric surface and be uniform in width. Fabrics must be dimensionally stable to the tensions exerted during the coating application and to the temperatures employed during the drying and curing of the coated fabric.

5.8.3 Waterproof breathable fabrics

Waterproof breathable fabrics are designed specifically for garments to protect the wearer from the effects of wind, rain and loss of body heat [10–13]. Waterproof fabrics completely prevent the penetration and absorption of liquid water (for example, raindrops) whereas water-repellent or shower-resistant fabrics only delay the penetration of water. While water-repellent garments are more comfortable to wear because they allow the perspiration of the wearer to permeate through them, keeping the wearer warm and dry, the water-resistant properties do not compare with those of a waterproof garment.

The term ‘breathable fabric’ is not used in the sense that active ventilation is taking place; it is used to indicate that water vapour can passively diffuse through the fabric but the fabric can still prevent the penetration of liquid water [13]. The human body core temperature of 37 °C is normally accompanied by a skin temperature in the range 33–35 °C and production of water vapour by the skin is essential for the correct maintenance of the body temperature. The greater the amount of physical activity, the greater is the heat energy and the corresponding perspiration rate (Table 5.14) [114]. The passage of water vapour from perspiration through a breathable fabric in a garment must therefore mirror the appropriate perspiration rate for the activity shown in Table 5.14 if the wearer is to remain at the physiologically required temperature. Modern waterproof breathable fabrics have been claimed to achieve moisture transmission rates of up to 10 000 g m⁻²day⁻¹, and the values of the major types are shown in Table 5.15 [115].

Waterproof breathable fabrics may be divided into three major types [10,13,115,116]:

- (1) densely woven fabrics (maximum pore size 10–4 µm);
- (2) membranes (maximum pore size less than 0.001 µm);
- (3) coatings (maximum pore size 3–0.1 µm).

Table 5.14 Heat energy produced by various activities, and corresponding perspiration rates

Activity	Work rate (W)	Perspiration rate (g day ⁻¹)
Sleeping	60	2280
Sitting	100	3800
Gentle walking	200	7600
Active walking	300	11 500
With light pack	400	15 200
With heavy pack	500	19 000
Mountain walking with heavy pack	600–800	22 800–30 400
Maximum work rate	1000–1200	38 000–45 600

Table 5.15 Typical water vapour resistance (Tarl dish test method) of fabrics [120]

Fabrics	WVR (mm still air)
Outer (shell) materials	
Neoprene, rubber or PVC coated	1000–1200
Conventional polyurethane coated	300–400
Waxed cotton	1000+
Wool overcoating	6–13
Leather	7–8
Woven microfibre (nylon or polyester)	3–5
Closely woven cotton	2–4
Ventile™ L28	3.5
Other Ventiles	1–3
Two-layer PTFE laminates	2–3
Three-layer laminates (PTFE, PE)	3–6
Microporous PU (various types)	3–14
open pores	3–5
sealed pores	6–14
Hydrophilic coated	4–16
Witcoflex Staycool	9–16
on nylon, polyester	9–16
on cotton, poly/cotton	5–10
Super Dry	6–14
on nylon, polyester	4–7
on cotton, poly/cotton	3–4
on liner fabrics	3–4
Waterproof, breathable liners (coated and laminated)	2–4
Inner clothing	
Vests (cotton, wool)	1.5–3
Shirting (cotton, wool)	0.8–3
Pullover (light-weight wool)	3–5

Densely woven fabrics

The first effective waterproof breathable fabric was developed in the 1930s and 1940s for military purposes, and was termed Ventile fabric [10,13,19,36]. Fine, long staple cotton fibres were combed and spun into yarn which was then plied. This improved the regularity, the fibres being as parallel as possible to the yarn axis with no large pores into which water could penetrate. Using an Oxford weave (plain weave with two threads woven as one in the warp) gave minimum crimp in the weft so that the fibres were as parallel as possible to the fabric surface. On wetting the fabric surface the cotton fibres were subject to transverse fibre swelling which decreased the size of the pores in the fabric from 10 µm down to 3–4 µm across [13,19,36]. As a result, a very high hydrostatic pressure was required to allow water to penetrate the Ventile fabric, yielding a waterproof fabric without the need for a water-repellent treatment, the pore size when dry being around 10 µm and only 3–4 µm when wet [19,36,117]. Modern Ventile fabrics for military end-uses may use a thread density of up to 98 cm⁻¹, but in other applications lower thread densities necessitate the application of a water-repellent finish [13].

Microfilament yarns made from polyester or polyamide microfilaments with a filament diameter of less than 10 µm are now used to produce densely woven waterproof breathable fabrics [10,13,115]. Silicone or fluorochemical finishes may be applied to improve the fabric resistance to liquid water penetration, but the treated fabric is still permeable to moisture vapour [10,13].

Membranes

Membranes are manufactured as extremely thin polymeric films specifically engineered to exhibit a high resistance to liquid water penetration but still allow the passage of water vapour. Typical microporous or hydrophilic membranes are only 10 µm thick and are laminated to conventional textile fabric to provide a suitable barrier to liquid water and to maintain adequate mechanical strength [10,13,115,116,118].

A microporous membrane, such as Gore-Tex (WL Gore), consists of a thin film of expanded polytetrafluoroethylene polymer, which is claimed to contain 1.4 billion very small holes per square centimetre. The smallest raindrops (100 µm) cannot penetrate through these holes (2–3 µm), but molecules of water vapour (0.0004 µm) can still penetrate [10,13,119]. Microporous polyvinylidene fluoride can also be cast directly onto a fabric by other manufacturers [13]. Usually microporous membranes are used with a layer of hydrophilic polyurethane to decrease the effects of contamination of the hydrophobic membrane by body oils, particulate dirt, and so on [120].

Hydrophilic membranes are very thin films of chemically modified polyester or polyurethane, which incorporate up to 40% by weight of hydrophilic poly(ethylene oxide) chains [117]. The membrane is solid but the poly(ethylene oxide) forms amorphous regions that act as intermolecular ‘pores’ allowing water molecules to diffuse through the membrane. Such membranes are sometimes termed non-porometric because the solid nature of the membrane contains no holes and hence prevents the penetration of liquid water.

Coatings

Both microporous coatings and hydrophilic coatings are used for waterproof breathable fabrics [10,13,115–117]. Microporous coatings may be produced by wet coagulation, thermocoagulation or foam-coating methods and lead to a coating containing a myriad of fine interconnecting physical channels [10,11,117–119]. These are much smaller than the smallest raindrop, but much larger than a water molecule. Hydrophilic coatings utilise a similar basic water vapour permeability mechanism to that proposed for hydrophilic membranes. These are based upon polyurethanes modified with hydrophilic groups such as polyvinyl alcohols and poly(ethylene oxides) [120]. Water molecules arriving at one side of the coating are absorbed and diffuse through the coating by a molecular diffusion process involving the hydrophilic groups. The water molecule finally arrives at the other surface of the coating and is desorbed, the energy for the diffusion process being derived from the wearer's body heat, the normal core temperature of which (37°C) is usually higher than that of the ambient temperature. Appropriate coating methods and other relevant information are to be found in Chapter 13, and in many other publications [121–123].

Stomatex coatings

Another application of biomimetics has been the introduction by Akzo Nobel of Stomatex, which is a closed foam insulating neoprene material incorporating a series of small convex domes that are vented by a small aperture at the dome apex (Figure 5.14) [13,124]. These mimic the action of naturally occurring leaf stomata that regulate plant moisture transpiration, opening to increase transpiration rate and closing to decrease transpiration rate. Stomatex is claimed to respond to the level of physical activity exhibited by the wearer, pumping faster as more heat is produced. However, this pumping action decreases progressively to a passive state when the wearer is at rest. The use of Stomatex in conjunction with Sympatex (Akzo Nobel) – a waterproof breathable membrane – can provide an effective breathable waterproof insulating barrier suitable for clothing and footwear applications, which has a very high level of comfort in wear.

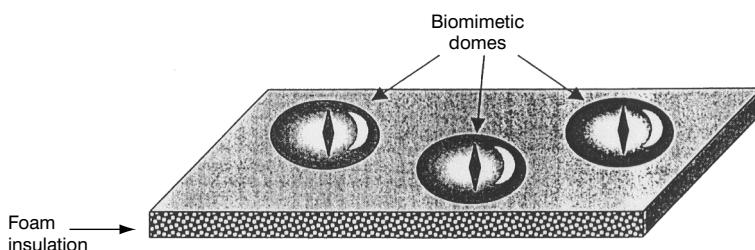


Figure 5.14 Stomatex biomimetic material (AkzoNobel) [13]

5.9 TEST METHODS FOR WATER-REPELLENCY, OIL-REPELLENCY AND STAIN-RESISTANCE

5.9.1 Test methods for water-repellency

There are three main types of test method used to evaluate the water-repellency of fabrics, which should be suitably preconditioned prior to testing under standardised conditions [8,125,126]:

- Class I spray tests to simulate exposure to rain;
- Class II hydrostatic pressure tests – these measure the water penetration as a function of pressure exerted by water standing on the fabric;
- Class III sorption of water by the fabric immersed in water.

The most widely used test methods will now be briefly discussed. The precise details of the test methods are given elsewhere [8,13,125,126].

Class I – Spray tests to simulate exposure to rain

In the 'AATCC Test Method 22 – 1996, Water-repellency: spray test', water is sprayed against the taut surface of a test specimen preconditioned four hours prior to testing under controlled conditions. This produces a wetted pattern whose size depends upon the relative water-repellency of the fabric. Evaluation is carried out by comparing the wetted pattern with pictures on a standard chart. This rapid, simple method, which is technically equivalent to ISO 4920 and BS EN 24920 [125], is suitable only for production control work.

The 'AATCC Test Method 35 – 1994, Water resistance: rain test' [125] measures the fabric resistance to the penetration of water by impact and can therefore be used to predict the probable fabric rain penetration resistance. This test method is applicable to any fabric, which may or may not have been given a water-resistant or water-repellent finish. In the test, a test specimen (preconditioned at $65 \pm 2\%$ relative humidity and $21 \pm 1^\circ\text{C}$ for at least 4 hours prior to testing) is backed by a weighed blotter and is sprayed with water in the AATCC Rain Tester for 5 minutes under controlled conditions. The severity of the simulated rain is altered by changing the height of the water column to give pressures of 60–240 cm water gauge. The blotter is then reweighed to determine the amount of water that leaked through the specimen during the test. The fabric performance is given by determining the maximum pressure at which no fabric penetration occurs, the change in fabric penetration as pressure is increased, and 'breakdown', the minimum pressure required to cause a penetration of more than 5 g of water.

The 'AATCC Test Method 42 – 1994, Water resistance: impact penetration test' [125] is applicable to any textile fabric, which may or may not have been given a water-resistant or water-repellent finish. The fabric resistance to impact by water is measured. This can be used to predict the probable rain penetration resistance of garment fabrics. 500 ml of water are allowed to spray from a height of 2 feet (50.8 cm) against the taut surface of a test specimen backed by a

weighed blotter. The blotter is reweighed to determine water penetration and the specimen classified accordingly.

'ISO 9865: 1991, Textiles, Determination of water-repellency of fabrics by the Bundesmann rain-shower test' (International Standards Organisation, 1991) and 'BS EN 29865: 1993, Textiles, Determination of water-repellency of fabrics by the Bundesmann rain-shower test' (British Standards Institution, 1993) both determine the water-repellency of water-repellent fabrics that are permeable to air [13]. Water is fed from the mains through a filter and de-ioniser to an upper reservoir with a large number of jets of specified size in the base. Four test specimens are placed over four inclined cups and sealed at the edges and are simultaneously exposed to a heavy rain-shower of controlled intensity while the under-surface of each specimen is subjected to a rubbing action. Any water penetrating the fabric is collected in the cups, which are fitted with taps. The penetrated water can therefore be run out, collected and its volume determined. The percentage of water retained by the fabric is measured on a mass basis [127].

It should be noted that all rain simulation tests should, in theory, replicate the rain conditions occurring in practice. An example of the difficulties inherent in this approach can be seen in Table 5.16 in which the conditions in a Bundesmann simulated rain-shower test are compared with the conditions to be observed under actual rain conditions [34]. The drop size in the Bundesmann test is over twice that observed in a cloud burst. The drop kinetic energy in the Bundesmann test is some 5.8 times that in a cloud burst and 21 000 times that observed in light rain.

Table 5.16 Comparison of Bundesmann simulated shower and actual rain

Type of drop	Diameter (mm)	Terminal velocity (cm s ⁻¹)	Kinetic energy (J × 10 ⁻⁶)
Cloud burst	0.30	700	346
Excessive rain	0.21	600	87
Heavy rain	0.15	500	22
Moderate rain	0.10	400	4.2
Light rain	0.045	20	0.095
Drizzle	0.02	75	0.0012
Bundesmann	0.64	540	2000

In the 'WIRA (Wool Industries Research Association) shower tester', adopted as a British Standard, a standard volume of water from a funnel flows slowly into a transparent reservoir with a perforated polytetrafluoroethylene base, which is covered with a filter paper [13]. This produces separate drops, which fall onto the fabric test specimens located a standard distance below the reservoir base. The fabric specimens are under tension over ribbed glass plates to form the top surface of an inclined box. Water that penetrates the fabric runs down the ribbed plates onto the box and then into a 10 cm³ measuring cylinder. Should this become full the excess water overflows into a beaker so that the total water volume can be measured. The percentage fabric absorption on a mass basis, the total water volume penetrating the fabric, and the time taken for the first 10 cm³ of water to penetrate may be determined [128].

Class II – Hydrostatic pressure tests

For many high-performance fabrics that are rendered waterproof, a hydrostatic pressure test may be conducted in one of two ways [13,129]:

- (1) by subjecting the fabric to an increasing hydrostatic pressure and measuring the pressure required to cause penetration;
- (2) by subjecting the fabric to a constant hydrostatic pressure for a long period of time and noting whether any penetration occurs.

Both the International Standard and the British Standard tests subject fabric to an increasing hydrostatic pressure and measure the pressure required to cause penetration:

- ISO 811: 1981, Water textile fabrics, Determination of resistance to penetration – Hydrostatic pressure test (International Standards Organisation, 1981);
- BS EN 20811: 1992, Resistance of fabric to penetration by water – Hydrostatic head test, (British Standards Institution, 1992).

In the 'AATCC Test Method 127 – 1995, Water resistance: hydrostatic pressure test' (related to ISO 811: 1981) [125], preconditioned fabric is placed over a recessed base filled with water. The fabric face exposed to the water is on the outside of the garment, and the fabric is clamped using an annular clamp [13,125]. The pressure of the water applied to the recessed base is increased at a standard rate and the fabric surface observed for any signs of penetration by water. The pressure when the third penetration occurs (that is, three points of leakage) is determined to be the penetration pressure, which is measured in centimetres water gauge [125].

Class III – Sorption of water by the fabric immersed in water

'AATCC Test Method 70 – 1997, Water-repellency: tumble jar dynamic absorption test' [125]. This test method measures the absorption of water into fabrics, which may or may not have been given a water-resistant or water-repellent finish, under dynamic conditions similar to those often encountered during actual use. Preconditioned and preweighed specimens are tumbled in water for a fixed period of time and then are reweighed after the excess water has been removed by a wringer method. The percentage weight increase of the specimen is taken as a measure of the absorption or resistance to internal wetting.

5.9.2 Test methods for oil-repellency

'AATCC Test Method 118 – 1997, Oil-repellency: hydrocarbon resistance test' (technically equivalent to ISO 14419) [125] is used to detect the presence of a fluorochemical finish or other low-surface-energy finish, by evaluating the fabric resistance to wetting by a selected series of liquid hydrocarbons of different surface tensions. Drops of the standard test liquids are placed on the fabric surface and observed for wetting, wicking and contact angle. The oil-repellency grade is the highest numbered test liquid that does not wet the fibre surface. The test liquids used are given in Table 5.17.

Table 5.17 Standard test liquids (AATCC Test Method 118 – 1997) [125]

AATCC Oil-repellency grade number	Composition	Surface tension at 25 °C (mN m ⁻¹)
0	None (Fails Kaydol)	
1	Kaydol	31.2
2	65 : 35 Kaydol : <i>n</i> -hexadecane by volume	28.7
3	<i>n</i> -hexadecane	27.1
4	<i>n</i> -tetradecane	26.1
5	<i>n</i> -dodecane	25.1
6	<i>n</i> -decane	23.5
7	<i>n</i> -octane	21.3
8	<i>n</i> -heptane	19.8

The visual evaluation of the liquid drop on the fabric surface is graded as follows:

- A = Pass – clear well-rounded drop;
- B = Borderline pass – rounding drop with partial darkening;
- C = Fail – wicking apparent and/or complete wetting;
- D = Fail – complete wetting.

The 3M test uses mixtures of Nujol Oil and *n*-heptane in various proportions numbered from 50 (100% Nujol) to 150 (100% *n*-heptane) [130].

It should be noted that the oil-repellency test is conducted under static conditions and depends completely upon the contact angle of the oil on the fibres. The test method does not measure the resistance of the fabric to the spreading of an oil that can wet the fibres [8].

5.9.3 Test methods for stain-resistance

In the 'AATCC Test Method 175 – 1998, Stain resistance: pile floor coverings' [125], all carpet samples are conditioned, pile side uppermost, on a non-absorbent surface for 24 hours at $65 \pm 2\%$ relative humidity and 21 ± 1 °C. A test specimen of pile floor covering is stained with a small volume of a diluted aqueous solution of Food Drug and Cosmetic (FD and C) Red 40 (100 mg l⁻¹ adjusted to pH 2.8 ± 0.1 with citric acid). After allowing the stained specimen to remain at controlled conditions for 24 ± 4 hours, it is rinsed in water to remove all unused FD and C Red 40 dye. Any residual stain is then assessed visually by means of the AATCC Red 40 Stain Scale where a grade of 10 is 'no staining' and a grade of 1 is 'severely stained'. The rater may interpolate to the nearest half-grade where the colour depth of the stained specimen is between the steps of the scale.

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CHAPTER 6

Flame-retardant finishes and finishing

A R Horrocks

6.1 INTRODUCTION

Flame-retardant finishes for textiles, which would otherwise ignite and burn in air, have been recognised for many years [1] but only since the Second World War have they become firmly established. This is a consequence of the recognition of the flammability hazard posed by textiles and the need to produce effective and durable finishes and treatments, which have minimal effect on the desirable features such as handle, comfort and general aesthetics.

The full chemistry of flame-retardant finishes for textiles was intensively reviewed by Horrocks in 1986 [2] as well as by other authors [3,4] and few, if any, really new finishes have been developed within the intervening period. A major reason for this absence is a consequence of the effectiveness of these chemical finishes in the first place, coupled with the greater awareness, legislative requirements and costs associated with the invention, development and introduction of new flame-retardant molecules and their associated chemistry. These follow from consumer and government demands for environmentally more acceptable textiles with minimal and preferably zero associated health and safety implications. However, the need to increase the safety of textiles by the introduction of a chemical finish or treatment must be balanced by the health and safety consequences of its presence.

This review will not present a detailed analysis of all aspects of flame-retardant finishing – which includes the nature of the burning process, means of conferring flame retardancy, chemical mechanisms of the flame-retardant finishes, and so on – because recent and extensive reviews exist [2–6]. It will, however, provide an overview of the general hazard of burning textiles and means of its reduction using the range of commercially available flame-retardants, and then focus on issues of current importance. These include improving the chemical technology of the finishing processes, maximising flame-retardant performance by encouraging char promotion, and minimising environmental impacts of flame-retardant finish use.

6.2 HAZARDS OF BURNING TEXTILES

The hazards posed by the textiles may be exemplified by the tragic fire in Saudi Arabia on 16 April 1997 during the haj killed over 340 pilgrims as flames swept through a tented camp at Mena within the vicinity of Mecca. In addition, many other pilgrims sustained burn injuries as

the fire spread quickly through the estimated 70 000 tents. It is most likely that all the tents were fabricated from woven cotton and that the fire was a consequence of the highly flammable behaviour of cotton, which was aggravated by the hot, dry environment, the high winds present and the denseness of the pitched tents. During the haj in 1998, flame-retardant tents were used in order to decrease the chance of a repeat of such an incident.

Cotton and cellulosic textiles in general, while being among the most flammable of materials, may be rendered flame-retardant by well-established means [2]. Cotton is the most commonly used of all textile fibres and, with regenerated cellulosics such as viscose, comprises 60% of the world annual fibre consumption. Because of the availability and usefulness of cotton and cellulosic fibres, and their relative ease of flame-retarding, they are – unsurprisingly – the most commonly used flame-retardant textiles. Flame-retarded cotton and viscose probably hold 80% or so of the total flame-retardant textiles market.

Other conventional textile fibres burn, although to varying extents determined by their chemical composition and whether or not they are thermoplastic.

Across the world very few comprehensive fire statistics exist, especially those that attempt to relate deaths and injuries to the cause of the fire, such as ignition and burning propagation properties of textile materials. While reflecting the behaviour of a European industrial society, the UK Fire Statistics are some of the most comprehensive available and do attempt to provide such information. For instance, up to 2000 [7], these statistics have demonstrated that while about 20% of fires in dwellings are caused by textiles being the first ignited material, over 50% of the fatalities are caused by these fires. Figure 6.1 presents typical data from the last two decades of the twentieth century, although since 1993, such detailed data have not been as freely available. This shows that generally deaths from fires in UK dwellings have fluctuated around 700 per annum, between 1982 and 1988; since then, they have fallen to the 500 level. Fatalities from textile-related fires show a similar pattern and it has been demonstrated that legislation associated with the mandatory sale of flame-retarded upholstered furnishing fabrics into the domestic UK market since 1989 has played a significant factor in these reductions [8]. At the present time, similar regulations are being considered for introduction by the US Government by the Consumer Product Safety Commission. If adopted, these will not only give rise to a fall in the number of fire-related casualties in the USA, but also offer great opportunities for the textile finishing industry and the sale of flame-retardant chemicals.

Within the EU, however, the planned implementation of the 1990 Upholstered Furniture Directive [9] and associated harmonisation of the UK regulations and test methods has not happened except for the small ignition sources, the so-called ‘cigarette’ and ‘match’ equivalent tests (EN 1021: 1994 and EN 597: 1994). Detailed examination of the currently available test methods used with the UK, EU and USA is beyond the scope of this chapter, but recent attempts to cover this changing area have been published [10,11].

The major UK and EU legislation driving the need for durable flame-retardant finishes and textiles is listed in Table 6.1. In addition to these are local, regional and national codes of practice, which often relate to interior textiles in public buildings, and regulations enforced by purchasing bodies, such as the Department of Health (for hospitals), the Ministry of Defence

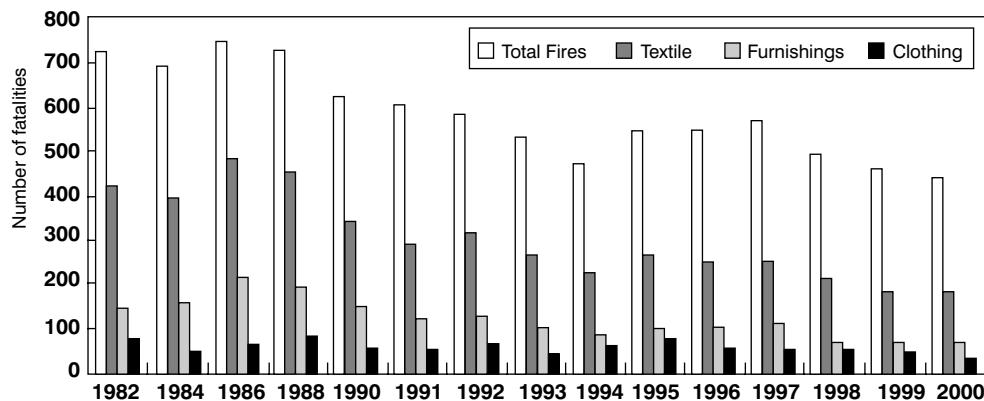


Figure 6.1 UK Fire Statistics for textile-related deaths, 1982–2000

Table 6.1 Selective legislative drivers influencing flame-retardant textiles usage in the UK

Domain	Legislation/regulation
UK only	The Fabric (Misdescriptions) Regulations, 1959, SI 616 Consumer Safety Act, 1978: The Nightwear (Safety) Regulations, 1985, SI 2043 Consumer Protection Act, 1987(a): The Furniture and Furnishing (Fire) (Safety) Regulations, 1998, SI 1324 The Fire and Precautions Act, 1971 (amended 1979) The Health and Safety Act, 1984 The Building Act, 1984
EU Directives	Upholstered Furniture, 1990 Toy Safety, 1990 Personal Protection Equipment, 1992, 1995
International	Aircraft Interior Textiles: US and European Airworthiness Regulations – for example: US Federal Aviation Regulation FAR 125, UK Civil Aviation Authority Airworthiness Notice No. 62

(for clothing and other defence-related textiles) and the Home Office (for firefighters' clothing) within the UK.

6.3 BURNING AND FLAME RETARDANCY

In Table 6.2 are listed examples of flame-retardant fibres, some of which are flame-retarded conventional fibres and others of which are inherently flame-retarded.

The burning behaviour of these fibres is influenced by, and often determined by, a number of thermal transition temperatures and thermodynamic parameters. Table 6.3 [12] lists the commonly available fibres with their physical glass (T_g) and melting (T_m) transition

Table 6.2 Durably-finished and inherently flame-retardant fibres in common use

Fibre	Flame-retardant structural components	Mode of introduction
Natural:		
Cotton	Organophosphorus and nitrogen-containing monomeric or reactive species – e.g. Proban CC (Rhodia, formerly Albright and Wilson), Pyrovatex CP (Ciba), Aflammit P and KWB (Thor), Flacavon WP (Schill and Seilacher)	F
	Antimony–organohalogen systems – e.g. Flacavon F12/97 (Schill and Seilacher), Myflam (Noveon, formerly Mydrin)	F
Wool	Zirconium hexafluoride complexes – e.g. Zirpro (IWS) Pyrovatex CP (Ciba), Aflammit ZR (Thor)	F
Regenerated:		
Viscose	Organophosphorus and nitrogen/sulphur-containing species – e.g. Sandoflam 5060 (Clariant, formerly Sandoz) in FR Viscose (Lenzing)	A
	Polysilicic acid and complexes – e.g. Visil AP (Sateri)	A
Synthetic:		
Polyester	Organophosphorus species: phosphinic acidic comonomer – e.g. Trevira CS (Trevira GmbH, formerly Hoechst), phosphorus-containing additive, Fidion FR (Montefibre)	C/A
Modacrylic ^a	Halogenated comonomer (35–50% w/w) plus antimony compounds – e.g. Velicren (Montefibre), Kanecaron (Kaneka Corp.)	C
Polypropylene	Halo-organic compounds usually as brominated derivatives – e.g. Sandoflam 5072 (Clariant, formerly Sandoz)	A
Inherent:		
Polyhaloalkenes	Polyvinyl chloride – e.g. Clevyl (Rhodia, formerly Rhone-Poulenc)	H
	Polyvinylidene chloride – e.g. Saran (Saran Corp.)	
Polyaramids	Poly (<i>m</i> -phenylene isophthalamide) – e.g. Nomex (Du Pont), Conex (Teijin)	Ar
	Poly (<i>p</i> -phenylene terephthalamide) – e.g. Kevlar (Du Pont), Twaron (Enka)	Ar
Poly (Aramid–Aramid)	For example: Kermel (Rhodia)	Ar
Polybenzimidazole	For example: PBI (Hoechst-Celanese)	

Key:

F: chemical finish

A: additive introduced during fibre production

C: copolymeric modifications

H: homopolymer

Ar: aromatic homo- or copolymer

^a Acrylic fibres comprise at least 85% acrylonitrile repeat units; modacrylics contain less than 85%, and more usually about 50%, acrylonitrile repeat units

temperatures, if appropriate, which may be compared with their chemically related transitions of pyrolysis (T_p) and ignition and the onset of flaming combustion (T_c). Generally, the lower the respective T_c (and usually T_p) temperature and the hotter the flame, the more flammable is the fibre. The natural cellulosic fibres cotton, viscose and flax, as well as some synthetic fibres like acrylic fibres, typify this generalisation. In Table 6.3, the respective Limiting Oxygen Index (LOI) values are listed, which are measures of the inherent burning character of a material [13]. Fibres that have LOI values of 21 or below ignite easily and burn rapidly in air (which contains 20.8% oxygen). Those with LOI values above 21 ignite and burn more slowly and generally when LOI values rise above values of about 26–28, fibres and textiles may be considered to be flame-retardant and will pass most small flame fabric ignition tests in the horizontal and vertical orientations. Nearly all flammability tests for textiles – whether based on simple fabric strip tests, composite tests (for example, BS 5852: 1979, ISO 8191/2, EN 1021 and 597) or more product/hazard related tests (for example, BS 6307 for carpets, BS 6341 for tents and BS 6357 for molten metal splash) – are essentially ignition resistance tests.

Table 6.3 Thermal transitions of the more commonly used fibres [12]

Fibre	T_g (softens) (°C)	T_m (melts) (°C)	T_p (pyrolysis) (°C)	T_c (ignition) (°C)	Limiting oxygen index, LOI (%)
Wool	–	–	245	570–600	25
Cotton	–	–	350	350	18.4
Viscose	–	–	350	420	18.9
Nylon 6	50	215	431	450	20–21.5
Nylon 6.6	50	265	403	530	20–21.5
Polyester	80–90	255	420–447	480	20–21
Acrylic	100	>220	290 (with decomposition)	>250	18.2
Polypropylene	-20	165	470	550	18.6
Modacrylic	<80	>240	273	690	29–30
PVC	<80	>180	>180	450	37–39
Metaaramid (e.g. Nomex) ^a	275	375	410	>500	29–30
Paraaramid (e.g. Kevlar) ^a	340	560	>590	>550	29

^a Fibres manufactured by Du Pont

Within the wider community of materials fire science, it is widely recognised that under real fire conditions, it is the rate of heat release that determines burning hazard. While their heats of combustion indicate that little difference exists between all fibres, and indeed some fibres like cotton appear to have a low heat of combustion, it is the speed at which this heat is given out that determines rate of fire spread and severity of burns.

Currently, only textiles used in building materials and aircraft and transport seating require to have minimal levels of rate of heat release, which is measured using instruments such as the

cone calorimeter [14,15] and the Ohio State University calorimeter [16] (used to assess aircraft interior textile performance). It is likely that rate of heat release will become a more important textile fire parameter within the next 10 years.

6.3.1 Flame-retardant strategies

Figure 6.2 [12] presents the combustion of any textile as a feedback mechanism in which fuel (from thermally degraded or pyrolysed fibres), heat (from ignition and combustion) and oxygen (from the air) feature as the main components. In order to interrupt the mechanism, five modes, (1) to (5), are proposed and flame-retardants may exert one or more of these. Each stage with a relevant flame-retardant action is listed below:

- (1) Removal of heat: high heat of fusion and/or degradation and/or dehydration (for example, inorganic and organic phosphorus-containing agents, aluminium hydroxide or 'alumina trihydrate' in back-coatings);
- (2) Enhancement of decomposition temperature: not usually exploited by flame-retardants; more usual in inherently flame- and heat-resistant fibres (for example, aramids);
- (3) Decreased formation of flammable volatiles, increase in char: most phosphorus- and nitrogen-containing flame-retardants in cellulose and wool; heavy metal complexes in wool;

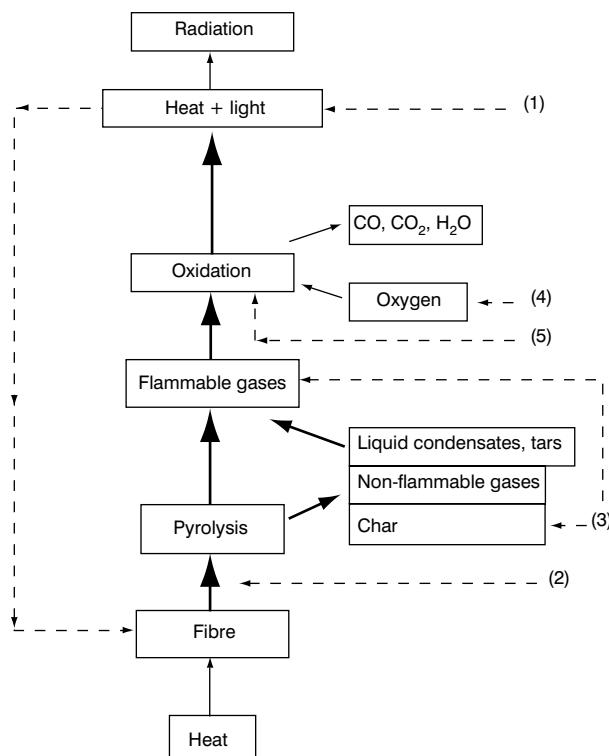


Figure 6.2 Combustion as a feedback mechanism

- (4) Decreased access to oxygen or flame dilution: hydrated and some char-promoting retardants release water; halogen-containing retardants release hydrogen halide;
- (5) Interference with flame chemistry and/or increase in fuel ignition temperature (T_c): halogen-containing flame-retardants, often in combination with antimony oxides.

From the above, it can be seen that some generic flame-retardants function in more than one mode and this is true of the most effective examples. Some flame-retardant formulations, in addition, produce liquid phase intermediates, which wet the fibre surfaces thereby acting as both thermal and oxygen barriers – the well-established borate/boric acid mixtures act in this manner as well as promoting char. In order to simplify the clarification of different modes of chemical flame-retardant behaviour, the terms ‘condensed’ and ‘gas or vapour’ phase activities may be used to distinguish them. Both are composite terms and the former will include modes (1) to (3) above and the latter (4) and (5). Physical mechanisms often operate simultaneously, and these include exclusion of oxygen and/or heat by coating (mode (4)), increased heat capacity (mode (1)) and dilution or blanketing of the flame by non-flammable gases (mode (4)).

6.3.2 Thermoplasticity

Whether or not a fibre softens and/or melts (as defined by physical transitions in Table 6.3) determines whether it is thermoplastic or not. Thermoplasticity can influence considerably how a flame-retardant behaves because of the associated physical change. Conventional thermoplastic fibres like polyamide, polyester and polypropylene will shrink away from an ignition flame and avoid ignition – this can give the appearance of flame retardancy when in fact, if the shrinkage was prevented, they would burn intensely. This so-called scaffolding effect is seen in cotton/polyester and similar blends where the molten polymer melts on to the non-thermoplastic cotton and ignites. Similar effects are seen in composite textiles comprising thermoplastic and non-thermoplastic components.

Added to the above is the problem of molten and often flaming drips of polymer, which, while removing heat from a flame front and encouraging flame extinction (and hence achieving a ‘pass’ in vertical flame tests), can lead to burns or secondary ignition of lower surfaces (for example, carpets or human skin).

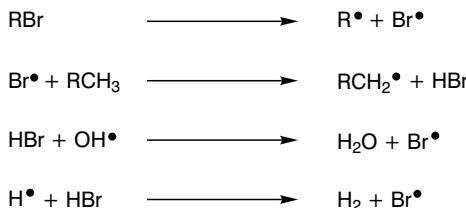
Most flame-retardants applied to conventional synthetic fibres during manufacture or as finishes function by increasing melt dripping and/or promoting extinction of flaming droplets. None to date decrease the fibre thermoplasticity and/or promote significant char formation as is the case in flame-retarded viscose fibres [5].

6.3.3 Flame-retardant mechanisms and char formation

Flame-retardants that function in the vapour phase by modes (4) and (5) (Figure 6.2) share the advantage that they will decrease ignition propensity and aid in flame extinction of any textile

fibre-forming polymer. This is because once the volatile products or fuels formed from thermal degradation enter into the oxidative reaction with oxygen in the flame, their chemistries are similar. Thus starvation of oxygen (mode (4)) or generation of interfering free radicals (mode (5)), for example, will assure the flame-retardant's effectiveness.

Antimony–halogen flame-retardants are the most successful within both the bulk polymer sectors and back-coated textile areas, based on cost and effectiveness. Unlike the fibre-reactive, durable phosphorus- and nitrogen-containing flame-retardants used for cellulosic fibres, they can only be applied topically in a resin binder, usually as a back-coating [17]. For textiles, most antimony–halogen systems comprise antimony III oxide and bromine-containing organic molecules such as decabromodiphenyl oxide (DBDPO) or hexabromocyclododecane (HBCD). On heating, these release HBr and also Br[•] radicals, which interfere with the flame chemistry by the following general scheme, where R[•], CH₂[•], H[•] and OH[•] radicals are part of the flame oxidative chain reaction [17,18] that consumes fuel (RCH₃) and oxygen (Scheme 6.1).



Scheme 6.1

The role of antimony has been studied by a number of authors [18–20] and is considered to involve formation of flame-active species such as antimony trihalides (for example, SbBr₃) and oxyhalides (for example, SbOCl). More recent research in this author's own laboratories confirms the importance of SbBr₃ as the effective retardant species in antimony III oxide–DBDPO back-coatings applied to fabrics [21].

The recent concern regarding bromine-containing molecules generally (whether justified or otherwise [22,23]) is causing end-users of Sb–Br formulations to demand decreased flame-retardant levels or alternatives (see Table 6.4 and Section 6.6.1 below).

Depending on the nature of the resin binder, often an acrylic copolymer or ethylene-vinyl acetate copolymer [17], these coated systems may have some char-forming character [21]. This enables them to be used successfully on furnishing fabrics containing synthetic fibre, for example, which must have a means of counteracting the effects of fibre thermoplasticity if they are to pass composite tests such as BS 5852, ISO 1891/2 and EN 1021.

However, without doubt, the most effective flame-retardants are those that promote char formation – they convert the organic fibre structure to a carbonaceous residue or char and hence decrease volatile (fuel) formation (mode (3)). Indirectly, these flame-retardants, which require absorption of heat for them to operate, will offer in addition flame retardancy via mode (1) and, by releasing non-flammable molecules like CO₂, NH₃ and H₂O during char formation,

mode (4). In addition, the char behaves as a carbonised replica of the original fabric, which continues to function as a thermal barrier, unlike flame-retardant thermoplastic fibres.

Char-forming flame-retardants, therefore, offer both flame and heat resistance to a textile fibre and so can compete with many of the so-called high performance flame and heat resistant fibres like the aramids and similar fibres (see Tables 6.2 and 6.3).

For char formation to be most effective, the polymer backbone must comprise side-groups, which on removal lead to unsaturated carbon bond formations and eventually to a carbonaceous char following elimination of most of the non-carbon atoms present. Most phosphorus- and nitrogen-containing retardants, when present in cellulose, decrease volatile formation and catalyse char formation. They act in this double capacity because on heating they first release polyphosphoric acid, which phosphorylates the C(6) hydroxyl group in the anhydroglucopyranose moiety, and simultaneously acts as an acidic catalyst for dehydration of these same repeat units. The first reaction prevents formation of laevoglucosan, the precursor of flammable volatile formation [6,21], and this ensures that the competing char-forming reaction is now the favoured pyrolysis route. The acidic catalytic effect of the released polyacid further increases the rate of this favoured route. While considerable research has been undertaken into char formation of flame-retarded cellulose, the actual mechanisms of both unretarded and retarded cellulose charring are not well understood [6].

Hirata in his review [24] supports the general view that for pure cellulose, the major char-forming mechanism is still that based on Kilzer and Broido's competition between dehydration to char and depolymerisation to laevoglucosan [25]. Work in one of the author's own laboratories [26] and reviewed previously [5,6] suggests that this mechanism is influenced by the presence and type of flame-retardants.

Figure 6.3 shows this modified mechanism and includes the 'activated cellulose' intermediate state proposed by Bradbury and coworkers [27]. Evolved gas DTA (differential thermal analysis) studies of a series of flame-retarded cotton fabrics identified seven transitions (Figure 6.3) associated with formation of activated cellulose (T_2), flame-retardant, low temperature-induced formation of char at 200 °C (T_1), higher temperature (250–300 °C) competitive formation of volatiles (and oxidation to CO at T_3 and CO₂ at T_5) and char oxidation above 400 °C to CO (T_6) and CO₂ (T_7). Generally, T_1 to T_7 represent sequentially increasing temperatures of the various transitions. Oxygen-dependence of some stages of the pyrolysis is seen, but of particular interest is the low temperature char formation transition T_1 seen only for certain phosphorus- and nitrogen-containing flame-retarded cottons. Subsequent pyrolysis GC (gas chromatography) studies [28] confirmed the char-forming and volatile fuel-decreasing tendencies of the phosphorus- and nitrogen-containing flame-retardants used. Flame-retardants producing the greatest char within the 300–500 °C range, such as the phosphonium salt condensates – for example, Proban CC (Rhodia, formerly Albright and Wilson), ammonium polyphosphate and the phosphonamide-based Pyrovatex CP (Ciba) – when pyrolysed at temperatures above 400 °C, generated high levels of aromatic volatiles including benzene, toluene and phenol. These observations therefore support the proposed aromatisation of carbonaceous chars that occurs following the initial cellulose dehydration reactions.

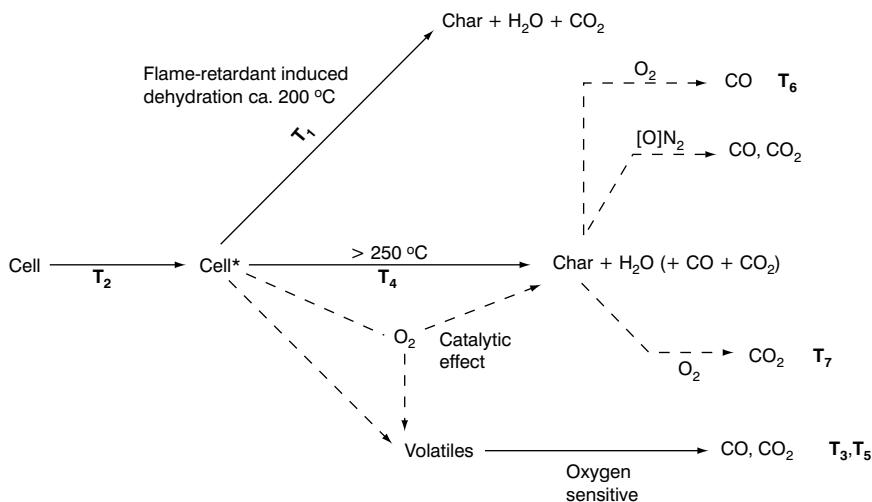


Figure 6.3 Schematic modified mechanism for cellulose pyrolysis

Char studies of flame-retardant cellulose have indicated that most phosphorus remains in the char [29]. However, subsequent research by Drews and Barker [30] showed that phosphorus retention in chars is related to flame-retardant efficiencies and the reactivity of phosphorus moieties with cellulose. Oxygen bomb calorimetric studies of all chars produced from different flame-retardants at different phosphorus contents suggested that they had similar structures, possibly derived from phosphorylated cellulose in the first instance. For phosphorus-containing species to be effective, the additional presence of synergistic nitrogen is essential and although nitrogen-containing species show little if any flame-retardant activity in cellulose, values of P:N molar ratios have a crucial influence on flame-retardant effectiveness [2] (see Section 6.4). The presence and role of nitrogen in P/N synergistic flame-retardants is understood even less than that of phosphorus and evidence exists that char structure is enhanced by formation of P–N bonds [31].

It may be stated that in the current quest for more effective flame-retardants in polymers and textiles, char formation is now one of the most significant and desirable properties. Currently, effective char-forming solutions exist only for the flame-retarding of cellulosics and wool textiles. Future challenges lie in the area of rendering the thermoplastic synthetic fibres char-forming, which will significantly enhance their fire-resisting behaviour.

6.4 CURRENT FLAME-RETARDANT FINISHES

Table 6.4 lists a simplified selection of suitable flame-retardants for cellulosic textiles, which indicates that a major criterion used for selecting a finish is its durability to aftercare or end-use exposure conditions such as wetting or laundering. In fact, many flammability performance tests demand that the fabric be tested after some form of wetting or laundering test. The British Standard BS 5651: 1989 defines a series of such conditions from water soaking at 40 °C (to

simulate resistance to spillage from hot drinks, and so on), through dry-cleaning to hot detergent washes of increasing severity. Flame-retardant finishes present on specific textiles are, therefore, defined as non-durable or durable with respect to a given condition. In some cases, the term ‘semi-durable’ is used and this may relate to a finish that withstands a hot water soak treatment but not a full laundering process. It is generally true to say that any treatment that withstands five or so laundering treatments will also resist 50 or more, as required by certain purchasing bodies such as hospital trusts in the UK (where up to 200 simulated hospital wash cycles are usually demanded for flame-retardant cottons).

One or more of the following factors determines the durability of any finish:

- (1) functionality and reactivity of the finish;
- (2) hydrophilicity and accessibility of fibres;
- (3) internal voidage within the fibres;
- (4) resistance of the applied finish to hydrolytic and oxidative bleach conditions, typically present in detergent solutions.

6.4.1 FLAME-RETARDANT CELLULOSICS

In principle, any Lewis acid will promote the char-forming action in Figure 6.3 and, in practice, many acidic salts act as flame-retardants for cotton. However, while solubility and durability are important issues, the ideal non-durable finish should be able to penetrate the fibre and minimise surface deposits. Secondly, the release of Lewis acidic properties should not occur significantly below 150 °C if the treated textile is to resist normal drying and curing temperatures. While traditional finishes like borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) and boric acid (H_3BO_3) in a 7:3% (w/w) ratio at add-ons of 10–15% (w/w) have been used for many years [32], this finish does start to decompose and release acid above 130 °C and has poor afterglow retardancy. Afterglow (flameless or smouldering combustion) must be prevented because it may lead to the slow burning of the fibres, which can revert back to flaming combustion if there is sufficient air present. The current main non-durable finishes, as Table 6.4 shows, are ammonium phosphates and polyphosphates, although addition of ammonium bromide can confer vapour phase activity to either salt. These salts offer excellent afterglow retardancy as well. Table 6.5 lists a typical range of currently available non- and semi-durable finishes based on these salts available in the UK. Those available in the USA are listed annually elsewhere [33].

Ammonium polyphosphate (APP) has a significant advantage: not only is its solubility less than that of the simple phosphates, but it depends on the degree of polymerisation of the linear $-\text{[P(O)(ONH}_4\text{)O]}_n-$ chains and the type of crystalline structure. Table 6.6 lists a range of commercially available ammonium polyphosphates and associated solubility data. In addition, APP has a phosphorus content as high as 32% (w/w) and so add-ons of 5–15% (w/w) are required to achieve phosphorus levels of about 1.5–4.5% (w/w). The presence of urea (see Table 6.5) is believed to have two major effects: it increases the degradation temperature of APP by acting as a buffer, and by improving penetration into the fine structure of the fibre. Its higher concentration in Antiblaze LR2, for example, enables the curing temperature to be raised to 150 °C and this will

Table 6.4 Summary of flame-retardant treatments for cotton [5]

Type	Durability	Structure/formula
Salts:		
(i) Ammonium polyphosphate	Non- or semi-durable (dependent on n)	$\text{HO}-\left[\begin{array}{c} \text{O} \\ \\ \text{P}-\text{O}-\text{H} \\ \\ \text{NH}_4 \end{array}\right]_n$
(ii) Diammonium phosphate	Non-durable	$(\text{NH}_4)_2\text{HPO}_4$
Organophosphorus:		
(i) Cellulose reactive methylolated phosphonamides	Durable to more than 50 launderings	$(\text{CH}_3\text{O})_2\overset{\text{O}}{\underset{\text{ }}{\text{P}}}\text{CH}_2\text{CH}_2\text{CON}(\text{CH}_2\text{OH})\text{H}$
		e.g. Pyrovatex CP (Ciba), Amgard TFR 1 (Rhodia, formerly Albright and Wilson), Aflammit KWB (Thor), Flacavon WP (Schill and Seilacher), Pekoflam DPM (Clariant)
(ii) Polymeric tetrakis (hydroxymethylol) phosphonium salt condensates	Durable to more than 50 launderings	THPC-urea- NH_3 condensate e.g. Proban CC (Rhodia), Aflammit P (Thor)
Back-coatings:		
(i) Chlorinated paraffin waxes	Semi-durable	$\text{C}_n\text{H}_{(2n-m+2)}\text{Cl}_m$ e.g. Flacavon FK (Schill and Seilacher)
(ii) Antimony-halogen (aliphatic or aromatic bromine-containing species)	Semi- to fully durable	Sb_2O_3 (or Sb_2O_5) + decabromodiphenyl oxide or hexabromocyclododecane + acrylic resin e.g. Myflam (Noveon, formerly Mydrin), Flacavon F12 (Schill and Seilacher)

enable a degree of cellulose phosphorylation to occur, thereby improving durability. Furnishing fabrics treated with Antiblaze LR2 are able to pass the water soak requirements (BS 5651) demanded by the UK furnishing regulations of 1988 [8] prior to achieving a pass according to BS 5852: 1979 Part 1 for cigarette (Source 0) and small flame (Source 1) ignition. Similar finishes are available from other manufacturers, as seen in Table 6.5.

Higher durability requires either the use of functional finishes based on organophosphorus compounds – for example, alkylphosphonamide derivatives such as Pyrovatex CP and CP New (Ciba), TFR1 (Rhodia, formerly Albright and Wilson), tetrakis (hydroxy methyl) phosphonium (THP) salt condensates (Proban CC, Rhodia) – or, more recently, back-coatings that usually

Table 6.5 Typical commercial non- and semi-durable flame-retardants for cellulosic fibres

Trade name	Chemical constitution ^a	Dry/cure Temperature (°C)
Rhodia, formerly Albright and Wilson:		
Antiblaze FSD ^d	Ammonium polyphosphate (APP) + ammonium bromide	105 (dry only)
Antiblaze DP	Diammonium phosphate (DAP)	100 (dry only)
Antiblaze RD1	Ammonium salt of phosphonic acid	≤ 130
Antiblaze TR ^e	APP + urea (8.2% w/w N)	105/135
Antiblaze LR1	APP + urea (9.0% w/w N)	105/135
Antiblaze LR2 ^{b,c}	APP + urea (9.9% w/w N)	105/150
Antiblaze LR3 ^c	APP powder (30% w/w P) for use in coatings	–
Antiblaze LR4 ^c	APP powder (27% w/w P) for use in coatings	–
Ciba:		
Flovan ASN	Ammonium compounds	100–130/140–150
Flovan BU ^d	Ammonium halide (bromide?)	110–120/140–150
Flovan FD	Ammonium phosphate (APP?) + urea	110–120 (dry only)
Flovan CGN	Ammonium acid phosphonate	110/140–150
Pyrovatim 7627 ^b	Phosphate salt of organic base	110–130/160
Pyrovatim SB ^c	APP + melamine formaldehyde for use in coatings	–
Thor:		
Flammentin ASN	Ammonium phosphate (APP or DAP?)	100–120 (dry only)
Flammentin BL ^d	Ammonium compounds (halides?)	100–140 (dry only)
Flammentin FMB ^b	Organic phosphorus–nitrogen compound	110–130/150–170
Flammentin HM	Ammonium salts (phosphates?)	100–110 (dry only)
Flammentin KRE	Organic phosphorus–nitrogen compound	110–160 (dry only)
Flammentin UCR ^c	Phosphorus–nitrogen compound	100–140/150–160
Flammentin MCFC ^c	Crosslinking silicone + P- and N-containing compounds	100–120/170
Schill and Seilacher:		
Flacavon B45 and HS	Organic + inorganic salts	100–110 (dry only)
Flacavon BST ^b	Nitrogen and phosphorus compound (APP?)	100–110/160–180
Flacavon GP	Organic P- and N-containing compound	100–120 (dry only)
Flacavon H12/10	Organic P- and N-containing compound	100–120 (dry only)
Flacavon RNEU	Organic P- and N-containing compound	100–110 (dry only)
Flacavon F12/937 ^c	Aliphatic bromine compound + phosphate + binder	
Clariant:		
Pekoflam OP liq.	Organic aminocompound and P-containing salt	110–120 (dry only)
Pekoflam ABU liq.	Inorganic bromine- and organic aminocompound	110–120 (dry only)
Sandoflam SPN liq.	Derivative of phosphonic acid	110–120/140
Sandoflam SPF liq. ^b	Nitrogen and phosphorus compound (APP?)	110–120/140

a Most formulations contain small amounts of other agents such as wetting agents and stabilisers

b These finishes may be termed semi-durable in that they resist a 40 °C water soak (BS 5651) prior to testing to BS 5852

c May be used in back-coating formulations

d May contain ammonium halides (usually bromide) and so are effective on cellulosic/synthetic blends as well as fabrics containing 100% synthetic fibre

e Available with additional fluorochemical finish

Table 6.6 Types of ammonium polyphosphate, APP

APP	Phase ^a	DP ^b	Solubility (g/100 cm ³)
Hoechst:			
Exolit 422	2	700	<1
Great Lakes:			
FR CROS 480	1		3.5
FR CROS 485	1		2.2
FR CROS 484	2	1000	0.3
Rhodia:			
Antiblaze PI	1	160	8
Antiblaze LR4	1	200	4–10
Antiblaze MC	1	220	4.5
Antiblaze MC(M)	1	290	3.5
Solutia:			
Phos-Chek P/30	1	>50	1.5

a Phase refers to the crystalline form

b DP = degree of polymerisation

comprise a resin-bonded antimony–bromine flame-retardant system [2,17]. Table 6.4 includes a summary of the currently popular treatments with selected commercial examples.

Most of these treatments have become well-established during the last thirty years and few changes have been made to the basic chemistries over that time [2]. Those changes that have been made usually involve minor alterations influencing properties such as handle [34] or decreased levels of formaldehyde release during application, as seen in Pyrovatex 7620 (Ciba), for example. However, during the same period, many other flame-retardants based on phosphorus chemistry and reviewed extensively elsewhere [2], in the main, have ceased to have any commercial acceptability for reasons that include toxicological properties during application or during end-use, antagonistic interactions with other acceptable textile properties and cost. The examples cited above may be considered to be those that continue to satisfy technical performance and enable flammability regulatory requirements to be met, while having acceptable costs and meeting current health and safety and environmental demands.

While the chemistry of functional organophosphorus finishes is quite complex [2,5], it is important to consider those important features that influence the application process and the overall flame-retarded textile performance. Figure 6.4 outlines the essential chemical and processing stages for a THP salt–urea complex such as Proban CC (Rhodia), which requires an ammonia cure and a final oxidative stage. The THP salt (usually the chloride, THPC) and urea are probably in a 2:1 molar ratio with a molar P:N ratio of 1:1. The chloride is generally preferred relative to other salts, such as the sulphate (THPS), because as a univalent anion, the salt–urea complex achieves a higher degree of penetration into the fibre microstructure. Experience has shown that the divalent sulphate complex, which is considerably larger, leads to lower levels of penetration with consequent reduction in durability.

The THPC–urea complex solution is applied by a pad or foam application method (see

Section 6.5) in the presence of wetting and softening agents. To ensure a high degree of penetration, the cotton fabric must have been scoured and bleached to a high degree of absorbency. After application (at a level commensurate with 2.0–3.0% (w/w) P on the final cloth), the fabric is dried to about 8–10% moisture level. This dried fabric is passed in open-width form to an ammonia-cure reactor into which ammonia gas is fed at a controlled rate. An exothermic crosslinking reaction (see Figure 6.4) occurs, preferably within the component fibre microstructure, yielding an insoluble polymeric phosphine having a molar P:N ratio of 1:2. This ratio yields a high degree of synergy, which if P > 2% (w/w or o/wf), gives an acceptable level of flame retardancy for most applications.

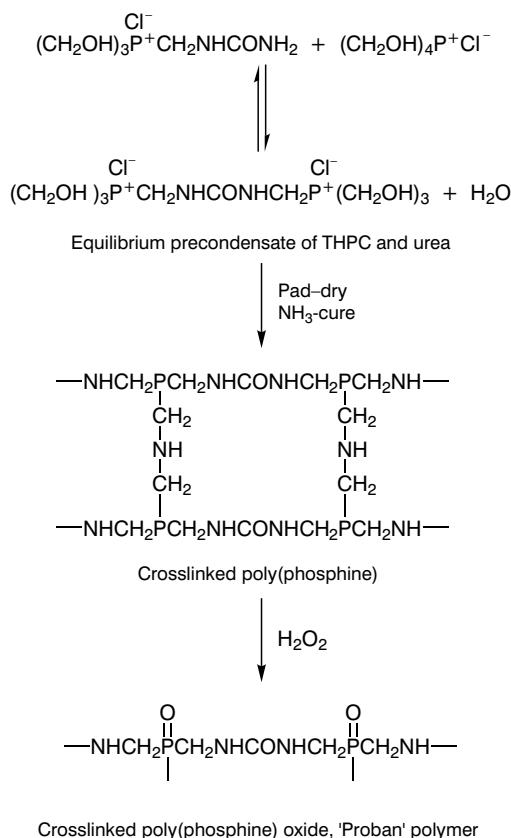


Figure 6.4 Outline chemistry of the THPC–urea–NH₃ (Proban) process

In order to stabilise the highly reducing phosphine polymer, after ammonia-curing fabric is passed through a dilute hydrogen peroxide bath to oxidise the polymer to a poly(phosphine oxide). After this the fabric is washed and dried. If the fabric has been correctly prepared and impregnated and the ammonia cure controlled, then the final fabric will have a durable finish with little surface deposit and good handle. Finished softness is improved by inclusion of softeners but increases after laundering as surface polymer is removed [35].

A similar situation exists during the application of phosphonamide finishes such as Pyrovatex

CP and similar finishes (see Table 6.4) as shown in Figure 6.5. Here, as above, a well-prepared fibre is essential and careful padding or foam application of the formulation is required in order to maximise penetration. The applied formulation is more complex, however, because in addition to the main *N*-methylol dimethyl phosphonamide flame-retardant component, it may only bond to the cellulose molecules via a methylolated resin bridge molecule (see Figure 6.5). Typically, this is a methylolated melamine derivative or dihydroxydimethylethylene urea (DHDMEU) in the presence of an acidic catalyst. Orthophosphoric acid has been shown to be the most effective catalyst in that it is sufficiently acidic to promote crosslinking reactions and yet it is not too acidic to create excessive hydrolytic degradation of cellulose chains and hence cause a decrease in both the fabric tear and tensile strengths. A typical formulation for application to a 150–200 g m⁻² cotton fabric at 80% expression or wet pick-up would be:

- (1) Pyrovatex CP 280.00 g l⁻¹;
- (2) melamine resin 35.00 g l⁻¹;
- (3) softener 25.00 g l⁻¹;
- (4) acid catalyst 20.00 g l⁻¹;
- (5) wetting agent 1.25 g l⁻¹.

After application, the padded fabric is dried at 130 °C and then passed to a curing oven or baker at 150 °C for 4–5 min, or at 170 °C for 1 min. Generation of gaseous formaldehyde is a serious problem and must be contained, extracted and removed by water scrubbing along with other emitted volatile organic compounds (VOCs); recent work by the author and his colleagues [36] has indicated that formaldehyde emission can be decreased by optimising the bath formulation (see Section 6.6).

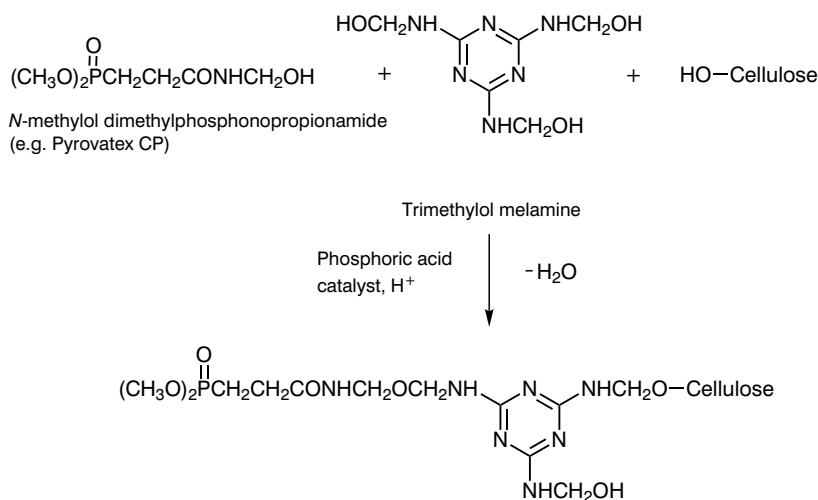


Figure 6.5 Chemistry of the Pyrovatex CP system

Curing must be followed by an immediate alkaline (caustic soda, NaOH, or soda ash, Na_2CO_3) neutralisation at 40–45 °C, if acid tendering is to be minimised. This neutralisation removes all residual phosphoric acid catalyst, uncrosslinked phosphonamide and some surface crosslinked polymer. Subsequent water washing-off and drying completes the process.

If controlled, the finishing process will yield high levels of durable flame retardancy at phosphorus levels of 1.5–2.0% (w/w or owf), and a fabric that has some degree of crease resistance, minimal losses in tensile and tear strengths (about 20–25%) and acceptable handle. Disadvantages are the need to minimise formaldehyde emissions and tensile property loss plus high losses of active flame-retardant from poor fixation and reagent purity. Because of the influence of two of these factors upon effluent discharges, they will be explored in greater detail in Section 6.6.

Compared to the THPC–ammonia cure systems, the cured phosphonopropionamide flame-retardant has better dye compatibility (hence its preferred use on printed upholstery fabrics) and better flame retardancy per unit level of phosphorus, but yields inferior tensile properties and poor resistance to bleaches during laundering.

On a final note, however, it must be emphasised that the chemical characteristics of the respective crosslinked resins are different to those of the respective precursor molecules and become a part of the fibre fine structure. As far as is known, flame-retardant cotton and other cellulose fabrics finished by such treatments pose no known toxicological hazards.

Durable, flame-retardant, topical treatments containing halogenated species in a wax or a resin base (see Table 6.4) have found use over the years in outdoor fabrics such as tentage and tarpaulins. More recently, and since the 1980s, coating and back-coating formulations comprising antimony–bromine compounds present in an acrylic or similar resin – for example, Flacavon F12/937, Schill and Seilacher (see Table 6.5) – have become significant competitors to the Pyrovatex CP treatment and similar systems for cellulosic upholstered finishing fabrics. This is probably a consequence of their relative cheapness (of raw materials), simple application techniques (see Section 6.5), flame-retardant efficiency of antimony–bromine formulations and an increased understanding of their underlying science [17–21]. Assuming that the flame-retardant present in the back-coating can transfer its activity through the fabric and to its face (against which the igniting source in BS 5852: 1979 Part 1, for example, is applied), then they have the advantage of not affecting the aesthetic properties of the fabric face. A typical back-coating formulation would be:

- (1) decabromodiphenyl oxide (DBPO) 3% (w/w);
- (2) antimony III oxide 17% (w/w);
- (3) acrylic binding resin 50% (w/w);

applied to the back of the fabric at 20–30% (w/w) total solids add-on. Commercially available formulations are far more complex and rarely published; typically, they will contain plasticiser, anti-foaming agents, viscosity modifiers and so on, and the resin component may be halogen-containing and thus add to the overall flame resistance [21]. The above weight ratio for Sb_2O_3 :DBPO of 1:2 relates to a mole ratio for Sb:Br of 1:3 and a bromine concentration of about

5–10% (w/w) on fabric. This relates to the proposed synergistic effect being associated with formation of SbBr_3 as the effective flame-retardant [18–21].

During application of these finishes, choice of resin and its viscosity during application are important if excessive fabric penetration (yielding 'grin through') and stiffness are to be avoided. Low second order transition resins ($T_g < 10^\circ\text{C}$) are to be recommended. The recent concerns about antimony- and bromine-containing species in the environment, however, have led to the decreased use of such finish formulations. This issue will be discussed in Section 6.6.1.

6.4.2 Flame-retardant finishes for wool

The dyeing and finishing of wool continues to pose a challenge for textile and protein chemists as the complexity of its chemical and physical structure and the need to find effective processes are in competition in recent years with its almost constant world tonnage production and diminishing share of world fibre markets and textile economy. Within the area of flammability, of all so-called conventional fibres, wool has the lowest inherent flammability and for some end-uses, where high density of structure and horizontal orientation (for example, carpets) are required in the product, wool fabrics will pass the required flame retardancy tests untreated. Table 6.3 above shows it to have a relatively high LOI value of about 25; wool also has a relatively low flame temperature of about 680°C . Its similarly high ignition temperature of 570 – 600°C is a consequence of its higher moisture regain (8–16% depending upon relative humidity), high nitrogen (15–16%) and sulphur (3–4%) contents and low hydrogen (6–7%) content by weight. While organo-sulphur compounds are generally flame-retardant to some degree, the disulphide cystine links are easily oxidisable and so this can offset some of the anticipated natural flame retardancy. Pre-oxidation of wool, and hence cystine to cysteic acid residues, restores this expected activity and oxidised wools can have greater inherent low flammability.

Notwithstanding the above, if wool is to be effective in applications such as curtains, upholstery, protective clothing and barrier fabrics, flame-retardant finishing is essential, although durability needs only to extend to dry-cleaning in most instances. When heated, wool – like cellulose – tends to form a char and this reaction is highly favoured in untreated wool. Furthermore, because wool chars via a semi-liquid state, char formation is accompanied by intumescence to give an expanded, though brittle, char that is often thicker than the original fabric. Thus the charred structure provides an equivalent, if not superior thermal barrier, provided that the char remains coherent, relative to the original fabric. This makes wool an ideal fibre for use in protective clothing, especially where the hazard of molten metal splash exists, because the intumescent char provides a thermal barrier to the solidifying metal splash (and its associated emission of latent heat of fusion), and the mass of the metal enables it to fall away as the weak encapsulating char fractures. Furnace and foundry workers' clothing and aprons are often based on flame-retardant wool fabrics.

An added advantage of the char is that following its formation by a point source of short duration (for example, brief cigarette or match contact) it can be brushed away leaving little if any sign of damage, assuming that only the fabric surface has been exposed.

Finally, the absence of significant inorganic salt concentration means that natural wool gives few if any afterglow problems, which can be a feature of cellulosic textiles.

From the above, it will be obvious that char-promoting flame-retardants will be particularly beneficial, although bromine-containing, vapour-phase-active surface treatments are also effective. The review by Horrocks [2] comprehensively discusses developments in flame-retardants for wool up to 1986 and very little has changed since that time. Given that a number of traditional non-durable finishes based on boric acid/borax (1:2 w/w) mixtures and sulphamic acid (as the ammonium salt) are still used, those currently supplied by a selection of major flame-retardant manufacturers are listed in Table 6.7. They are mostly based on phosphorus-based salts and complexes and some also function on cellulosics, as seen in Table 6.5.

It is significant that ammonium phosphates and derivatives will function as Lewis acids on any functional polymer that has pendent –OH groups and so will promote char formation in wool. Released phosphorus acids will probably promote the deamination of wool protein and so further encourage char promotion. These salts, when dried and cured at temperatures up to 130 °C, will give dry-clean durability up to as many as 10 cycles. Even the highly water-soluble ammonium bromide gives some degree of durability on wool as seen in Table 6.6 (see Antibleaze FSD and possibly Flovan BU (Ciba) in Table 6.7).

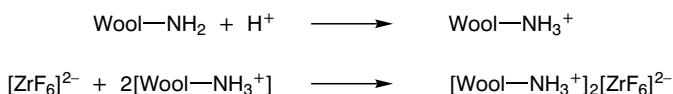
Table 6.7 Non- and semi-durable flame-retardant finishes for wool and wool blends

Trade name	Chemical constitution	Durability
Rhodia, formerly Albright and Wilson:		
Antibleaze FSD	Ammonium polyphosphate (APP) + ammonium bromide	Dry-cleaning
Antibleaze RD1	Ammonium salt of phosphonic acid	–
Antibleaze LR3	APP powder (30% w/w P) for use in coatings	Dry-cleaning
Antibleaze LR4	APP powder (27% w/w P) for use in coatings	Dry-cleaning
Ciba:		
Flovan BU	Inorganic (ammonium?) halide (bromide?)	Dry-cleaning
Flovan CGN	Ammonium acid phosphonate	–
Thor:		
Flammentin ASN	Ammonium phosphate (APP or DAP?)	Dry-cleaning
Flammentin HM	Ammonium salts (phosphates?); useful up to 30% wool in blends	Dry-cleaning
Flammentin KRE	Organic phosphorus–nitrogen compound	–
Flammentin MCFC	Crosslinking silicone + P- and N-containing compounds	40 °C water soak, dry-cleaning
Schill and Seilacher:		
Flacavon R _{NEU}	Organic P- and N-containing compound	Dry-cleaning

In spite of considerable research into the use of functional phosphorus-based finishes, including the more recent study of the effectiveness of methylolated phosphonamides (for example, Pyrovatex CP) by Hall and Shah [37], and substantive halogenated species like chlorendic, tetrabromophthalic and dibromo-maleic anhydrides and brominated salicylic acid derivatives, the most commonly used durable flame-retardants are based on Benisek's Zirpro (IWS) system [2] (see Table 6.2). Major advantages of this treatment are the absence of any discolouration or other effect on wool aesthetics, coupled with its application via a simple exhaust process.

The Zirpro process is based upon the exhaustion of negatively charged complexes of zirconium or titanium onto positively charged wool fibres under acidic conditions at a relatively low temperature of 60 °C. Zirpro treatments can be applied to wool at any processing stage from loose fibre to fabric using exhaustion techniques either during or after dyeing. The relatively low treatment temperature is an advantage because this limits the felting of wool.

The processor has the choice of potassium hexafluorozirconate (K_2ZrF_6) or a mixture of this and potassium hexafluorotitanate (K_2TiF_6). Both components are stable metal fluoride complexes that are substantive to wool. Exhaustion is rapid, achieving 80% or so after 30 minutes. The simple chemistry of application is shown in Scheme 6.2.



Scheme 6.2

Some hydrolysis of the complex does occur but Benisek demonstrated that acceptable flame retardancy occurs if the molar ratio F:Zr ≥ 5 when maximum exhaustion occurs [38] and the zirconium concentration on the fabric is 2.3% (w/w). The use of the titanium complex, because of the smaller ionic size and hence the greater penetrative character of titanium, enables an equivalent or higher level of flame retardancy to be achieved at similar bath concentrations. K_2TiF_6 , however, causes discolouration and so it is used as a mixture with K_2ZrF_6 to minimise this and decrease both concentrations and cost [2].

It is important to maintain a low pH (≤3) in order to maximise fibre penetration and wash fastness to as many as 50 washes at 40 °C or 50 dry-cleaning cycles in perchloroethylene. Acids like hydrochloric and formic acid are preferred because, unlike sulphuric acid, for example, they do not have anions that compete with the metal fluoride ions for protonated amino groups in wool. However, the general simplicity of the whole process enables it to be used either concurrently with 1:1 premetallised and acid levelling dyes or after dyeing when applying acid milling reactive 1:2 premetallised and chrome dyes. Furthermore, the treatments are compatible with shrink-resist, insect-resist and easy-care finishes.

Should smoke emission be a problem, then because the above Zirpro treatments can increase smoke generation with respect to untreated wool, a low-smoke variant may be used, which

comprises a fluorocitratozirconate complex. This is applied from formic acid to achieve a molar ratio F:Zr = 2 and a zirconium concentration of at least 2–3% (w/w).

The effectiveness of the Zirpro treatment is not fully understood from the mechanistic point of view and while Benisek [39] attributes it to enhanced intumescent char formation, Beck and coworkers contest this view [40]. Clearly, however, its ability to create extremely effective flame and heat barrier properties at high heat fluxes, is associated with the char structure generated.

Recently the process has come under the critical eye of environmentalists (see Section 6.6) as a consequence of the release of heavy metal ions into effluent discharges. In attempts to decrease effluent problems, replacement of the exhaust method by padding methods has not been successful because both the potassium metal fluoride complexes are not very soluble ($\sim 10\text{ g l}^{-1}$) at room temperature.

In spite of these concerns, research during recent years has been limited. For instance, Lewin and Mark [41] have demonstrated that sulphation with ammonium sulphamate followed by curing at 180–200 °C in the presence of urea can give a 50 hard water wash-durable finish for wool fabrics with little change in handle. Clearly there is an opportunity to develop a commercial process not dependent on heavy metal complexes based on this procedure. More recent research discussed in Section 6.6 has shown that intumescents may also offer effective flame retardancy to wool and wool-containing blends.

One final point to be mentioned concerns the need to impart a number of finishes to wool fabrics if they are to achieve the many performance requirements demanded by protective clothing and aircraft upholstery applications, for instance, coupled with the need for easy-care properties. Developments in this area have been reviewed [2] and certain factors are worthy of note:

- (1) oxidative shrink-resist treatments should be applied before Zirpro treatment;
- (2) insect-resist treatments should be added to a Zirpro bath first;
- (3) resin-based shrink-resist treatments can promote flammability unless, like the Hercosett (Hercules) resin, they contain elements like chlorine and nitrogen;
- (4) such resins should be applied after Zirpro treatment;
- (5) co-application of water-repellent (for example, resin-wax dispersions) and oil-repellent (for example, fluorocarbon) finishes should follow Zirpro treatment, by a pad–dry–cure–rinse–dry process, for example.

6.4.3 Flame-retardant finishes for man-made fibres

Synthetic fibres may be rendered flame-retardant during their production, thereby creating a degree of inherent flame retardancy. Apart from viscose and, more recently, lyocell fibres, the conventional synthetic fibres are hydrophobic with physical structures inaccessible to the salt-like materials used for non-durable flame-retardants. Consequently, only regenerated cellulose fabrics and blends are amenable to non-durable flame-retardant finishing with the formulations described above in Table 6.5. Viscose, in particular, is more delicate than cotton and lyocell fibres, and so must be finished with care to avoid undue strength losses during drying and curing.

The remaining common synthetic fibres – namely polyamide, polyester, polyacrylic and polypropylene – are candidates for semi-durably and durably flame-retarding if suitable finishes are available, unless alternative inherently flame-retardant analogues are commercially acceptable. Table 6.8 lists examples of those currently available for polyester and polyamide (and blends). In the case of acrylics, because of the difficulty of finding an effective flame-retardant finish, modacrylic fibres are preferred unless a back-coating is considered as an acceptable solution, as it would be for finishing fabrics to be tested to BS 5852 : 1979 or EN 1021-1/2. While back-coatings may be similarly effective on other synthetic fibre-containing fabrics and may offer sufficient char-forming character and char coherence to offset fibre thermoplastic and fusion consequences (see Flacavon H12 and H14 examples in Table 6.8), this is less easily achieved for polypropylene fabrics.

The low melting point, non-functionality and high hydrocarbon fuel content (see Table 6.3) of polypropylene are three factors that have created problems in finding an effective durable flame-retardant finish and also pose difficulties in the design of effective back-coatings.

This leaves only polyamides and polyesters as possible candidates for durable flame-retardant treatments. While the scientific literature contains possible solutions [2], few have entered the commercial arena, as examples in Table 6.8 show [33].

The Antiblaze CU product (formerly Antiblaze 19 [2]) is claimed to be effective on polyamides and polypropylene as well as polyester, for which it was initially developed. It is essentially monomeric although available as the high-boiling dimer Antiblaze 1045, for use as a melt additive. Antiblaze CU has a high phosphorus content (21.5% w/w) and is a clear viscous liquid that is applied to polyester at 3–6% (w/w) add-on buffered at pH 6.5 with disodium phosphate and a small amount of wetting agent. After padding at about 40–60% expression or wet pick-up, fabric is dried at 110–135 °C followed by thermofixation at 185–205 °C for 1–2 min. Thermofixation usually only results in about 80% retention of the original finish because of the finish volatility at high temperature. After rinsing and drying, the finish should resist 50 washes at 60 °C or 10 dry-cleaning cycles with 90% retention.

The finish may be incorporated in a resin for coating polyester and its blends. Durability is not as great but loss does not occur during processing, as in the thermofixation treatment. Inclusion of melamine increases the finish effectiveness on 100% polyester. A typical binder ratio of Antiblaze CU : melamine : binder would be 8:13:34, with the residual weight made up of water and a viscosity modifier. Antiblaze CU has also been used to partly replace brominated flame-retardants in Sb–Br back-coating formulations [21]. Thor's Aflammit PE and Schill and Seilacher's Flacavon AZ are believed to be similar if not the same as Antiblaze CU.

A number of US-manufactured flame-retardants, which are able to confer BS 5852: 1979 Part 1 or EN 1021-1/2 passes on polyester fabrics (presumably after exposure to the required 40 °C water soak requirement), are included in Table 6.8 and tend to be halogen-based [33].

For the flame-retardant treatment of nylon fabrics, few treatments are satisfactory. Application of 10% (w/w) ammonium bromide or 18% (w/w) ammonium dihydrogen phosphate by a pad–dry route is effective but non-durable. The use of urea-formaldehyde resins or aminotriazine-aldehyde condensates can be used with ammonium bromide using a pad–dry–cure process to improve the

Table 6.8 Durable finishes for synthetic fibre-containing textiles

Trade name	Chemical constitution/comments
Rhodia, formerly Albright and Wilson:	
Antiblaze CU/CT	$\text{CH}_3\text{O}\text{P}(\text{O})(\text{CH}_3)_2 - \left[\begin{array}{c} \text{O} \\ \\ \text{OCH}_2\text{C}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{O} \\ \\ \text{CH}_2\text{O} \end{array} \right]_n \text{P}(\text{O})(\text{CH}_3)_2\text{O}$ <p><i>n</i> = 1; cyclic oligomeric phosphonate; pad-dry(110–135 °C)–cure(185–200 °C) Primary use: polyester Secondary uses: polyamide, polypropylene</p>
Thor:	
Aflammit PE	As above for Antiblaze CU, polyester
Aflammit NY	Organic nitrogen and sulphur compound (probably a thiourea derivative) and a reactive crosslinking compound; polyamide. Cure at 150–170 °C for 45–60 s.
Schill and Seilacher:	
Flacavon AM	Nitrogen- and sulphur-containing compound (thiourea derivative?); polyamide; 100–110 °C dry only; durable to dry-cleaning
Flacavon AZ	Organic phosphorus compound (as for Antiblaze CU?); polyester
Flacavon H12/10	Organic phosphorus and nitrogen-containing compound (+ binder)
Flacavon H14/587	Antimony oxide + bromine compound (+ binder); all fibres especially polyester/cotton blends
Clariant:	
Pekoflam PES new liq.	Cyclic organic phosphorus compound (as for Antiblaze CU?); polyester
Apex Chemicals (US):	
Apex Flameproof 334	Organohalogen compounds: polyester
Apex Flameproof 1510	Organohalogen compounds: polyester, polyamide
Emco Services (USA):	
Flame Out PE-60	Organohalogen compounds: polyester
Flame Out PE-19	Cyclic phosphorus compound: polyester
Flame Out N-15	Organic nitrogen compound: polyamide
Glo-Tex International (USA):	
Guardex PFR-DPH	Organohalogen–phosphorus compound: polyester, polyamide, polypropylene
Guardex FR-MEHN	Organophosphorus compound: polyamide
Sybron Chemicals (USA):	
Flame Gard PE conc	Organophosphorus compound: polyester
Flame Gard 908	Organic nitrogen compound: polyamide

durability of the finish. Durable but stiff flame-retardant finishes based upon methylated urea formaldehyde with thiourea formaldehyde have been successfully applied to nylon nets for evening wear and underskirts. Some 15–20% (w/w) thiourea formaldehyde precondensate is padded with ammonium chloride (1% on the weight of the resin) as a latent catalyst followed by low temperature drying and then curing at 170 °C for 1 min.

Examples of these finishes are probably included in Table 6.8, although the exact chemical constitutions of polyamide-specified retardants are not available.

6.4.4 The challenges of finishing blends

Experience has shown that flame-retardants that are effective on one fibre, when in contact with a second differently flame-retarded fibre, may prove to be antagonistic and render the blend flammable [2]. Consequently, the current rules for the simple flame-retarding of blends are either to apply flame-retardant only to the majority fibre present or apply halogen-based back-coatings, which are effective on all fibres because of their common flame chemistries in the vapour phase.

The widespread use of cotton/polyester blends coupled with the apparent flammability-enhancing interaction in which both fibre components participate (the so-called scaffolding effect, reviewed elsewhere [2,13]) mean that cotton/polyester has promoted greater attention than any other blend [2]. However, because of the observed interaction, only halogen-containing coatings and back-coatings find commercial application to blends that span the whole blend composition range; the earlier (1975) Caliban F/R P-44 decabromodiphenyl oxide and antimony III oxide in a 2:1 mass ratio (equivalent to a molar ratio of Br:Sb = 3:1) in a latex binder [42] has been the model for current coating and back-coating formulations for cotton/polyester blends as well as for back-coatings in general [17] (see examples from Noveon (formerly Mydrin) and Schill and Seilacher in Tables 6.2, 6.5 and 6.8).

Most non-durable finishes for cellulosics (see Table 6.5) function on cellulosic-rich blends with polyester although the converse does not hold true unless some bromine is present. Antibleaze FSD, Flovan BU and Flammentin BL are examples in Table 6.4 of those able to flame-retard cellulosic blends rich in polyester (and other synthetic fibres) because they contain ammonium bromide.

In the case of durable, phosphorus-containing cellulose flame-retardants, they are generally only effective on cellulose-rich blends with polyester. THP-based systems like Proban CC (Rhodia, formerly Albright and Wilson) are effective on blends containing no less than 55% cotton if a combination of flame retardancy and acceptable handle are required. This is because the THP condensate is substantive only on the cellulose content, which would require over 5% (w/w) phosphorus to be present on this component in order to confer acceptable flame retardancy to the whole blend. High phosphorus and hence finish levels lead to excessive surface deposits on fibres and decreased durability to laundering, and create unacceptable harshness of handle. Furthermore, such an application only works well on medium- to heavy-

weight fabrics ($> 200 \text{ g m}^{-2}$) and so is particularly effective for protective clothing applications. The use of a cotton-rich blend here is particularly advantageous because the lower polyester content confers a generally lower thermoplastic character to the fabric with a smaller tendency to produce an adhesive molten surface layer when exposed to a flame.

In order to achieve the high finish levels necessary, often a double pass pad-dry (or foam-dry) stage is required before the THPC-urea-impregnated fabric is ammonia-cured in the normal way. If a lower degree of durability is required, then the cheaper semi-durable Antiblaze LR2 (at phosphorus levels of about 6%) and 5–6% Antiblaze CU applied to cotton and polyester components respectively in the blend will give a 40 °C, 30 minute water-soak-resistant finish.

Application of methylolated phosphonamide finishes – for example, Pyrovatex CP (Ciba) – is effective on blends containing 70% or greater cellulose content. This is because the phosphorus present is less effective on the polyester component than in THP-based finishes [2]. The reasons for this are not clear but are thought to be associated with some vapour-phase activity of phosphorus in the latter finish on the polyester component.

Wool blends pose different challenges, but given the complexity of wool and the position of the Zirpro process as the currently major durable FR treatment, its specificity ensures that little if any transferability occurs to other fibres present. Furthermore, Benisek reported antagonisms between Zirpro and other flame-retardant fibres in 1981 [43]. In the absence of any back-coating treatment, acceptable flame retardancy of Zirpro-treated blends is obtainable in 85/15 wool/polyester or polyamide combinations. For lower wool contents in blends, and without the possibility of using alternative FR treatments, flame retardancy can be maintained only if some of the Zirpro-treated wool is replaced by certain inherently flame-retardant fibres, except for Trevira CS polyester [43]. Chlorine-containing fibres such as PVC and modacrylics are particularly effective in this respect.

6.5 APPLICATION OF FLAME-RETARDANT FINISHES

Successful flame-retardant finishes are those that combine acceptable levels of flame retardancy at an affordable cost and are applicable to textile fabrics using conventional textile finishing and coating equipment. Without wishing to enter into great detail of such established techniques, which are well-documented in the general textile literature, Figure 6.6 attempts to present an overall summary of these.

Four basic processes are shown schematically and each relates to one or more of the flame-retardant finishes for cellulosic textiles identified above in Table 6.4 as well as for most other textiles discussed above. It is of interest to note that alternative application methods to padding (1)–(3) – such as foam application – may be used, although padding represents the most commonly used technique. Each process (1)–(4) in Figure 6.6 relates to finish type as follows:

- (1) This simple pad-dry technique is applicable with most non-durable and water-soluble finishes such as the ammonium phosphates and similar finishes.
- (2) This sequence is typical of those used to apply crease-resistant and other heat-curable textile finishes applied to cellulose-containing fabrics. In the case of flame-retardant

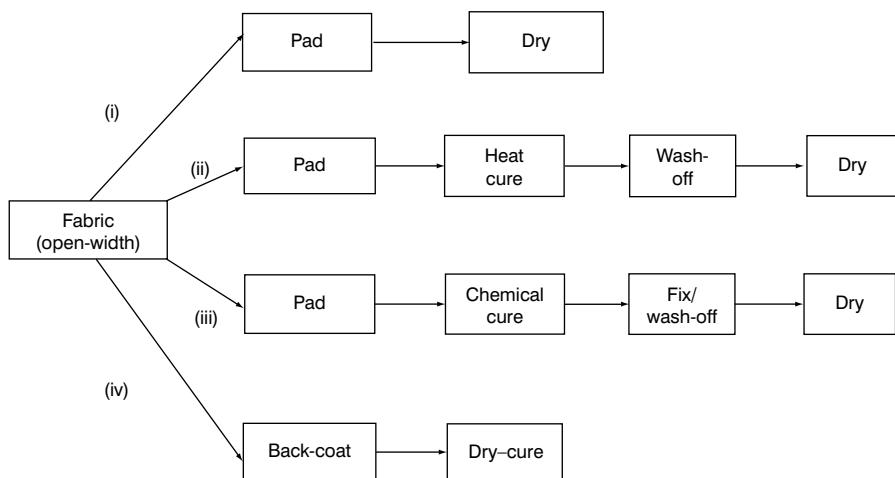


Figure 6.6 Schematic representation of flame-retardant finishing and coating techniques

finishes it finds best use for application of the phosphonamide systems such as Pyrovatex CP (Ciba), Aflammit KWB (Thor) and TFR1 (Rhodia, formerly Albright and Wilson) which are applied with resin components such as methylolated melamines. Because the process requires the presence of acidic catalysts (for example, phosphoric acid), the wash-off stage will include an initial alkaline neutralisation stage as shown in the detailed schematic in Figure 6.7 [36]. This same sequence without the washing-off stage may be used to apply semi-durable finishes where a curing stage allows a degree of interaction to occur between the finish and the cellulose fibres. Typical examples are the ammonium phosphates, which during curing at about 160 °C, give rise to phosphorylation of the cellulose. Thus the finish develops a degree of resistance to water soak and gentle laundering treatments. Thermally fixed finishes like Antiblaze CU would use this process modified with the baker being replaced, if necessary, with a radiant heater and, of course, no alkaline neutralisation stage.

- (3) This is best exemplified by the Proban process, which requires an ammonia gas curing stage in order to polymerise the applied finish within the internal fibre voids. In this way the Proban CC condensate of tetrakis (hydroxy methyl) phosphonium chloride and urea after padding and drying onto the fabric, is passed through a patented ammonia reactor, which crosslinks the condensate to give an insoluble polymeric finish. In order to increase the stability and hence durability of the finish, a subsequent oxidative 'fixation' stage is required before finally washing-off and drying (see Figure 6.4).
- (4) Back-coating, as discussed above, describes a family of application methods where the flame-retardant formulation is applied in a binding resin to the reverse surface of an otherwise flammable fabric. In this way the aesthetic quality of the face of the fabric is maintained while the flame-retardant property is present on the back or reverse face. Careful use of viscosity modifiers and general back-coating application variables ensures that 'grin-through' is minimised. Recent work in the author's own laboratory has attempted

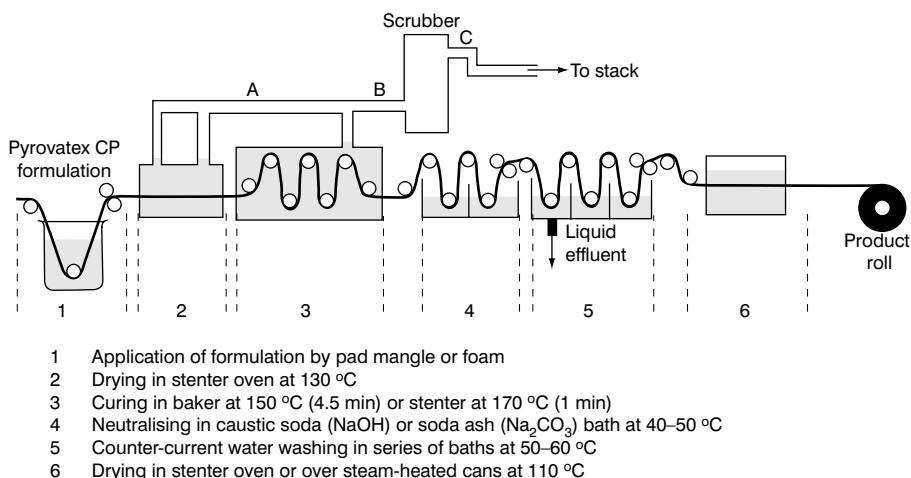


Figure 6.7 Detailed schematic diagram of the Pyrovatex CP application process

to correlate the various back-coating variables and hence show how an optimised process may be achieved [44]. Application methods include doctor blade or knife-coating methods and the formulation is as a paste or foam. These processes and finishes are used on fabrics where aesthetics of the front face are of paramount importance, such as furnishing fabrics and drapes.

The vapour phase activity of the typical Sb–Br flame-retardants presence ensures effectiveness of the finish if the coating is truly on the rear face of the fabric. With the pressure to replace Sb–Br by less environmentally-questionable retardants based on phosphorus (see Section 6.6), the need for greater fabric penetration towards the front face is required. This means that closer control of back-coating variables is essential if grit-through is to be prevented. Use of chlorine-containing resins, such as PVC-vinyl acetate and PVC-ethylene-vinyl acetate copolymers decreases the amount of the less effective phosphorus-containing replacement retardants required and hence coating application levels. Typical coating levels of 20–30% by weight are required in order to achieve passes during testing. Coating methods generally, unlike those requiring impregnation (for example, methods (1)–(3)), lead to little or no waste of application chemical formulation and hence minimal effluent problems.

The relatively high application levels necessary for all flame-retardants can adversely influence fabric handle, drape and appearance; these effects are minimised by ensuring that finishing application is carried out so that in processes (1) to (3) minimal finish remains on fibre and fabric surfaces. In process (4), however, the coating is applied solely to the surface fibres of the fabric reverse face. In addition, softening agents may be included within the formulations during application; careful selection of these is essential if compatibility with the formulation is to be assured and they are to have minimal effect on the resulting flame-retardant property.

6.6 CURRENT ISSUES

Apart from the inevitable pressure to decrease costs throughout the textile industry and use the most cost-effective finishes and application processes available, a major issue is the influence of environmental factors and the related current concerns levelled at the use of flame-retardants in general. A secondary and not unrelated issue is the use of flame-retardant treatments that combine enhanced performance and efficiency with decreased environmental impact, namely the role and potential of intumescents [5].

6.6.1 Environmental factors

While Holme [45] has addressed and reviewed environmental concerns of textile processing in general, Horrocks and coworkers [46,47] have attempted to quantify the environmental impact of the currently available flame-retardant fibres including finished and inherently flame-retardant types. A simple model has been devised, which identifies each stage in the processing and end-use history of each fibre from 'cradle to grave'. Each stage is ranked from 0 to 5, for zero to maximum environmental impact respectively, and then summed and expressed as a percentage environmental impact index. Figure 6.8 shows the results for the most common and high performance flame-retardant fibres and indicates that, in spite of very different process histories, these span a very small range of 39–51%. Assuming that the model is valid, then the similarity of values might suggest that since all fibres and textiles are produced by the most economically efficient processes and raw material sourcing, then environmental impact minimisation is already a factor. Obviously as process efficiency, energy and waste minimisation and recycling of by-products and even end-products improves, such environmental impact will decrease further.

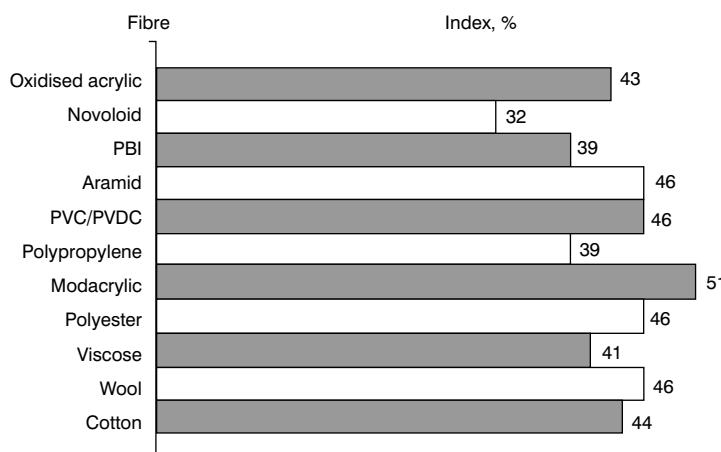


Figure 6.8 Environmental impact index values of flame-retardant fibres

The antimony–bromine question

However, notwithstanding the above, considerable concern has been shown regarding the possible formation of polybrominated dioxins associated with incineration of organobromine compounds, especially those based on polybrominated diphenyl oxides (PBDPOs) [22]. Following the initial concern in Germany in 1986, the EU published in 1991 a draft amendment to EC Directive 76/769/EEC, which would essentially ban use of all polybrominated diphenyl oxides or ethers within five years. In 1994, this Directive was withdrawn as subsequent studies cast doubt on the earlier concerns. Simultaneously with its publication, however, the US Environmental Protection Agency in 1991 demanded vigorous testing of five flame-retardants including decabromodiphenyl oxide (DBDPO). Meanwhile, the Organisation for Economic Co-operation and Development (OECD) had already established in 1990 a pilot programme to decrease risk associated with chemicals and PBDPOs were selected as one of five chemical groups for testing. At the same time the World Health Organization initiated an evaluation of the risk to health of DBDPO, which in 1994 indicated that it did not pose a significant hazard. The full details of the OECD programme are complex [48], but one outcome has been an industrial commitment to address environmental exposure and purity of PBDPOs and minimisation of the presence of non-commercial congeners.

As a consequence of these concerns, European companies like Schill and Seilacher now offer DBDPO alternatives such as hexabromocyclododecane, and Wragg [23] has reviewed the current position.

Even more recently, the role of antimony III oxide in ‘cot deaths’ or sudden infant death syndrome (SIDS) was raised on UK Television in 1994, and although refuted [49] and subsequently shown to be without foundation [10,50], the image of Sb–Br finishes in general is poor within the media and environmental circles.

Antimony–bromine alternatives

Efforts to decrease Sb–Br concentration and eventually replace Sb–Br in back-coating formulations have continued since the early 1990s and this has been alluded to in previous sections.

Table 6.5 lists a number of ammonium polyphosphate formulations (for example, Antiblaze LR3/LR4, Pyrovatim SB and Flammentin UCR) that may be used to partially or even wholly replace Sb–Br systems in back-coating formulations, and are recommended for cellulosic furnishing fabrics. Their effectiveness is enhanced by use of chlorine-containing binding resins (see Section 6.5) [21]. One drawback lies in the solubility of APP (see Table 6.6), however, and so they need to be used with care if they are to pass the 40 °C water soak test (BS 5651) as required by UK furnishing fabric regulations [8]. In addition, because these phosphorus-based formulations are not vapour-phase active, there is a need to increase and control coating penetration, which has also been briefly discussed in Section 6.5. In an attempt to provide a deeper understanding of the back-coating application process, recent work by Davis and Horrocks has shown that multivariate analytical techniques are able to define the

interdependencies of variables such as paste viscosity, blade angle and penetration [44]. As a consequence, the means of assuring correct coating penetration may be more scientifically implemented.

An alternative to APP is the use of phosphorus compounds in the Flammentin NAH range of products from Thor, which may be used in coating formulations. This and other flame-retardants that do not contain Sb–Br – including the cyclic oligomeric phosphonate Aflammit PE (Thor, see Table 6.8), an APP-based formulation, alumina trihydrate and zinc hydroxystannate – were recently studied by the author and coworkers [21]. It was shown that each could partly replace the antimony III oxide-DBDPO present and still maintain a pass to the simulated match requirements of BS 5852. However, only alumina trihydrate, the oligomeric phosphonate and ammonium polyphosphate were able to fully replace the Sb–Br and still yield a pass, although marginal, at 30% (w/w) add-ons to cotton. Figure 6.9 shows the add-ons of both pure and mixed Sb–Br and non-Sb–Br components required to pass the simulated match (BS 5852) test; only three formulations (marked 'F') were unable to achieve passes. Subsequent work has suggested that for phosphorus-containing flame-retardants to be effective as back-coating formulations, they must be able to melt or decompose to liquid intermediates, which can wet the fabric back surface and diffuse through to the front face [51].

One other recent innovative approach has been reported by Wragg [23], which uses a modified carbon pigment – possibly an intumescent (see Section 6.6.2 below) exfoliated graphite – applied in a resin, and is recommended for technical non-woven fabrics comprising

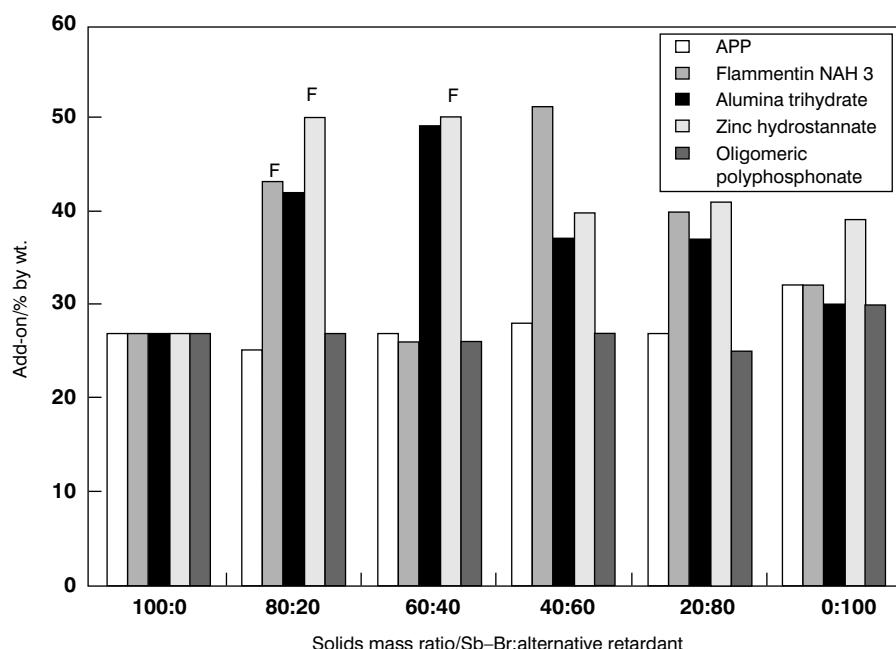


Figure 6.9 The minimum percentage add-on required to achieve a pass for different back-coating formulations on 264 gm⁻² cotton (F denotes failure) [21]

the common synthetic fibres polyester, polyamide and polypropylene. Flacavon DPL from Schill and Seilacher is an example, although other grades are available.

Effluent and water minimisation

As a consequence of current environmental legislation (the UK Environmental Protection Act, 1990) and EU demands for stricter controls over effluent discharge, a number of problems particularly associated with flame-retardant applications have been identified. These relate to the following:

- (1) effects of discharge to effluent of unused flame-retardant liquors;
- (2) effects of emissions of formaldehyde to the atmosphere, especially during curing (currently required to be ≤ 20 ppm);
- (3) emissions of volatile organic compounds (VOCs) (currently ≤ 50 ppm);
- (4) use and emission of ammonia in THP-based treatments;
- (5) discharge of unfixed flame-retardants from washing-off effluent.

In order for most commercial textile finishers to achieve acceptable formaldehyde and VOC emissions when applying formaldehyde-based finishes such as Pyrovatex CP and its analogues, gaseous exhausts from the drying and curing stages pass through scrubbers before release into the environment. Liquid effluents require neutralisation and dilution before release. Particular problems posed by the N-methylol dimethyl phosphonopropionamide ($\text{RCONHCH}_2\text{OH}$) finishes stem from the impurity of the reagent itself and the difficulty of optimising the chemistry to minimise formaldehyde release. Recent research by Kapura [52] has shown that the percentage solids active species in commercial Pyrovatex CP is as little as 27% (w/w) with the methyl ether derivative of N-methylol dimethyl phosphonopropionamide ($\text{RCONHCH}_2\text{OCH}_3$) present at 28% (w/w). If these are considered to be similarly effective, this is equivalent to a total effective solids content of still only 55% (w/w). Remaining components include the non-methyloated form, RCONH_2 (8% w/w), and the dimer, $\text{RCONHCH}_2\text{OCH}_2\text{NHCOR}$ (37% w/w). In 1990, Ciba introduced a purer version, Pyrovatex CP New, which according to Kapura, comprises 61% (w/w) main reagent $\text{RCONHCH}_2\text{OH}$, 10% (w/w) of the methylated derivative, 21% (w/w) of the non-methyloated form and a much decreased dimer content of 8% (w/w). This product has given higher levels of fixation after curing and decreased levels of resin deposits in the curing/baking zones. More recently, Ciba have introduced Pyrovatex 7572, possibly the dimethylolated derivative $\text{RCON}(\text{CH}_2\text{OH})_2$, to increase fixation further. An alternative product, Pyrovatex 7620, is also available giving decreased formaldehyde emissions.

Recent research at Bolton Institute under a UK Environmental Technology Best Practice Programme [36] has shown that during the application of Pyrovatex CP (see Figures 6.5 and 6.7), the objectives of decreasing formaldehyde emissions by up to 75%, and decreasing levels of phosphorus in effluent by improved finish fixation, and hence decreased application costs, were achieved. By using a chemometrics software package, the five-component liquor (see Table 6.9) could be analysed in terms of identifying those component concentrations that significantly affected flame resistance (measured as LOI), formaldehyde emission levels and degree of fixation.

Subsequently, the software predicted a minimum number of experiments required to optimise the application recipe. The standard and optimised recipe with associated fabric properties and formaldehyde levels measured at the curing stage (position B in Figure 6.7) are presented in Table 6.9 for laboratory-based experiments. While the optimised recipe is little different from the standard formulation, the analytical software predicted and demonstrated that the latter is on a 'knife edge' with regard to sensitivity of the concentration of formaldehyde emission. On scaling up to full plant scale, the four-fold decrease in formaldehyde from 20 to 5 ppm previously obtained under laboratory conditions is shown in Table 6.10 to yield between 36 and 59% reductions.

Table 6.9 Pyrovatex CP standard and optimised application recipes and pilot-scale results [36]

	Standard recipe	Optimised recipe
Recipe component (g l ⁻¹)		
Pyrovatex CP	280.00	260.00
Melamine resin	35.00	32.00
Softener	25.00	27.00
Acid catalyst	20.00	15.00
Wetting agent	1.25	1.25
Fabric response (%)		
LOI	28.00	30.00
Phosphorus on fabric	1.90	2.00
Emission level after curing stage (ppm)		
HCHO, formaldehyde	20.00	5.00

Table 6.10 Industrial trial results for formaldehyde emissions from optimised Pyrovatex CP application [36]

Site	Standard recipe formaldehyde emissions (ppm)	Optimised recipe formaldehyde emissions (ppm)	Reduction (%)
1	11	4.5	59
2	7	4.5	36
3	4.3	2.5	42

This work also demonstrated that formaldehyde levels could be monitored directly from plant emissions using Fourier Transform infrared (FTIR) spectroscopy and also that phosphorus emissions in liquid effluent were decreased by 50% following improved fixation as a consequence of modifying the formulation.

Finally, the project demonstrated that chemometrics software should be applicable to a whole range of multicomponent dyeing and finishing formulations in order to optimise application and

minimise waste. Clearly such processes, if used with minimum add-on (for example, foam application) and waste water recycling systems can minimise waste even further, thus achieving environmental and economic savings.

6.6.2 The potential of intumescent application

Intumescence is a phenomenon where heat or another agent promotes formation of an expanded or swollen condition; in the case of a flame-retardant, this is an expanded char [5,53]. Intumescent coatings may be applied to textile fabrics, which once activated by heat generate a foamed insulating layer on the fabric surface. This intumescent layer prevents any further ignition until the fire consumes the intumescent layer itself. Thus the primary aim is to prevent or retard the rate at which flammable substrates ignite, or non-flammable, thermoplastic substrates soften. The stable and thermally insulating char barrier created by the mechanism of intumescence is resistant to both radiant heat and flame. The mechanism operates within the solid phase and is designed to delay the combustion or softening of the textile material.

Intumescent coatings normally contain four major components – namely a ‘carbonific’ or char-former, a catalyst, a ‘spumific’ or gas-former and a binder. Other components that may be used include fillers, pigments, viscosity-modifiers and fibres. A typical intumescent coating [54] has the same surface appearance as that of a conventional coated textile, but on heating the surface of the binder melts and spreads, forming a skin over the fabric surface that inhibits exposure of the underlying fibres to atmospheric oxidants. The heat then activates the catalyst, which decomposes to yield an inorganic acid, which chars the carbonific compound by a dehydration mechanism. Under the action of the heat the specific compound generates non-flammable gases, which are released and trapped within the viscous carbonaceous char, ‘blowing’ up the layer to form a thick thermally-insulating foam.

Clearly, any enhancement of the char barrier in terms of thickness, strength and resistance to oxidation will enhance the flame and heat barrier performance of textiles. Generation or addition of intumescent chars as part of the overall flame-retardant property will also decrease the smoke and other toxic fire gas emissions.

The application of intumescent materials to textiles has been reviewed [5] and is exemplified in the patent literature by the following fibre-intumescent structures, which offer opportunities in textile finishing.

- (1) More conventional, flexible textile fabrics to which an intumescent composition is applied as a coating have been reported [54]. In one example of this patent, the glass-fibre-cored yarns used in the woven or knitted structure complement the flame and heat resistance of the intumescent coating. Presence of sheath fibres of a more conventional generic type ensures that the textile aesthetic properties may be optimised. More recently, the Flammentin IST flame-retardant from Thor is based on the use of intumescents as replacements for antimony–bromine systems in coating and back-coating formulations.
- (2) The recent development of a back-coating for technical non-wovens based on modified carbon and developed by Schill and Seilacher has been described in Section 6.6.1 [23].

- (3) Most recently, Horrocks and coworkers have patented [55] a novel range of intumescent-treated textiles that derive their unusually high heat barrier properties from the formation of a complex char that has a higher than expected resistance to oxidation. These require the intumescent to be in intimate contact with the surfaces of flame-retarded, char-forming fibres and for respective char-forming mechanisms to be physically and chemically similar. Exposure to heat promotes simultaneous char formation of both intumescent and fibre to give a so-called ‘char-bonded’ structure.

The integrated fibrous-intumescent char structure in (3) above has a physical integrity superior to that of either charred fabric or intumescent alone and, because of decreased oxygen accessibility, demonstrates an unusually high resistance to oxidation when exposed to temperatures above 500 °C and even as high as 1200 °C. Furthermore, these composite structures show significantly decreased rates of heat release when subjected to heat fluxes of 35 kW m⁻², thus demonstrating additional significant fire barrier characteristics [56].

More recent work has shown that the intumescents, which are based on ammonium and melamine phosphate-containing intumescents applied in a resin binder, can raise the fire barrier properties of flame-retarded viscose and cotton fabrics to levels associated with high performance fibres such as aramids [57]. Furthermore, charred residues are considerably stronger than those from flame-retarded fabrics alone [58]. Applications of these same intumescents to wool-containing fabrics have shown that enhanced barrier properties are possible and this occurs for both flame-retarded (Zirpro) and unretarded wool fibres present [59,60]. Current research is now focussed upon enabling these intumescent formulations to be applied to conventional fabric structures using normal application technologies. In addition, some success has been achieved at creating durable intumescent finishes based on the reaction of phosphorylated polyols (for example, pentaerythritol diphosphoryl chloride) with cellulose, flame-retarded cellulose, wool and nylon [61,62].

Clearly there is increasing interest in the development and use of intumescent flame-retardants across the whole spectrum of flame-retardant polymeric materials as the need to decrease the concentrations and usage of the common Sb–Br formulations increase, coupled with the superior fire barrier and decreased toxic combustion gas properties that they generally confer. In the next few years, there will be increased use of these materials in the textile and related sectors.

6.7 CONCLUSIONS

In summary, very little has changed regarding the fundamental chemistries of flame-retardants for use in the finishing of textiles during the last ten years or so. However, major concerns regarding the environment and health and safety have decreased the large numbers developed and reported during the 1960–1980 period [2]. Environmental interests continue to question the usefulness of some systems – in particular, antimony–bromine-based formulations – and the use of intumescent and similar systems are being investigated and introduced as possible replacements.

Two independent studies have recently been undertaken into the possible toxicological consequences of using flame-retardants in textiles, one in the EU and the other in the USA. The former is as a consequence of an EU Mandate demanding a general study into the burning behaviour of nightwear [62], the outcome of which has been the instruction to the CEN/TC248 Textiles and Textile Products Committee to draft an appropriate test method. The second is a consequence of the US National Academy of Sciences having been tasked by Congress during 1999 [64] with undertaking a risk assessment of a number of flame-retardants used for furnishing fabrics, as a prelude to the possible introduction of US Federal regulations that will require simulated match flame resistance for such fabrics. The recent report is the most authoritative toxicological risk assessment of flame-retardant chemicals to date. It also used stringent exposure scenarios for dermal, oral and inhalation exposure to reach its conclusions. Table 6.11 lists the flame-retardants considered and the results of the assessment. Those in the upper half were considered safe to use on residential furniture with minimal risk even under worst-case assumptions. It was recommended that those in the lower half be subject to exposure studies to determine whether further toxicity studies should be undertaken. Subsequent work by the US Consumer Product Safety Council (CPSC) has confirmed the findings in Table 6.11 and provided evidence that cyclic organophosphates like Antiblaze CU (see Table 6.8) should be 'above the line' and so may be deemed to be 'acceptable'[65]

Finally, while application methods are those based on normal textile finishing procedures, minimum application systems such as foam application and decreased use of water and energy and effluent minimisation continue to receive attention. Any developments in new flame-retardant types and processes will probably be in the synthetic fibre arena where the goal will be the generation of char-promoting finishes or other treatments [66].

Table 6.11 Risk analysis of 16 selected flame-retardants [63]

Acceptance	Chemical	Use in furnishings
Acceptable:	Hexabromocyclododecane (HBCD)	✓
	Decabromodiphenyl oxide (DBDPO)	✓
	Alumina trihydrate	✓
	Magnesium hydroxide	✓
	Zinc borate	✗
	Ammonium polyphosphates	✓
	Phosphonamide ('Pyrovatex' type)	✓
	Tetrakis(hydroxymethyl) phosphonium derivatives ('Proban' type)	✓
Exposure studies needed:	Antimony trioxide	✓
	Antimony pentoxide and antimonates	✓
	Calcium and zinc molybdates	✗
	Organic phosphonates	✓
	Tris (1,3-dichloropropyl 1-2) phosphate	✗
	Tris (monochloropropyl) phosphates	✗
	Aromatic phosphate plasticisers	✗
	Chlorinated paraffins	✓

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CHAPTER 7

Chemical softening

W Mooney

7.1 INTRODUCTION

The feel of a textile garment is largely determined by the fabric construction [1] and the fineness of its component fibres. For example, low-twist yarns made from fine fibres will produce soft fabrics. Conversely, a very harsh unpleasant handle will result from coarse fibres in a tightly woven structure. The increasing use of microfibres [2–4], has made it possible to produce fabrics with outstanding softness and drape. The introduction of open end spun yarns, particularly for economy quality cottons, has lead to an undesirable surface harshness. Chemical soft finishes can go a long way to imparting ring spun characteristics to such fabrics.

Most mechanical finishing operations improve fabric handle. Such processes include abrasive sueding, napping, teaselling of wool piece, stone-washing of denim and brushing of fleece-backed casual wear. Sanforizing of woven cotton and compaction of knitted cotton leads to reduced shrinkage during laundering but the fabrics are stiffer and consequently are perceived as having reduced softness and a less desirable handle. Treatment with a chemical soft finishing agent regenerates the softness and drape of such preshrunk fabrics [5–7].

Chemical shrink-resist or easy-care finishes likewise produce a stiffening effect on the fabric, resulting in increased harshness and poor drape. More important here is the reduced abrasion resistance and tear strength. The addition of a lubricative soft finish to the resin treatment bath not only restores the fabric's wear properties but can impart very desirable handle characteristics.

But chemical soft finishes are not restricted to such corrective treatments. In fact, practically all finished textile materials will contain some form of handle modifier. Selected chemical finishes can be used to produce a degree of softness that cannot otherwise be achieved whether by mechanical finishing or fabric construction. It is also possible to further improve the handle and therefore add value to naturally soft fibres like lambswool and cashmere. As a marketing tool, improving the handle of a garment at the 'point of sale' is very powerful – a prospective customer will always assess the overall feel of a garment, often quite subconsciously [8,9]. This can be a vital deciding factor as to whether a sale is made. Careful selection of the type of finish effect is also important. A bulky hand is required for towelling whereas a smoother, crisp, hand may be more appropriate for cotton summer dress wear.

7.2 CHEMICAL SOFT FINISHING

The use of soft finishes is now universal. The cost of such a simple final treatment is low yet the result is a dramatic improvement in perceived fabric quality. This is accompanied by a very practical improvement in fabric processability. With present day high-speed mechanical finishing and sewing operations most types of fabric could not be made into garments without a lubricative finish. Proprietary finishes are formulated from several different chemical constituents to meet the varying requirements of textile manufacture.

Many softener formulations are designed to give point-of-sale appeal to garments in the store and have limited durability. This is an acceptable circumstance when we consider two facts. First, domestic washing loosens up fabric structure so that fabrics get softer as they are subjected to repeated wash cycles. Secondly, softeners are widely used in home laundering either in the detergent formulation or as rinse conditioners. This is a result of a general increase in the level of comfort demanded by the consumer. Softener build-up can be a problem [10] especially from rinse conditioners, so that the low durability of the industrially applied finish is usually unimportant.

The chemical formulations applied as industrial finishes are almost always required to be multifunctional. Proprietary domestic formulations traditionally offer softening as the main function. A domestic product will be advertised as giving a good bulky handle along with antistatic properties and ease of ironing [11]. Often a subtle mixture of perfumes will be present. Industrial formulations offer additional lubricative functions to improve cutting, sewing and brushing operations.

Formulations for use by textile finishers can have different selection criteria depending on the intended method of application and whether the product needs to be compatible with other non-softening finishes. Functional compatibility with showerproofers and anti-soil treatments may be necessary. Durable press finishes use strong acids and high electrolyte concentrations as part of the catalysing requirements. A soft finish must form a stable mixture under these conditions if the pad treatment bath is to have a worthwhile life, usually several hours at least. The use of foam application has found its niche with finishers, putting further demands on the softener formulator to maintain foam quality.

The ionic nature of the product is important for applicational reasons such as compatibility with other finishes, likely effects on dyestuffs and type of handle required. Most important is the fact that cationic products can be applied by the very convenient exhaust method. Products with other polarities are usually pad-applied. The term 'cationic' is derived from the fact that the surfactant head-group is positively charged (+ve) and migrates towards the cathode, which is the negative electrode in an electrolytic cell. The counter-anion – for example, chloride (Cl^-), or methosulphate (CH_2SO_3^-) – represents only 5% of the molecular mass and plays only a minor part in the performance of the product, remaining in solution at all times. Of course, anionic products are anodic by the same reasoning. Therefore the ionic nature of soft finishes can be summarised as shown in Table 7.1.

Table 7.1 Classification of finishes by ionic nature

Product type	Electrical charge	Characteristics
Cationic	Positive (+)	Best softeners
Pseudo ionic	Mostly positive (+/-)	Lubricative finishes
Amphoteric	Varies with pH (+/-)	Surfactant compatible
Non-ionic	Neutral (0)	Best compatibility
Anionic	Negative (-)	Special properties

7.2.1 The mechanism of softening

The exact mechanism by which softeners impart their desirable effects is elusive and continues to receive the attention of researchers. However, recent workers have made good progress in this area [12]. Softeners contain one or two long, hydrophobic chains, usually C₁₈ hydrocarbon. These are attached to a water-soluble polar 'head' group to form an amphiphilic, and therefore surface-active, molecule. Unlike detergents, softeners have very low aqueous solubility and exist as cloudy micellar dispersions. Shortening the hydrophobic alkyl chain results in greater solubility as indicated by higher critical micelle concentration (CMC) [13,14] in Table 7.2.

Table 7.2 The effect of increasing alkyl chain length of alkyltrimethylammonium bromide (CH₃)₃N⁺R Br⁻

Aliphatic chain	Critical micelle concentration (mol l ⁻¹)	Surfactant end-use
-C ₁₀ H ₂₁	0.015	Biocides
-C ₁₄ H ₂₉	0.003	Surfactants and biocides
-C ₁₆ H ₃₃	0.001	Surfactants and biocides
-C ₁₈ H ₃₇	0.0003	Softeners

The CMC is the surfactant or amphiphile concentration in water at which aggregates or 'micelles' begin to form. The onset of micelle formation is easily detected by measuring physical properties such as viscosity, density or electrical conductivity at increasing concentration. Plotting this data reveals the CMC as an abrupt change in the slope of the curve (see Figure 7.1). The formation of micelles is the result of the insoluble nature of the long alkyl chains – the hydrophobic effect [15]. The strong interaction between water molecules squeezes out the hydrophobic chains of the amphiphile to the nearest surface. As the surface becomes saturated, aggregates of surfactant begin to collect within the water away from any surface. This process takes place over a very small increase in concentration, producing a sharp inflection on the curve, defining the CMC. The CMC can also be deduced from solubility–temperature curves,

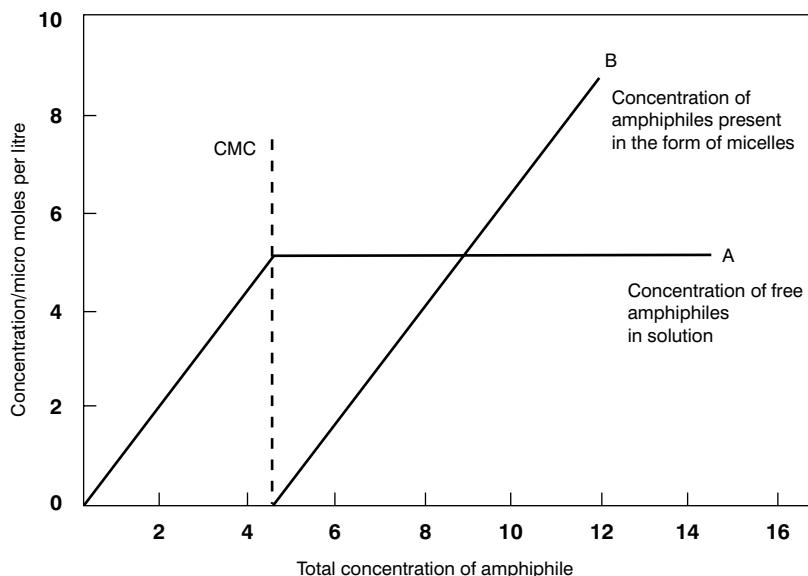


Figure 7.1 Relationship between concentration of free amphiphiles in solution and amphiphiles present as micelles

which show a similar inflexion referred to as the Kraft point. As the total concentration of amphiphile in the system increases, the free monomer reaches a steady value at the CMC and above this point any added monomer will rapidly form micelles. A reversible equilibrium is set up between monomer and aggregate as shown in Figure 7.2.

The structure of the micelles in a softener formulation has an important bearing on the efficacy as a softener. The attraction between the long alkyl chains in a micelle is low so that the hydrocarbon core can be considered as liquid hydrocarbon. Micelles can take several forms – spherical, cylindrical, planar bilayers, and so on. The shape depends on the physical conditions, such as temperature, pH and electrolyte concentration. The shape will alter in response to a change in its environment. The most important factor determining the micellar construction is the geometry of the amphiphile molecule. The molecular volume, the area of the head-group, the hydrocarbon chain length and the counter-anion are the most important

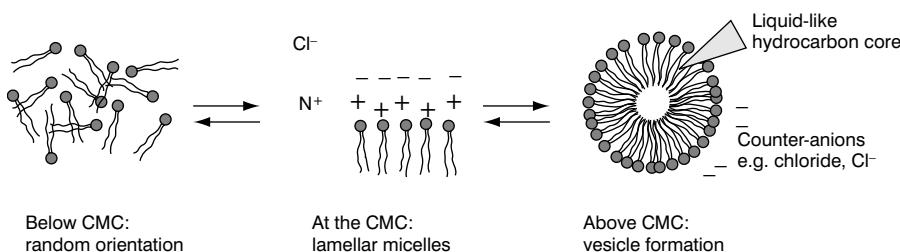


Figure 7.2 Development of micelles in a typical softener dispersion

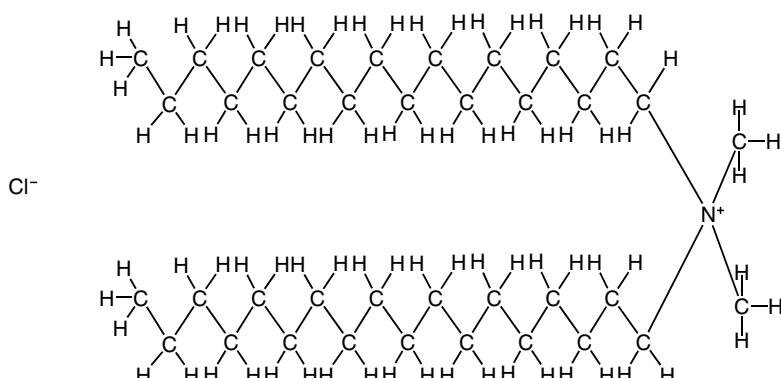
parameters. Softener molecules favour the formation of micelles and multi-walled, lamellar phase vesicles with an onion-like structure (Figure 7.2, 7.4).

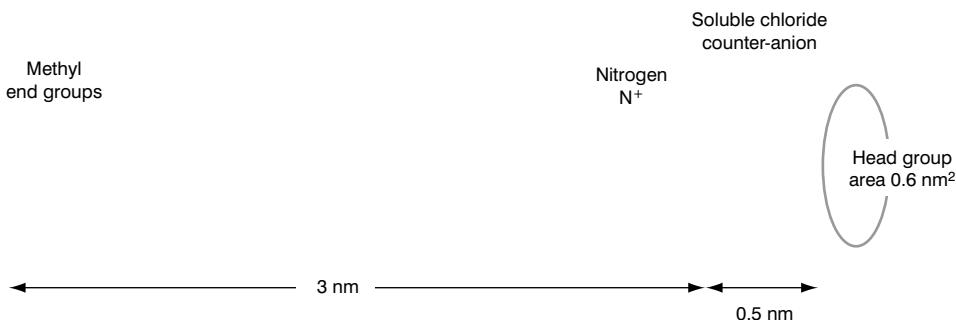
There are many types of chemical species that could be classified as softeners, all with unique properties. In fact, the addition of a C₁₈ alkyl chain to most radicals will induce some softening efficacy. But, as with dyestuffs, only carefully selected molecules reach final acceptance by industry. The fact that a soft finish remains in the finished goods and will in many cases be worn next to the skin means that we need to be especially careful to avoid physiological effects. Cationic compounds are widely used as biocides in mouth washes, cleaners, disinfectants, dressings and preservatives. The cationic biocides are very potent and have hydrophobic chains in the range C₈ to C₁₆. They will adsorb onto surfaces but produce little or no softening effect. Most cationics have no effect on animals but reactions can vary from mild sensitising to poisons with strong curarising effects. These effects diminish rapidly at the high molecular mass needed for effective softening and any residual biocidal effect can be advantageous. A very small sector of the population displays specific reactions to cationic softeners but numbers are tiny. Softening finishes are nonetheless used extensively on medical goods such as cotton wool and bandages, and also on food packaging and in hair care products.

Of all the compounds used as softeners the most effective is the highly favoured distearyl dimethyl ammonium chloride, often referred to as DSDMAC. As a commercial raw material it is widely available as the less pure di-hydrogenated tallow dimethyl ammonium chloride (DHTDMAC) in the form of a 75% slurry containing isopropanol or propylene glycol (Structure 7.1 and Figure 7.3).

As a consequence of its popularity over several decades, the behaviour of this molecule is well known, following numerous studies by pure and applicational researchers. In aqueous formulations, DSDMAC molecules form back-to-back bilayers with their hydrophobic chains in contact with each other and the polar head-groups in contact with the water. These bilayers eventually fold into multi-walled vesicles between 1 and 10 µm in diameter. The vesicles

Structure of DSDMAC



**Figure 7.3** Dimensions of the DSDMAC molecule**Figure 7.4** Structure of a liposome showing bilayers and entrapped water

formed by this material can be engineered, by the addition of formulating aids, to contain reduced amounts of water. This reduces their size and hence the viscosity of the dispersion. The DSDMAC compound has a very low solubility, CMC 4.6×10^{-6} mol l⁻¹. The co-anions are largely dissociated from head-groups but remain close to the outer surface of the vesicle. The large multi-layered colloidal particles or 'liposomes' have a high water content of over 90%. In practice, several sizes of colloidal particle are produced depending on shear and other manufacturing conditions. The structure of a DSDMAC liposome is shown in Figure 7.4.

As a cationic softener dispersion is diluted to proprietary product concentration, and finally to working strength in a treatment bath, several phases will spontaneously form. Formulation specialists find phase diagrams very useful for predicting performance of their products [16]. A typical phase diagram for the DSDMAC material is shown in Figure 7.5.

At very low temperatures the amphiphile is crystalline and the water is in the form of ice, 'Lα'. At room temperature the amphiphile is still crystalline with a liquid water phase, 'Lβ'. Increasing the temperature above 42 °C results in a liquid hydrocarbon phase, 'Lα'. Simple, but highly engineered, dispersions of quaternary compounds like DSDMAC are common in domestic usage where maximised perceived softness is the main aim. Such products are

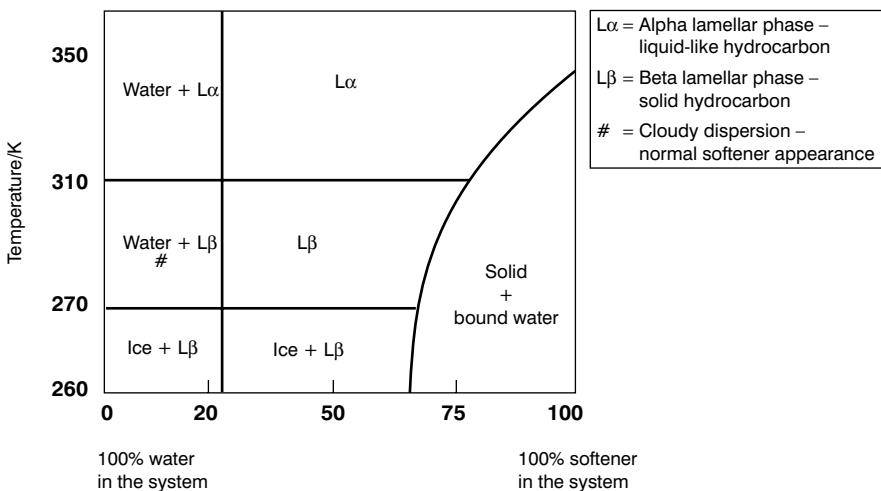


Figure 7.5 Idealised phase diagram of DSDMAC–water system

primarily 'L β ' in structure. The phase structure is far more complex when lubricants and other functional materials are present, as is the case with most industrial products.

The most basic model for softener action involves discrete cationic molecules depositing on the fabric. All fibres develop a small negative potential (–ve) in water, referred to as the zeta potential, at the fibre surface. The cationic charge on the softener molecules or aggregates results in concentration at the fibre surface [17]. The hydrocarbon chains of the softener protrude outward from the surface to give the lubricating effect perceived as softness [18–20]. Undoubtedly single molecules deposit onto the surface but in the main whole aggregates or fragments deposit, forming one or more layers. It is evident that a certain amount of unfolding of the liposomes takes place on drying of the treated fabric to form the favoured layered deposition. The 'integrity' or lateral strength of the softener layers has been shown to be most important for effective softeners and corresponds to the 'L β ' structure in Figure 7.5. To achieve the required integrity, the alkyl chains must be C₁₈. At this length there is sufficiently strong side-to-side attraction to effect crystallisation. Low inter-layer cohesion is also an important requirement so that sliding is possible. Attempts to link softening to a plasticising of the fibre by internal modification suggest that this is, at best, a minor mechanism. But it should be noted that there are obviously several mechanisms in operation. The picture is even less clear when we consider that many non-polar chemicals can be used as softeners. Paraffin waxes, polyethylenes, esters, certain clays and silicones are important examples. These finishes deposit on the surface as multiple layers and function as hydrodynamic or boundary lubricants [21–25].

7.3 CATIONIC SOFTENERS

Cationic softeners reign supreme in the domestic and industrial softener market [22–24]. Home and laundry usage of cationics is mainly in rinse conditioners. Industrial products are also largely

cationic although they tend to incorporate a wider range of supporting chemicals in multifunctional formulations.

There are several reasons for the importance of cationics.

- (1) They are the most effective softening materials known, imparting the greatest degree of softening for a given weight; levels of 0.2% actives on the fibre can give a full soft hand.
- (2) They are substantive to all fibres including glass and particularly cotton, facilitating simple exhaust application from rinse baths.
- (3) The manufacturing technology is well established and prices are at a minimum as a result of the economies of scale and competition.
- (4) They provide a highly characteristic handle, which is well-liked – bulky but not too greasy.
- (5) They impart good antistatic and lubricative properties to fibres.
- (6) Many variants are possible by altering the molecular structure or by formulation.

A large number of cationic molecules have been developed, some of which offer specific useful attributes as softeners such as hydrophilicity, often at the expense of softening efficacy [26–29]. So the properties listed above do not apply to all cationics per se. The substantivity of cationics is certainly a most important attribute. By this mechanism a textile substrate placed in a dilute solution of the softener will slowly become coated with it in a manner similar to dyeing except that there is practically no diffusion into the fibre and levelness is relatively poor. The solution thus becomes exhausted as the finish builds up on the textile surface.

7.3.1 Exhaust application of cationic softeners

Exhaust application of soft finishes is very popular and usually takes place in the final rinse bath after dyeing or bleaching. Substrates can be treated in any convenient form – for example, fibre, yarn, fabrics and garments. All types of machinery can be used including winch, jet, beam, package and cage [30,31].

The rate of exhaustion of cationic softeners increases with temperature in most cases, but other factors need to be considered. Certain formulations, particularly lubricative wax-containing products, can become unstable at higher temperatures. However, most fabrics ‘run’ better in dyeing machines, particularly winches and jets, if the temperature is raised to 40–50 °C. The rate and evenness of softener exhaustion is greatly enhanced by good agitation, to achieve a continuous supply of softener to the fabric surface.

The pH of the application bath is important when applying cationics, especially the amino and amphoteric types, which are more strongly cationic in acid media. Such formulations are ideally applied at pH 5–6. More acidic conditions, especially below pH 4 can result in yellowing due to interaction with anionic fluorescent brighteners where these are present on the fabric. Quaternary softeners are more tolerant to pH, giving good exhaustion from pH 4 or less, up to mild alkaline conditions of pH 8–9. This tolerance is useful for bleached cotton treatment where alkali carryover is difficult to avoid as it is chemically associated with the cellulose. The use of a pH buffer can help to reduce this problem.

Flocculation is usually caused by water hardness, organic matter in the water (such as humic acid), or breakdown of a compounded finish by excessive shear or by live steam injection. In all cases there is a risk of an insoluble scum gathering on the surface of the bath. If this is deposited on the fabric it will cause staining. Such stains can be fixed by stentering and may be impossible to remove by normal scouring systems. Selection of the correct formulation for the conditions is therefore important [32–35]. It is common practice to apply cationic dye fixing agents in the same exhaust bath as cationic softeners. In this case, a five-minute pretreatment with the fixer alone is advisable before the softener is added. Typical application conditions for a jersey knit cotton fabric in a winch or jet are shown in Table 7.3.

Table 7.3 Exhaust application conditions for cationic finishes

Temperature	40 °C
Time	20 min
Liquor ratio	15:1
Bath pH	6.0
Finish level	2%

Most proprietary finish formulations should be pre-diluted with water immediately prior to addition to the rinse bath in order to reduce the viscosity and increase the rate of dispersion in the liquor. Undiluted or even diluted softener formulations should never be poured directly onto the fabric but should be added to a side tank or into the treatment liquor remote from the fabric. Pre-heating the bath to the application temperature before softener addition may reduce emulsion breakdown and scumming. A little foam generation is usually of no consequence but excessive foam can be a problem and a non-ionic antifoam or selection of a lower foam product may be necessary.

In after-rinse application, up to 100% exhaustion of the finish is possible under ideal conditions. More often, a much lower efficiency can be tolerated, 60% adsorption being quite acceptable. In some cases – for example, in garment laundering where softening only is required – a finisher will accept less than 50% exhaustion. A shorter time of perhaps 10 min is given, trading efficiency for increased production. This is practical when we take into account the rapidly diminishing returns in terms of softness achieved for application levels above about 0.25% chemical applied. Very dramatic effect on handle can be achieved with low levels, about 0.1%, of cationic softener actives. Where a lubricative finish is required for sewing or mechanical finishing, 3–5% of product is required and decreasing the level applied can be a dangerous practice. In this case, it is important to ensure maximum exhaustion as more than a boundary layer is required. Good fibre-to-metal lubrication and needle cooling, for example, require levels that ensure hydrodynamic lubrication.

Poor exhaustion can mean delivery of cationic substances to the effluent where they can disrupt biological treatment of sewage. Discharge of unabsorbed cationic to rivers is unacceptable due to their fish toxicity.

Cationic finishes can be applied at the same time as the dyestuffs in certain cases. Cationic softeners have the same polarity as basic (cationic) dyestuffs and will therefore not form insoluble complexes as with acid dyes. Acrylic fibres are therefore frequently dyed and softened in the same bath. Basic dye-retarding agents are almost always cationic and are therefore compatible with the softener. The particle size and shear stability of cationic emulsions is of particular importance when they are to be applied in package machines. Certain yarn packages – for example, continuous filament polyester and acrylic – are wound very tightly and filtration of the softener is a real danger. The shear on the circulating liquor is very high within the package and the softener formulation must be designed to withstand this. Simple filtration on the inside or outside of the package is usually visible. But uneven application throughout the package due to excessively rapid exhaustion is less visible and can lead to uneven friction coefficient and knitting problems. Fabric beam machines can pose similar problems. Microfibre yarn and fabric can also filter out large particles. In this case, a fine emulsion, less than 1 µm, will give better penetration into the yarn.

7.3.2 Pad application of cationics

The application of cationics by padding can be very efficient but care is required. Selected cationics can be applied by any of the methods that collectively come under this heading, including spray, lick-roller, minimum application (MA) techniques, foam and pad trough. The most important difference from other finishes is the tendency for cationics to exhaust from the pad liquor onto the fabric. The fabric therefore receives the desired quantity of finish due to liquor expression plus an extra quantity of finish resulting from exhaustion. This results in an accelerated decrease in pad bath concentration often referred to as 'tailing'. The effect can be decreased by selecting a more weakly cationic softener and by use of a suitable liquor feed system. A low capacity pad trough supplied from a holding tank containing the softener dispersion will not reduce the tendency to exhaust but will give a constant application level throughout the piece. Cationic finishes, especially those types that contain waxes for lubrication, will invariably coat the pad rollers and render them hydrophobic. This is usually not important and long runs are possible before cleaning.

7.3.3 Softeners for aftercare treatments

Unlike the very wide range of finishing chemicals used in industry, aftercare finishes are more limited in scope.

Most finishes used for fabric aftercare are applied in the rinse after aqueous machine washing. Proprietary products are described as rinse conditioners or softeners. Formulations are usually based on one of a limited number of cationic structures as the main active component, with low levels of several cosmetic adjuncts. On a world-wide basis, the DSDMAC compound is almost universal but imidazolines are also significant. In Europe, biodegradable esterquats have largely replaced DSDMAC [36–39]. The consistency, odour and colour of domestic rinse

conditioners have special importance for marketing reasons. Such properties are carefully controlled to cater for consumer preferences. More functional additives include silicones, soil-release agents, preservatives, optical brighteners, opacifiers, anti-shrink and pearlising agents [40,41].

Many domestic washing detergents now contain softening elements. The quantity deposited on the fabric is small and, although not as effective as rinse application, worthwhile handle improvements are achieved. Compared to industrial exhaust application conditions the domestic rinse is restrictive in time and temperature (Table 7.4).

Table 7.4 Domestic rinse application conditions

Time	5 min
Temperature	Ambient (20 °C)
pH	6
Level on fabric	0.25% (actives)
Bath concentration	0.1 g l ⁻¹
Liquor ratio	25:1

The short time and low temperature puts heavy demands on the formulation especially when high exhaustion levels in excess of 80% are expected in order to achieve the required high levels of softness. Carryover of anionic materials and alkali from the wash cycle can interfere with the efficiency. Commercial products contain about 5% actives for standard materials and 10–15% in concentrates [42,43].

Tumble-dryer application of domestic softeners represents what is in effect a form of pad application [44,100]. The excellent handle achieved by exhaustive application of cationics is in part due to orientation of the softener molecules on the fibre surface. However, excellent softening effects can be achieved by applying cationics in tumble-dryers from impregnated strips of paper or textile. The crumpled strip of substrate material is discarded when it is used up. For this application, the same type of cationic materials found in liquid conditioners can be used. But special low-melting-point compounds have been proposed [44,45] and carrier sheets composed of a solid gel are possible, which leave no residue whatsoever.

Novel methods of applying soft finishes have resulted in special formulating techniques. Foam applicable softeners are available for use in domestic tumble-dryers. Such proprietary preparations contain high levels of cosolvents such as isopropanol, a propellant, a blowing agent such as dichloromethane and perfumes. The softener is usually the DSDMAC compound.

Commercial laundry softeners are optimised for performance and ease of delivery, often in automatic liquid dosing systems. Aesthetic additives such as colour and perfume are less common. Softening efficacy can be lower than domestic products and extra performance additives for easy-iron, for example, are not usually required. The addition of a long-chain alkyl softener alone will impart several positive effects to a fabric other than softness. Treated fabrics will have better drape and handling properties and some degree of antistatic protection.

Softeners and other finishes can be applied in dry-cleaning machines. The most common

solvent system is perchloroethylene but hydrocarbon systems are being introduced for environmental reasons. Some exhaustion can take place from the non-aqueous solvent system but a dip or spray system is most common.

In solvent systems, the micelle structure will be reversed so that the exhaust mechanism is different. A small, strictly controlled water addition is sometimes made for improving finishing and scouring effects. Finishes include waterproofing, oil-repellents, mothproofing, re-texturing and softening. It is most important to control the amount of water in a dry-cleaning machine as even small quantities can damage certain garments which are designed for dry-cleaning only. Finish formulations tend to be of high concentration or are solvent based.

In the dip process, a calculated quantity of finish is added to the machine and the load is tumbled for a short time to achieve even distribution. The amount of exhaustion from the solvent is negligible. The load is then extracted to leave a small quantity of softener solution of known concentration. As the solvent evaporates, the softener remains on the fabric.

The spray process involves spraying the load after extraction with a solution of finish of known concentration. The spray technique requires a little more drying time but there is less danger of cross-contamination as fresh solvent is added each time. Since both these methods of application are essentially padding processes there is more diversity in the chemical type used and non-ionics are popular.

7.4 CHEMISTRY OF CATIONIC SOFTENERS

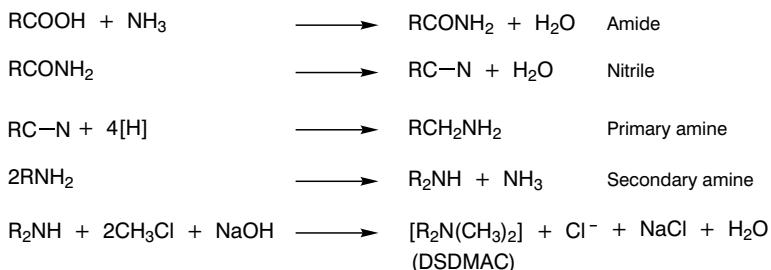
Several types of compounds meet the criteria for use as general purpose cationic finishes. Distearyl dimethyl ammonium chloride (DSDMAC) and distearyl amido imidazolinium chloride, and the alkyl sulphate versions, along with minor variants, make up the bulk of domestic softener usage and are important in industrial and laundry applications. For industrial use we can add a large array of amido amines. In all cases, fully hydrogenated tallow is most frequently the source of the octadecyl (C_{18}) alkyl chains. The DSDMAC compound has been widely investigated and represents a useful predictive model for the behaviour of other types of cationic. The physical and chemical properties of the DSDMAC compound have been described in some detail and the reader should consider this as a general model for all cationic softeners.

7.4.1 Dioctadecyl dimethyl ammonium chloride

As a commercial raw material, dioctadecyl dimethyl ammonium chloride is widely available as the less pure distearyl dimethyl ammonium chloride (DSDMAC) in the form of a 75% slurry containing isopropanol or propylene glycol. It is prepared from hydrogenated tallow (hardened) fatty acids (DHTDMAC) by the multi-stage process shown in Scheme 7.1.

First the di-tallow amine (R_2NH) is prepared by amidation, cyanoalkyl preparation, reduction and deamination. Finally the DSDMAC is prepared by exhaustive methylation with methyl chloride in isopropanol (propan-2-ol).

Preparation of DSDMAC compound

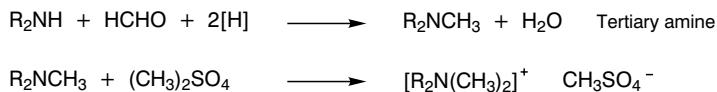
**Scheme 7.1**

The methyl sulphate (DSDMAMS) compound is also important commercially and is prepared by a slightly different route (Scheme 7.2).

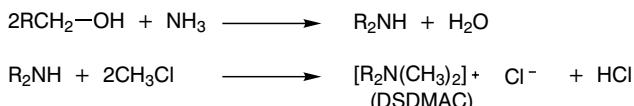
The secondary amine is converted to a tertiary amine by reductive methylation, and quaternisation is with dimethyl sulphate. The compound can also be prepared from a fatty alcohol by methylation and quaternisation with methyl chloride or benzyl chloride (Scheme 7.3).

The commercial grade DSDMAC is easily converted to a softener at a working strength of 4% or 8%. The 75% isopropanol slurry is melted at 80 °C and stirred into hot water at up to 80 °C, when it disperses with the aid of good mixing to form the characteristic viscous emulsion. The viscosity of many proprietary products is controlled by careful addition of common salt (sodium chloride). However, more sophisticated methods of achieving the required product consistency are available – for example, the use of deflocculating polymers in the external phase, controlling the inter-micelle layer water content, and interference with the micelle structure by addition of small amounts of unsaturation into the long-chain alkyl groups. A small

Preparation of methyl sulphate compound (DSDMAMS)

**Scheme 7.2**

Preparation of DSDMAC from fatty alcohol

**Scheme 7.3**

amount of unsaturation in a portion of the stearyl chain will result in a structure that cannot crystallise with its neighbours, breaking down the micelle structure at this point.

Although the DSDMAC compound is very effective, it does have limitations. The compound imparts a strong hydrophobic effect – for example, making towels ineffective – and is very sensitive to electrolytes and hardness in water. It is slow to biodegrade and is therefore the subject of recent legislation for environmental reasons. For such reasons, it is now less favoured, although it is widely used at low levels in multifunctional formulations by industrial users.

7.4.2 Amido amine compounds

Amido amines of various types represent an important group of compounds used in the textile industry as the basis for fabric finishes. These compounds are frequently found in multifunctional finishes designed to facilitate making-up operations, such as sewing and cutting, and where good fabric handling is essential for efficient production. They are easily prepared and have excellent compatibility with other formulation adjuncts such as waxes, fatty esters and polyethylenes. A large variety of cationic finishes of this type are possible by selection of original fatty acids, the degree of saturation and the degree of amidation.

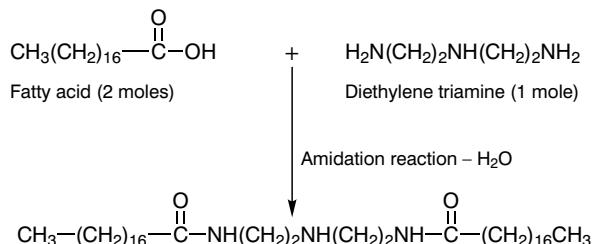
The starting point for many amino amides is often one of the ethylenic polyamines containing up to five nitrogen atoms. The alkanolamines may also be included in this group. Stearic acid condensation products of alkanolamines form the basis of a large number of proprietary products (Table 7.5).

Table 7.5 Amine starting materials for softer manufacture

Starting material	Amine structure
Ethylene diamine	$\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2$
Diethylene triamine	$\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2$
Triethylene tetramine	$\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2$
Tetraethylene pentamine	$\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2$
Amino ethyl ethanolamine	$\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{OH}$
Diethanol amine	$\text{HO}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{OH}$

Having selected an amine, the amidation can be carried out in several ways. The reaction requires vigorous conditions often involving temperatures approaching 200 °C and it is essential to exclude all traces of oxygen. The water of reaction must be removed (Scheme 7.4) and a suitable catalyst is required, such as sodium methoxide, to improve the reaction rate. The fatty acid source, particularly for alkanolamides, can be provided in the form of a triglyceride such as hydrogenated tallow or vegetable oils. The degree of hydrogenation and the fatty acid distribution gives the manufacturer a useful means of controlling the properties of the final product. The triglyceride reaction obviates the need to remove the water of reaction and the residual glycerol and diglycerides can have beneficial properties in the final formulation.

Production of a typical amido amine product

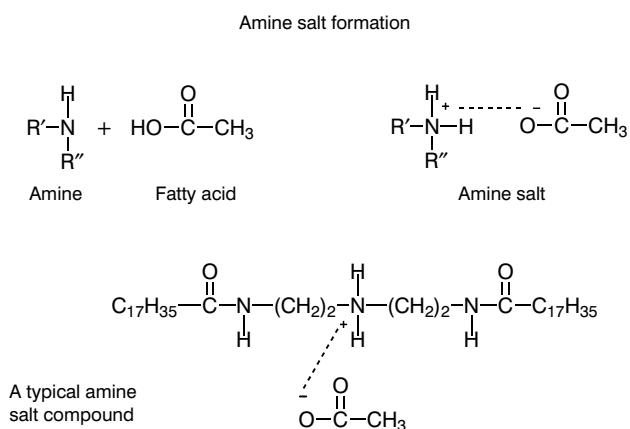


Scheme 7.4

Fatty acids shorter than C₁₈ (stearic acid) can result in a rapid decrease in the softening effect. Similarly, unsaturation – for example, mono-unsaturated C₁₈ (oleic acid) – results in decreased softening and changes in the type of handle achieved. Unsaturation results in lower melting point compounds, which are easier to formulate but thermal stability is diminished. Longer chain acids, particularly C₂₂ (behenic acid), give a noticeable improvement in handle but are more difficult to formulate due to their higher melting points. The longer-chain compounds are more expensive, and so tend to be used for special effects or for their much improved durability.

The excellent stability of this structure is reflected in the resistance to thermal yellowing of products of this type, and their widespread use on textiles treated with fluorescent brightening agents. The fully amidated versions (triamide) are difficult to formulate due to their lower solubility and higher melting points. The cationic strength is often too low to effect good exhaustion from aqueous treatment baths.

Leaving one amine group unreacted results in a strong cationic. In this case, the amine will be converted to a salt, usually the acetate (Scheme 7.5). To maintain this protonated form the product is formulated and used under acidic conditions in the range pH 4–7. It is usually



Scheme 7.5

possible to control the amine value to achieve negligible yellowing yet still have sufficient cationic strength to promote good exhaustion from the treatment bath. An increased cationic strength also results in better softening efficiency.

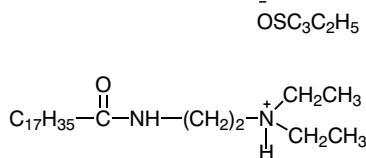
Selection of the fatty acid co-anion needs consideration. At first sight the mineral acids, such as hydrochloric, may seem attractive but the chloride salts are a little less stable than the fatty acid salts. Dibasic acids like sulphuric and polybasic phosphoric acids tend to produce amine salts of poor solubility because they can link two softener molecules to make an insoluble mass. The polybasic organic acids – citric and maleic, citramalic, malonic, and so on – have similar effects on solubility. Similarly, high-molecular-weight acids such as stearic acid tend to form insoluble salts. Low levels of stearic acid can be added, in practice, as a means of reducing formulation costs and it gives certain softening advantages – for example, when applied to wool. The free long-chain fatty acid has a strong substantivity for the proteinaceous wool substrate and therefore enhances the softening effect. The traditional method of scouring wool with fatty acid soaps improved the softness for the same reason. The lower polarity of the product gives a marginal improvement in the colour fastness of acid dyes on wool compared with strong cationics.

The most common acid in commercial use is acetic acid. It produces acetate salts of excellent solubility at low cost. Formic acid is similar to acetic acid and is also in common use. However, both acids are volatile and a large excess over the stoichiometric requirements can result in objectionable acidic odours [46]. For low-odour products, the more costly lactic and hydroxyacetic acids have been proposed [47].

Amido amines with free primary amine groups can be converted to much higher molecular weight compounds by further reaction with urea to form carbamides. Unfortunately, ammonia is evolved in the reaction, which must be performed at moderately high temperatures. The resulting weakly cationic materials have poor solubility and are difficult to formulate. However, they impart a less greasy handle and have higher thermal stability, which results in a lower tendency to yellow during drying and stentering.

Alkylation of amido amines leads to another important class of derivatives in the form of quaternary ammonium salts. These have improved softening efficiency, probably due to the higher polarity of the hydrophilic head-group, resulting in orientation on the substrate fibre more closely resembling the basic DSDMAC molecule. They have much better tolerance to high pH conditions than the amine salts and can be successfully applied over a very wide pH range from pH 4 or less to pH 8 or higher. This is useful for bleached cottons where alkali carryover from peroxide bleaching is inevitable. In this case, the alkali is chemically bound inside the cotton fibre and slowly leaches into the water at the fibre surface, upsetting the zeta potential. Complete rinsing out of the alkali is difficult. The use of a pH buffer in these circumstances only marginally improves matters. The finish must overcome a chemical concentration amounting to a pH gradient at the fibre surface. Near the fibre surface the pH may be much higher than the measured bath pH. A strong quaternary head-group will survive such conditions, unlike the amine salts, which will become non-ionic. Alkylation with diethyl sulphate gives the common ethosulphate salt (Structure 7.2). The chloride compound using methyl chloride is also useful.

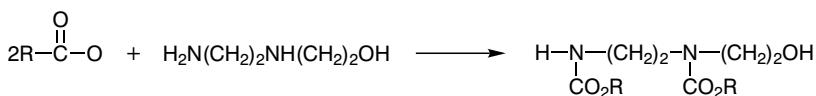
Quaternised amido amine ethosulphate compound



7.2

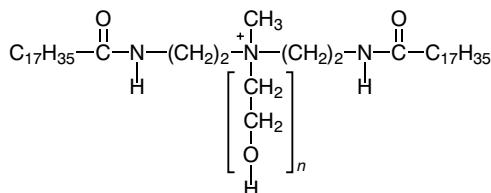
Alkanolamide derivatives of various kinds are found in industrial usage (Scheme 7.6). The hydrophilic hydroxy group improves solubility and makes formulation easier. The softening power for a given weight applied is somewhat decreased compared with dialkyl aminoamide derivatives but this is offset by the improved hydrophilicity of finished goods. The amides of alkanolamines are relatively easy to make and tend to give lighter coloured products. The cationic strength can be decreased to a degree where exhaustion is negligible, so that this type of finish is frequently designed for pad application. Higher-molecular-weight alkanolamides containing an amine salt or quaternary nitrogen can of course be applied by exhaustion [48].

A useful alkanolamide compound

**Scheme 7.6**

The diamide compound of diethylenetriamine can be ethoxylated with about five moles of ethylene oxide to give a very easily diluted base material for softener formulation (Structure 7.3). The alkoxylation of the central nitrogen facilitates quaternisation with diethyl sulphate. Such compounds have a useful degree of hydrophilicity and make excellent antistats, not just because of their ionicity but because of the tendency of the ethoxylate chain to hold associated water molecules. The softening efficiency drops off rapidly above five moles of ethylene oxide [49].

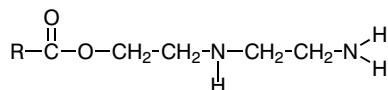
Ethoxylated amino amide



7.3

The amino esters comprise another interesting range of compounds, particularly in their salt form. Here, one or more long-chain alkyl groups are attached through ester groups (Structure 7.4). Such compounds are easily formulated to give stable emulsions and impart a characteristic handle with good lubrication. Hydrolysis of the ester group can be a problem, which can be alleviated to some extent by careful selection of the pH of the formulation. The quaternaries of these esters are also easily hydrolysed. Derivatives of monoethanolamine and diethanolamine are used but triethanolamine allows more variation by selection of the degree of esterification giving mono-, di- or tri-esters. The good availability of raw materials and ease of manufacture has assured this class of compound a sustained existence in the product range of many formulators.

Amino ester compounds

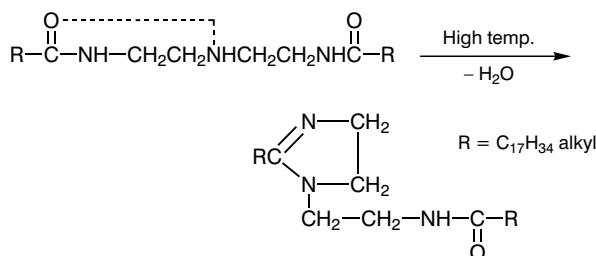


7.4

7.4.3 Imidazoline compounds

This is the second most important class of softener compounds, of which the stearyl amido ethyl imidazolinium methosulphate is highly favoured. Imidazolines are in essence derived from amido amines by ring closure under high temperature conditions with loss of water (Scheme 7.7). Some degree of hydrolysis back to the non-cyclic aminoamide is possible in aqueous solution. But this does not affect the performance of proprietary preparations [50].

Imidazoline production



Scheme 7.7

Further reaction of the imidazoline with dimethyl sulphate easily produces the quaternary imidazolinium compound, which is by far the most widely used (Scheme 7.8). This is a strongly cationic molecule giving a degree of softening comparable to the DSDMAC compound. As a commodity, it is most often supplied as a 75% active slurry in propylene glycol or isopropanol. A degree of unsaturation is often introduced into a portion of the long-chain alkyl groups, resulting

Imidazolinium formation

**Scheme 7.8**

in a more fluid raw material that is easier to formulate, particularly when higher working concentrations are required.

The unsaturated compound produces a different type of handle often described as more fatty or greasy. Imidazolines have lower melting points and this, coupled with a high level of cosolvent, can make cold water dispersible concentrates possible. Imidazolines are more easily degraded in effluents and are less irritant to skin and eyes than the DSDMAC product. They also have a lower tendency to make fabrics strongly hydrophobic and tend not to build up over several domestic washes.

Conventional domestic fabric softeners contain 5–8% of active softener. Non-hydrogenated (oleyl) or partly hydrogenated isopropanol containing slurries (75% solids) can be simply mixed at room temperature. The fully hardened compound should be mixed at about 60 °C. A typical formulation for domestic or industrial use is given in Table 7.6.

Table 7.6 A basic softener formulation for domestic or laundry use

	Proportion (%)
Water	89.8
Imidazolinium methosulphate (75%)	10.0
Perfume	0.1
Colour (basic dye 1% solution)	0.1
	<hr/>
	100.0

This simple formulation can be modified in several ways – for example, by the addition of lubricants to assist ironing, biocides, encapsulated perfumes and other desirable cosmetic additives [50]. The consistency and viscosity requires careful control as with DSDMAC formulations. Higher concentrations can be achieved by the incorporation of various additives such as special polymers to the external phase of the dispersion. Such formulations have uses in light industrial applications – however, most non-domestic products are made to a higher concentration in the region of 10–30% [51–57].

7.4.4 Miscellaneous cationic compounds.

The very desirable characteristic of exhaustibility of cationics has led to a variety of quaternary

compounds that approach the softening efficiency of DSDMAC but do not carry the disadvantages.

Properties that could be improved are:

- (1) lower tendency to cause waterproofing, especially for towelling applications;
- (2) reduction of the deleterious effects on optical brighteners and dyestuffs, such as change of shade, reduced fastness and yellowing;
- (3) reduced toxicity to biological effluent systems and reduced fish and aquatic toxicity;
- (4) reduced tendency to cause skin reactions in certain individuals;
- (5) enhanced thermal stability to severe drying conditions.

Most of these requirements have been overcome to a degree by expert formulating techniques. However, the ideal solution lies in the development of compounds that are intrinsically hydrophilic, non-toxic, biodegradable, and so on. This has not yet been achieved but interesting compounds have evolved, particularly biodegradable esterquats.

By far the greatest research effort has gone into the production of environmentally friendly cationics for the domestic market [58–62]. Unlike scouring and dyeing auxiliaries, finishing treatments remain on the fabric. The amount of product escaping into the effluent from a textile processor is therefore usually small and represents an inefficiency in the system. Industrial finishes are mostly non-cationic and often contain a large portion of degradable waxes. However, many finishes are intended for point-of-sale effect and have limited durability on the fabric. This means that some finish will end up in domestic discharges where it will represent a small fraction of the total loading. On the other hand, soft finishes applied as domestic after-rinse conditioners can reach significant levels. A typical cationic will be applied in the rinse to give 90% exhaustion and will remain on the goods until the next wash when it will be removed, mostly as an anionic complex with part of the detergent system.

The toxicity of cationics arises mostly from their tendency to adsorb on the cell membranes of micro-organisms and the gills of fish, with lethal consequences. It can be shown that given time a biomass will eventually breakdown the DSDMAC compound. But in normal systems the central quaternary is very persistent and toxic to the biomass even if it is present as an anionic complex. The most common solution is to use an 'esterquat' consisting of a quaternary compound in which requisite long-chain alkyl groups are bonded by ester linkage to the cationic foot of the molecule. The ester groups are readily hydrolysed to produce a less substantive low-molecular-weight fragment, which is accessible to the bacteria as a nitrogen source and therefore easily mineralised.

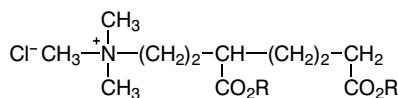
Several esterquat variants are possible depending on the position of the ester linkages. Structures 7.5 to 7.8 represent the kinds of structures under investigation and appearing in patents.

Another variant is prepared from aspartic acid giving excellent biodegradability and a full softening effect (Structure 7.6). The quaternary version is preferred for effectiveness.

A similar symmetrical structure is shown in Structure 7.7. The hydroxyethyl group improves hydrophilicity and ease of formulation.

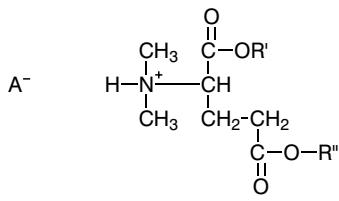
Biodegradable cationic based on aspartic acid

A typical biodegradable esterquat



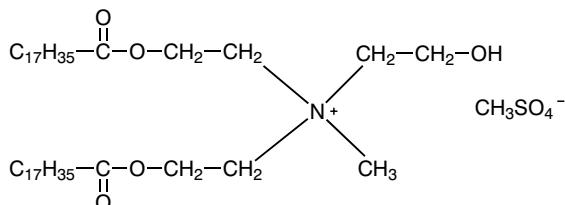
7.5

R = stearyl



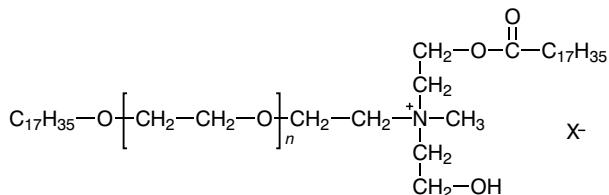
7.6

A commercial degradable esterquat



77

An etheramine ester hydrophilic compound



7.8

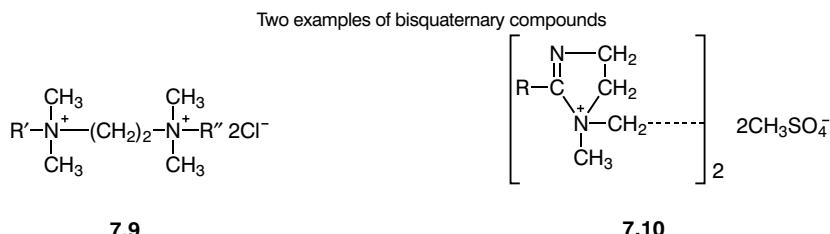
Etheramine ester compounds, based on one ester and one ether linkage, impart hydrophilicity and good biodegradability (Structure 7.8). The synthesis is complex and therefore costly.

This framework allows for considerable variation. Alkoxylated alcohol precursors up to 10 EO units can be employed to give increasing solubility and hydrophilicity but with decreasing softening efficacy.

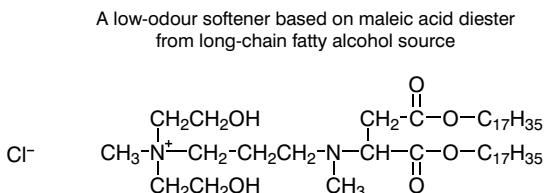
Another approach to producing environmentally friendly formulations is to combine an esterquat with a non-ionic softener such as ethylene glycol distearate and long-chain fatty acids. Such fatty insoluble materials become intimately mixed with the cationic and deposit on the fabric surface to give enhanced softening with a decreased portion of quaternary in the formulation. Non-quaternary compounds, such as fatty amines including imidazolines, are more easily degradable and can be used as useful finishes if acid pH is maintained and the amine value is minimised in order to offset undesirable skin reactions.

Several types of bis quaternary compounds are found in the literature (Structures 7.9 and

7.10). These have limited use in special industrial or domestic applications as softeners. The shorter chain compounds are used as emulsifiers and dyeing auxiliaries. The increased positive charge results in more rapid exhaustion and somewhat easier formulation. Both the dimethyl ammonium and imidazolinium compounds are used.



Cationic softeners, and indeed any finish that remains on the fabric surface, have the potential to develop objectionable odours in storage. This can result from tallow, which is the source of the bulk of the fatty matter in a finish, particularly if a degree of unsaturation remains. Rancidity can occur in a finish before it is applied to the fabric. Rancidity in emulsions is more likely with non-cationic or weakly cationic formulations because the strong cationics have a degree of biocidal action. It is highly advisable to incorporate one or more carefully selected biocides in any formulation. Bad odours can develop on treated fabrics even in dry storage conditions. Air oxidation can also produce bad smells particularly where unsaturated compounds are present. A number of intrinsically low-odour compounds have been proposed based on maleic, fumaric, citraconic and mesaconic acid diesters of long-chain fatty alcohols (Structure 7.11). Methods have been found to incorporate perfumes and masking agents into formulations – for example, by coacervation methods. Controlled release of perfumes of different volatility from microcapsules has also been investigated.



Non-nitrogen cationic softeners should be possible but research on them is limited [22]. The required -onium structure can be formed with phosphorous, sulphur, arsenic, selenium, tellurium, antimony and bismuth in aqueous media. But such cationics are expensive, more complex to produce and are often highly toxic or have potentially bad odours. Sulphonium, phosphonium and sulphonoxonium surfactants are the most likely to be of use as finishes.

7.4.5 Pseudo cationic wax emulsions

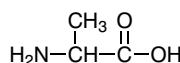
Formulations that contain lubricants other than the base cationic softener are sometimes referred to as ‘pseudo ionic’. In essence, the fatty lubricant takes on the characteristics of a cationic emulsion. The emulsification is prepared above the melting point of the lubricative wax. The cationic softener, along with a small quantity of cationic dispersant, provides the required surfactancy for emulsification. Cationic polar head-groups cover the outside of each particle so that they become substantive to fibres, as would a fully cationic material. Quite low levels of cationic emulsifier are effective in producing strongly exhausting wax emulsions. This is useful where softening is not too important and lubrication is the main requirement. Typical applications are sewing thread dressings, knitting and winding lubricants, where excellent fibre-to-metal lubrication demands quantitative delivery of a paraffin wax fatty ester mixture [63–65].

7.5 AMPHOTERIC SOFT FINISHES

Amphoteric soft finishes have a limited, but significant, use in textile applications. By far the most important area of application of amphoteric chemicals is in personal care products where their low toxicity, coupled with their isotonic properties, makes them ideal for shampoo formulations. The longer-chain components adsorb onto hair, which in essence is a protein fibre, imparting softness and other useful properties. For general textile use, amphotericics offer good compatibility with a number of pad bath adjuncts such as easy-care finishes, flame-retardants and hydrophilic finishes. Foam generators, typically based on alkanolamides are particularly effective for application of amphoteric softeners, which enhance the foam quality.

Amphotericics are surfactants that contain potentially anionic (carboxyl) and cationic (amine) groups within the same molecule. They are exemplified by the amino acids of nature which make up proteins when they are condensed into polymers. The simplest example is glycine (aminoacetic acid) $\text{H}_2\text{NCH}_2\text{COOH}$. Alanine contains a pendent methyl group, substitution of which by a long-chain alkyl group would yield a range of surfactants (Structure 7.12).

Alanine, a simple amphoteric compound



7.12

It will be observed that at low pH the molecule in Structure 7.12 would form an amine salt, and if the alkyl chain was sufficiently large it would behave as a cationic surfactant – for example, cocoamphocarboxyglycinate. At high pH the carbonyl group would ionise forming an anionic surfactant (Figure 7.6).

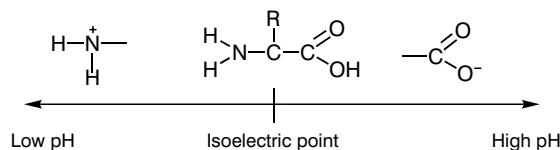
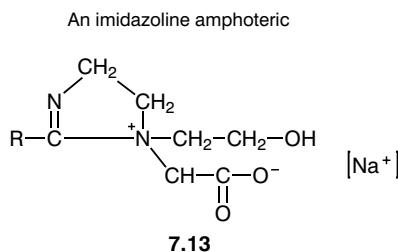
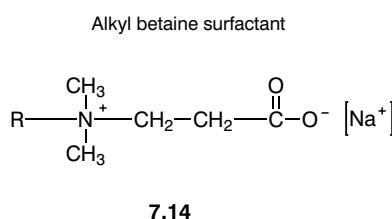
$R = \text{CH}_3 \text{ or } \text{C}_{16}$


Figure 7.6 Behaviour of amphoteric with pH

In practice, however, amino acids are less basic (pK_b 12) and less acidic (pK_a 10) than the individual carbonyl (pK_a 5) and amine groups (pK_b 4) would suggest. This is because there is partial internal acid–base interaction to give a ‘zwitterion’. The pH at which there is no net charge on the molecule is referred to as the isoelectric point. It is usually below pH 7 because of the difference in strength between the $-\text{NH}_3^+$ and $-\text{COO}^-$ functions. The molecule is in fact isoelectric over a range of pH values. Engineering this characteristic leads to many commercial products to suit varied applications. Typical are the imidazoline-derived amphoteric (Structure 7.13).



In the isoelectric pH range, the physical properties – including viscosity, solubility and foaming characteristics – all change to a greater or lesser extent, depending on the structure. If the charge on the nitrogen is permanent, as in the quaternary structure, the molecule is always strongly cationic, whatever the pH. Alkyl betaines (Structure 7.14) are very useful surfactants and many variants are commercially available. As softeners, they have use in hair preparations but industrial use is limited as they are expensive and not weight efficient compared to other materials. Temperature stability is also poor.



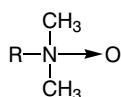
Betaines are used as softeners with special properties such as hydrophilicity. Glycine-derived betaines are used as tumble-dryer softener additives in gel-like compositions [54].

Another range of products that express amphoteric behaviour are the amine oxides (Structure 7.15) [55]. Here an oxygen atom is linked to a tertiary nitrogen by a coordinate covalent bond. The higher alkyl derivatives produce good softening effects although the thermal stability is poor and their use as softeners per se is secondary.

Amine oxides can be added to anionic detergents to impart softening to the wash load. They are excellent antistatic agents, helping to eliminate the static 'cling' found with synthetic fibres. In shampoo formulations the amine oxides, such as dimethyldodecylamine-N-oxide, give body and lustre to the hair and make it more manageable. Solid softener preparations for use in tumble-dryers employ amine oxides as the major finish component.

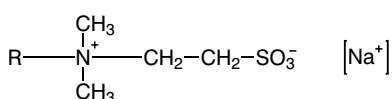
A more powerful range of primarily surfactant amphoteric is the sulphobetaines (Structure 7.16), in which a sulphur group provides the anionic portion of the molecule.

Amine oxide structure



7.15

Structure of sulphobetaine surfactant



7.16

7.6 NON-IONIC SOFT FINISHES

In industrial applications, non-ionic softeners probably dominate in terms of tonnage. Non-ionics are not only widely used as finishes in their own right but are also found as adjuncts in strongly cationic formulations, often performing multiple functions as softeners, emulsifiers, stabilisers, extenders and lubricants [66,67]. Large quantities of woven fabric are finished with non-ionics based on simple oxidised polyethylenes, glycerol monostearate and ethoxylated castor and similar materials. Included in this category are many different chemical species with the common feature of low polarity. For this reason they are applied by a padding technique, with a few exceptions. The characteristics that exemplify non-ionics as a class are listed in Table 7.7.

Table 7.7 Characteristics of non-ionic finishes

Compatibility	Selected compounds are tolerant to strong acids, alkalis and electrolytes found in easy-care and other finishes
Handle	Good control of handle and drape but never achieving the extremes of softness possible with cationics
Lubricity	Extensive control of lubricity is possible with the right choice of finish
Low yellowing	Non-ionics can be selected for operation at extremes of temperature without yellowing and to have minimal effect on fluorescent brighteners.

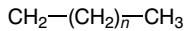
Non-ionic candidates for use as softeners can be extracted from a large pool of chemical types. Waxes are the most traditional and include paraffins, polyethylenes, ester waxes such as beeswax and synthetic beeswax, lanolin and its derivatives. Fatty esters can be selected from a large number of variants to provide lubrication needs. Ethoxylation of common fatty materials provides an invaluable source of softeners and emulsifiers.

7.6.1 Paraffin waxes

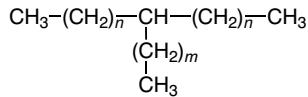
The most basic non-ionics are the paraffin waxes and related materials. Petrolatum waxes are the lowest melting (45–48 °C) and are very soft and pliable. They can have a high oil content depending on the grade and even very soft materials such as petroleum jelly are used as softener adjuncts. Paraffin waxes as such are the most useful and are derived from petroleum distillates by freezing, solvent de-oiling and other refining processes. They consist of linear and branched hydrocarbons of high molecular weight (C₂₃–C₂₈) (Structures 7.17 and 7.18). Melting points vary from 50 °C to 60 °C and they have a coarse crystalline structure. Another range of paraffin waxes referred to as ‘microcrystalline’ have higher melting points in the range 85–93 °C. These are much harder due to the very fine crystalline structure and can be better lubricants.

Paraffin waxes can be blown in air at about 150 °C, when a degree of oxidation occurs resulting in carbonyl groups on the hydrocarbon chain. Neutralisation with alkali such as sodium hydroxide or ethoxylated amines yields self-emulsifiable waxes.

Linear paraffin wax structure



Branched paraffin wax structure



7.17

7.18

Paraffin waxes have no polar groups and are totally insoluble in water. They must be applied as aqueous emulsions, which can be prepared with non-ionic, cationic or anionic emulsifiers, depending on the required method of application. The non-ionically-emulsified products have the best compatibility, maintaining the desirable non-ionic character.

Excellent results can be achieved by combination of non-ionics with other softener types including cationics. As finishes for facilitating sewing, knitting and promoting high resistance to flex abrasion, tear strength and so on, paraffin wax-based formulations give excellent results at low cost. Needle cooling is attributed in part to the low melting point when the heat of fusion extracts energy from the point of friction, therefore decreasing the needle temperature.

The water-repellency effect produced by paraffins cannot always be tolerated and could cause serious problems in subsequent fabric printing. On the other hand, water-repellent finishes often incorporate paraffin waxes to extend and improve performance.

7.6.2 Polyethylenes

Polyethylene is a wholly synthetic polymer produced by high pressure polymerisation of ethylene with a suitable catalyst. It is a thermoplastic resin, which is inert to most chemicals and is produced in a large variety of types. For finishing of textiles, the more wax-like polyethylenes are most effective. Oxidised homopolymers and copolymers are widely used for their ease of formulation. Selection of cationic, non-ionic or anionic emulsifiers gives products that can be applied by pad or exhaust methods and with the required compatibility with other finishes.

Polyethylenes have many advantages over paraffin waxes but they are more expensive. They have higher melting points from about 100 °C up to 140 °C, and produce more durable films than paraffins. Overall, the lubricating properties for making-up operations such as sewing and cutting are superior. Paraffins tend to discolour in sunlight whereas polyethylenes have excellent thermal and light stability. The softer nature of paraffins and their high residual oil content can result in scum build-up in application machinery and a tendency to soil more easily. Polyethylenes can be classified by melting point, hardness, density and acid number (Table 7.8).

Table 7.8 Characteristics of common polyethylenes

Polyethylene type	Melting point (°C)	Hardness (dmm)	Density (g cm ⁻³)	Acid no. (mg KOH g ⁻¹)
Low density	102	5.5	0.93	16
Medium density	110	1.5	0.94	16
High density	138	0.5	0.99	30

The hardness figure is the depth of penetration of steel point in deci-millimetres (dmm) for a given force. The acid number is a measure of the number of carboxylic acid groups on the polyethylene chains resulting from controlled oxidation. The acid number provides information on the neutralisation requirements so that emulsion characteristics can be engineered for particular end-uses. The differences in density are numerically small but have important performance implications, as indicated by the hardness. In performance terms, the selection of a particular polyethylene depends on a number of factors. The softest handle and best drape are produced by low density polyethylenes and in fact these are the most widely used [68].

Low density polyethylenes are used with easy-care and flame-retardant finishes (with caution) to overcome the harshness and loss of strength produced by such treatments. They improve fabric tear strength, seam strength, and general wear characteristics. The lubricity of polyethylenes is used to improve mechanical finishing treatments such as napping and brushing and to reduce needle damage in making-up. Medium and high density polyethylenes are noticeably less soft but are more permanent to washing and give improved lubricity on heavier-weight fabrics.

Copolymers of ethylene and acrylic acid offer the finisher a material that is colourless, unlike simple polyethylenes, which have a slight brown cast. They can be regarded as medium density but produce a somewhat more flexible film and slightly better lubricity.

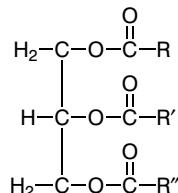
7.6.3 Fatty esters

Fatty esters, as a chemical category, are recognised for their excellent lubricating properties particularly for reduction of fibre-to-metal and metal-to-metal friction. Fibre-to-fibre lubrication is associated with perceived softness and therefore esters can make good softeners. The ester function is found in certain ethoxylates, degradable cationics and anionics, but here we are concerned with compounds where an ester is the only functional group. Esters are insoluble in water and are therefore applied as emulsions with certain exceptions such as wax ring disc formulations, which are used for yarn processing. Fatty esters can be prepared with any polarity to suit the required application method. The non-polymeric esters have limited durability to washing and will be applied mostly as processing aids with good point-of-sale handle.

The simplest esters that are of interest as finishes are short-chain alcohol reaction products with long-chain acids. Products such as methyl stearate reduce dynamic friction at very low levels of application and tend to be effective scrooping agents rather than softeners when used alone. Admixtures with a softening agent will produce a very greasy, slippery handle which is sometimes demanded but not generally considered desirable. A more satisfactory handle is achieved with longer chain compounds such as stearyl stearate or stearyl oleate, which are a little easier to formulate due to their lower melting points.

Probably the most common esters are those based on glycerine. The mono-, di- and tri-glycerides represent important variants (Structure 7.19). Different fatty acid chain lengths and degrees of saturation give a useful range of softener properties. The more surface-active mono- and di-glycerides find wide usage in softener formulations.

Fatty triglyceride ester



7.19

Stearate, palmitate and oleate esters of other polyhydric alcohols, such as sorbitan and pentaerythritol, are very common. The mono- and di-esters leave free hydroxy groups and can be used where a less hydrophobic finish is required. Ethylene glycol mono- and di-long-chain esters represent useful softening agents with good lubricating effects and excellent temperature stability. An obvious example is ethylene glycol distearate.

7.6.4 Ethoxylated compounds

Ethoxylated compounds are used extensively in softener formulations. As the degree of ethoxylation increases the aqueous solubility increases, but the softening efficacy diminishes rapidly. Ethoxylation improves product handling properties such as compatibility with pad bath

additives and increases the hydrophilicity of the finish. The basic reaction is the opening of the epoxy ring in the addition to alcohols, acids, esters, amines and so on (Scheme 7.9), or simple polymerisation of the ethylene oxide itself.

Reaction of ethylene oxide with fatty ester

**Scheme 7.9**

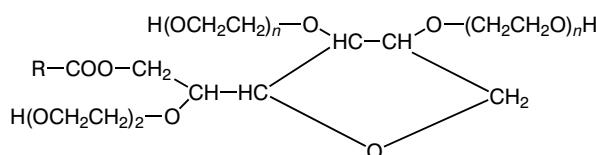
The polyethylene glycols (PEG) such as PEG800 are hard waxes and give an improvement in handle when padded onto fabrics but are more useful as formulating additions. However, the presence of one or more long alkyl chains, as in sorbitan ester ethoxylates, gives us useful finishing effects. The ethylene oxide (EO) chain length or 'n' number describes the number of moles ($-\text{CH}_2\text{CH}_2\text{O}-$) added. The degree of ethoxylate determines the hydrophilic–lipophilic balance (HLB) of the resulting surfactant and therefore allows the formulator to select optimum emulsification properties (Table 7.9).

Table 7.9 Sorbitan monostearate ethoxylates

EO addition 'n' number	HLB	Solubility (in water)	Description (physical form)
0	4.7	Insoluble	Hard solid
4	9.6	Soluble	Waxy paste
20	14.9	Soluble	Yellow liquid

Sorbitan mono-, di-, tri- and hexa-esters of oleic, stearic, palmitic and lauric acids, ethoxylated to different degrees, are available to the formulator. Sorbitan is a cyclic ether-alcohol resulting from the reduction of sorbitol, which is a hexahydric alcohol. Structure 7.20 shows its ethoxylated monoester. They are excellent lubricants, softeners and emulsifiers.

Structure of sorbitan ester ethoxylate

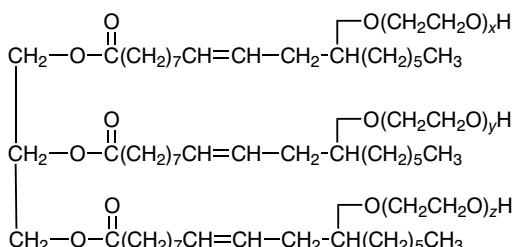


R = stearate, oleate or a mixture

Castor oil ethoxylates (Structure 7.21) have an enduring place in softener formulation [69]. They have good compatibility with all ionic species, particularly the lower ethoxylates, and produce useful softeners that can be used alone or in combination with fillers and crease-resist finishes.

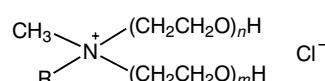
Ethoxylation of amines yields a useful range of surfactants, some of which can be used alone as soft finishes for textiles and in more diverse applications such as hair-care and in the scouring/softening of sheepskin rugs [70]. The more surface-active types of compound are effective emulsifiers for paraffin and other waxes, when making pseudo cationic formulations. A controlled residue of amine will result in weakly cationic emulsions at low pH, sufficient to effect exhaustion onto fabrics. A large number of amine ethoxylates are possible by varying the degree of ethoxylation and selection of starting material. Strongly cationic derivatives with good exhaustion and antistatic characteristics are the quaternised ethoxylated amines (Structure 7.22).

Castor oil ethoxylate



7.21

Ethoxylated quaternary compound



7.22

7.7 ANIONIC SOFT FINISHES

Although anionics were amongst the first soft finishes to be used commercially, they are still important. Early anionics were based on sulphonated tallow and on soaps. Anionics dominate the surfactant market and a number of chemical types have value as softeners. Alkylaryl sulphonates, alcohol sulphates, ether sulphates, phosphate esters, sulphosuccinates, sulphosuccinamates, alkane sulphonates, olefine sulphonates, sarcosinates, taurates and soaps are all commonly available (Table 7.10). Long-chain derivatives can be found in each group that will exhibit useful softening properties. More complex materials, such as sulphated castor oil, tallow, petroleum sulphonates and purified lecithin, also make good softeners and related lubricative products such as dyebath lubricants.

Fatty anionics are used directly as softeners for pad application. A degree of substantivity to cotton is possible at higher temperatures of 60 °C or above. Anionic softeners have specialised areas of application, such as medical textiles, where the physiological activity is low and they have a long history of use without problems. Most fluorescent brightening agents (FBAs) are anionic and are therefore highly compatible with anionic softeners. For resin finishing of white cellulosics, anionic softener and FBA can be added to make a stable pad bath.

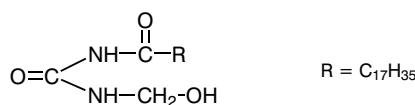
Table 7.10 Some typical anionic finishes

$\text{R}-\text{CO}_2-\text{Na}^+$	Fatty acid soap
$\text{R}-\text{OSO}_3-\text{Na}^+$	Sulphates
$\text{R}-\text{SO}_3-\text{Na}^+$	Sulphonates
$\text{R}-\text{C}-\overset{\text{O}_2}{\underset{\text{CH}}{\text{O}}}-\text{CH}$	Sulphosuccinates
$\text{R}-\text{C}-\overset{\text{O}_2}{\underset{\text{CH}-\text{SO}^-}{\text{O}}}-\text{CH}-\text{SO}^- \text{ Na}^+$	

7.8 REACTIVE SOFT FINISHES

Reactive soft finishes differ from all other types of softener in that they chemically react with the textile fibre to form a covalent bond and are therefore permanent to washing. This usually involves a cellulosic fibre, where the hydroxyl groups are the reactive sites. Synthetic blends such as polyester/cotton can also be finished with reactive softeners but care is needed to avoid poor rub fastness caused by disperse dye migration at the cure temperature. It is difficult to separate waterproofing from softening because permanent waterproof finishes require the same long-chain alkyl groups as a softener. Similarly, the subject of resin finishing is inexorably linked with handle and drape [71–76].

Several types of reactive chemical have been proposed [166,172]. The *N*-methylol derivatives of stearic acid amides and urea-substituted compounds are the most successful (Structure 7.23). The triazinyl-based reactivities similar to reactive dyestuffs have generated some interest but are not commercially important. Reactive silicones used alone or in combination with *N*-methylol compounds or epoxy resins can give an added dimension to the handle effects that can be achieved. All reactivities require baking at 90–130 °C or higher and this has been a distinct disadvantage compared with a simple after-rinse exhaust application.

Structure of *N*-methylol urea reactive softener

7.23

In reaction with cellulosic hydroxyl groups to form the ether linkages, the *N*-methyl compounds require an acid catalyst such as citric acid or an acid-liberating salt such as magnesium chloride. The levels of formaldehyde created under unfavourable application conditions can exceed present limits so that care is required when using this type of chemistry. The attraction of reactive finishes is their permanency to repeated washing. New fibre types, particularly microfibres, are proving to be a non-chemical means of producing fabrics that are soft for life [77–80].

7.9 SILICONES

The use of silicones (polyorganosiloxanes) in textile finishing has grown steadily in volume and variety [81–88] in the half-century since the preparation of the first commercial silicones. Polydimethylsiloxanes (PDMS) of varying viscosity soon became widespread in the textile and numerous other industries. Their excellent lubricating properties and chemical inertness gave finishers a truly new material to work with. The traditional PDMS [89] varieties are still widely used but are being replaced by a newer complex range of silicone derivatives producing diverse effects, from elastomers to supersofteners.

The physical presentation of silicones has steadily improved along with the chemistry. Early silicones based on dimethylsiloxane were invariably manufactured as white milky emulsions with droplet sizes as large as 300 µm. These had to be used with great care due to poor stability and the danger of silicone spotting on fabrics. Modern silicone emulsions have excellent mechanical and chemical stability. Whilst coarser emulsions have their place, the finisher can now choose from highly stable mechanical emulsions with particle sizes down to 1 µm or less. Such fine emulsion particles are of the same order as the wavelength of visible light so that the products have an opalescent or translucent appearance. However, developments have not stopped and several types of silicone are now available as microemulsions with particle sizes down to 50 nm or less. Microemulsions take on the appearance of a clear solution and apart from superb stability they have performance advantages as a direct result of the finer particle size. In particular, the improved penetration into microfibre fabric gives better internal lubrication and improved handle. On natural fibres, particularly cotton and cellulosics where fibrillation can take place, a similar mechanism operates to give perceptibly improved handle.

Silicone chemistry is special in that it bridges inorganic ($\text{Si}-\text{O}$, $\text{H}-\text{Si}-\text{O}$) and organic chemistry ($\text{Si}-\text{CH}_3$, $\text{CH}_3-\text{Si}-\text{R}$) in the same molecule. This is borne out by the partially ionic nature of the $\text{Si}-\text{O}$ bond. The silicon atom is slightly positive in nature so that the pendent methyl groups are much more stable than in an organic molecule. Not surprisingly, silicones applied to textiles have a characteristic ‘silicone-feel’, particularly when applied at higher levels. It can be argued that organics have a corresponding ‘fatty-feel’ for which humans have a slight preference. Silicone usage in finishes has in part been successful as a result of skilful formulation of silicones with organic finishes so that a synergy is achieved. The outstanding developments in silicone chemistry have to some extent been concerned with making silicones more organic yet retaining the useful properties of the silicone origin. This is exemplified by the recent introduction of aminofunctional silicones, which impart a much more acceptable type of handle. The desirable properties of silicones result from several unusual physical properties some of which are listed below [90,91]. Silicones used for textile treatment are invariably based on the polydimethylsiloxane backbone. The presence of the methyl group has a strong bearing on the properties of the finish. The presence of the methyl substituent – as opposed to, for example, phenyl groups – is largely responsible for most of the attributes of silicones:

- (1) Highly flexible backbone: the $\text{Si}-\text{O}$ bonds rotate freely, 0 kJ mol^{-1} bond rotation energy; films are extremely flexible and lubricative;

- (2) Very low surface tension: the low surface tension of 21 mN m^{-1} means that the film has little affinity for most organics and reduces fibre-to-fibre cohesion, maximising fabric bulk; it is also water-repellent;
- (3) High bond strength: the Si–O bond is very strong, 445 kJ mol^{-1} , compared to carbon–carbon at 346 kJ mol^{-1} and carbon–oxygen at 358 kJ mol^{-1} – silicones are therefore resistant to breakdown at high temperatures;
- (4) Low glass transition temperature: films remain flexible from -90°C to $+200^\circ\text{C}$ without any step-change in physical properties;
- (5) Very low vapour pressure: products above 50 cst have no volatiles and no odour whatsoever and almost no weight loss on heating;
- (6) Chemically inert: silicones are resistant to strong oxidative attack and only show weakness under strong alkaline conditions at high temperature; they are also resistant to UV and IR radiation and are physiologically benign;
- (7) Highly compressible: treatments have positive effects on fibre, yarn and fabric modulus;
- (8) Permeable to nitrogen and oxygen: this is associated with comfort in wear;
- (9) Temperature-stable physical properties: refractive index, surface tension, density and viscosity change little with temperature;
- (10) High dielectric stability and strength: widely used outside the textile industry in electrical applications;
- (11) Highly surface-active: very good spreading and film-forming properties on fibre surface; alkoxylated silicones are excellent wetting agents.

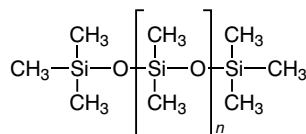
These factors undoubtedly contribute to the desirable effects imparted by silicones but the precise mechanism relating to softness and handle is not fully understood.

7.9.1 Polydimethylsiloxanes

Although the first silicon–organic compounds were prepared in 1863, it was military demands in the 1940s that resulted in the large-scale introduction of dimethylsiloxane polymers. Textile applications developed in the 1950s, where low-viscosity silicones were used as water-repellents. It was known that high-viscosity silicone fluids imparted softness but they were not economical until the development of emulsion polymerisation in the 1960s. High viscosity silicone finishes were used initially on synthetic fibres but soon became widespread either alone or in formulations with organics. Structure 7.24 shows the most basic type silicone used in textile finishing – polydimethylsiloxane (PDMS).

Polydimethylsiloxanes are marketed as white opaque emulsions containing up to 60% silicone oil. PDMS oils can be low-viscosity, volatile materials at less than 1 cst to greases with a viscosity of 1 000 000 cst. To produce softening, the polymer viscosity must be over 10 000 cst. The higher viscosity polymers are more difficult to formulate but give increased softening effect so that 100 000 cst materials represent a good compromise [92,93]. PDMS-based products have several

Structure of polydimethylsiloxane (PDMS)



n can range from 0 to 2500

7.24

uses as finishes from simple winding aids, components in sewing thread lubricant formulations and sewing lubricants for synthetics, to stand-alone softeners.

Delivery onto the fabric can be problematic unless care is taken. Emulsions can break down under the shear of the padding process, giving build-up on machinery and silicone spots on fabrics that are difficult to remove. If the correct formulation is selected and the use conditions are within the design limits, excellent results can be achieved. For exhaust application, cationic emulsions are available. The cationic emulsifiers can impart a degree of softening. To some extent the exhaust process is aided by dilution of the emulsion as it is added to the treatment bath. The reduced concentration of emulsifier results in instability of the oil droplets and a tendency to deposit more easily onto the fabric. Build-up of silicone on the insides of winches and jets is largely avoidable by choice of product and good working practices. Heating the exhaust bath to temperature before the silicone emulsion is added will reduce the risk of the emulsion splitting at the heat exchanger. Pre-dilution of the emulsion and slow addition to the bath from a side tank will also help.

Polydimethylsiloxane is very effective on synthetic fibres where the surface area is low. Deposition of very small quantities, as low as 0.1% of active softener, can eliminate fusing of polyester during cutting and high-speed sewing and produces a very noticeable improvement in handle and elasticity. Cotton fibre requires larger amounts of silicone to achieve a particular effect, due to its high specific surface. Nonetheless, silicones are commonly used on cotton and cotton blends to good effect. PDMS emulsions are particularly useful for application with easy-care resins. The non-ionic emulsions have excellent stability in the high electrolyte concentrations and low pH of the resin bath. This type of silicone is extremely stable under the severe conditions required to cure crease-resist resins, typically 1–2 min at 180 °C. The effect of PDMS in an easy-care finish is to give remarkable improvements in crease recovery, tear strength and softness, as well as abrasion resistance and similar wear parameters. Typical results obtained on 100% cotton woven fabric are given in Table 7.11.

Silicones, and PDMS in particular, can be beneficial to the colour of textiles. The smooth silicone film on the fabric surface produces a brightening effect in the same manner as varnish on wood. The effect is particularly noticeable on polyester, which has a high refractive index compared to other fibres. Light arriving at the surface of a material with a high refractive index is absorbed less than by a low refractive index material. A lower portion of the light is therefore absorbed by the dye inside the fibre. The silicone film, which has a low refractive index, will

Table 7.11 Improvements in easy care properties of 100% cotton woven fabric by addition of PDMS to resin system

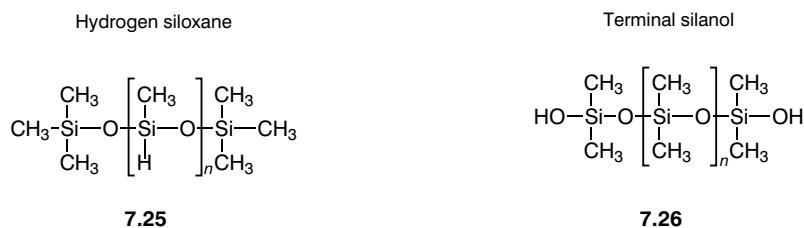
	Resin only	Resin + PDMS
Crease recovery angle warp plus weft	210°	240°
Elmendorf tear strength warp way (kg)	0.5	0.75
Softness rating (1 to 14, where 1 is the best)	9	5

therefore couple more light into the fibre. This effect is particularly useful for dyeing polyester microfibres where it helps to obtain a deep black colour. Although this is not a softening effect, the improved visual effect enhances the obvious handle improvement.

It is known by formulators that a small portion of hydrophobic silicone included in an organic softener formulation will give a small but useful reduction of hydrophobicity. The effect is associated with an improved rate of water wicking into the fabric and is particularly noticeable with the more polar anionic softeners used for pad application. This improvement is associated with greater comfort and better performance in the case of towelling. Additions greater than about 2% silicone in a typical anionic softener become ineffective [94,95]. Polydimethylsiloxanes are not permanent on textiles but the higher-molecular-weight materials in particular have a useful degree of durability on most fibres.

7.9.2 Reactive polydimethylsiloxanes

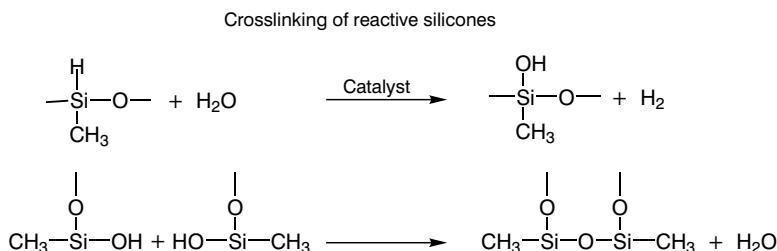
For waterproofing applications the durability of PDMS is limited. Reactive polydimethylsiloxanes were developed in the early 1970s in order to produce more permanent finishes. In this case a proportion of the methyl groups in the chain are replaced with hydrogen or a terminal methyl is replaced with a silanol (Structures 7.25 and 7.26) [96,135].



These first generation reactive silicones provide a good permanent soft finish to many types of fabric and are important additives to permanent press finishing formulations, water- and showerproof finishes, machine wash wool treatments and as general softeners and elastomers. Although the permanency on cotton can be satisfactory, the repeated swelling by hydration and dehydration during laundering weakens the attachment.

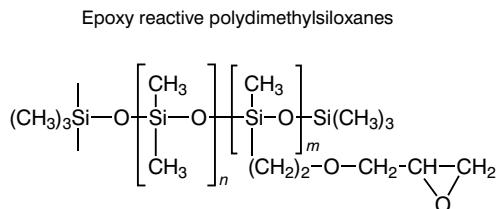
They are generally used with metallic catalysts. By altering the proportions of hydrogen silane to silanol, several different finishing effects are possible. A typical metallic catalyst is

tetrabutyl titanate, which has a secondary advantage of improving the bonding to the textile substrate. The more elastic effect is the result of cross-linking to form a three-dimensional matrix. The silicone can be supplied as a silane and is readily hydrolysed to give pendent hydroxy groups, which condense with the aid of the organometallic catalyst to give an elastic gel matrix with enhanced permanency. More effective results require short-chain tri-functional crosslinkers to produce a highly crosslinked rubber-like polymer with excellent elasticity (Scheme 7.10). This is particularly useful on knit goods in which dimensional stability and snap-back represent added value. Trifunctional crosslinkers are typically hydrosilane ($-\text{SiH}$), acyloxy ($-\text{SiOCOCH}_3$) or ester ($-\text{SiO}_2\text{R}$). These can link three silicone molecules to form a highly crosslinked gel network [97–99].



Scheme 7.10

The epoxy functional silicones comprise an important subset in the reactive polydimethylsiloxane range. These have the capability to react with the hydroxy groups on cotton and cellulosics to give permanent effects. Epoxy silicones (Structure 7.27) enhance dimensional stability and can be better softeners than PDMS. They are durable to many domestic laundering cycles and have very low yellowing properties. Compatibility with easy-care resin baths is very good and they are thermally stable at the cure temperatures. Their permanency makes them ideal for this purpose. Unfortunately, the softness attainable is well below the amino silicones.

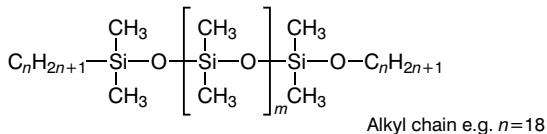


7.27

7.9.3 Organo modified polydimethylsiloxanes

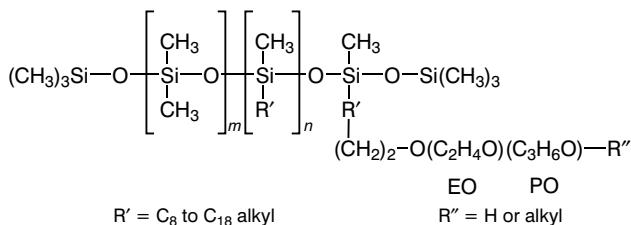
The introduction of side-groups other than hydrogen and hydroxy can result in dramatic changes in properties. Some interesting effects can be produced – for example, polydimethylsiloxanes with long alkyl groups can result in lubricants with glide properties for application to recording tapes (Structure 7.28). Other uses are scratch resistant finishes and fibre lubricants.

Polydimethylsiloxane with long alkyl chains as super lubricants



7.28

Structure of *n*-alkyl ethylene oxide propylene oxide polydimethylsiloxane



7.29

The *n*-alkyl polyethers with terminal alkyl groups are particularly useful. Many such products have uses outside the interest of finishers such as wetting agents and emulsifiers with HLB values that can vary greatly. The low physiological activity makes such emulsifiers particularly suitable for lotions and sunscreens. Similarly, they are used in finish formulations [100–107].

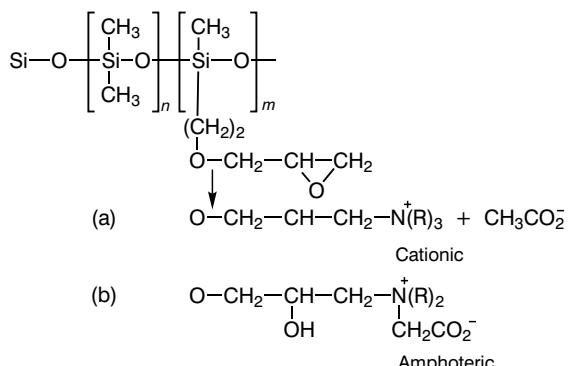
In the compound shown in Structure 7.29, the variables m and n and the alkyl chain length can be varied to produce emulsifiers, demulsifiers, stabilisers, and lubricants. It is also possible to introduce ionic end groups to PDMS substituents [104,105]. This can be done in many ways, one of which is to start with the addition of allyl glycidyl ether to a silane site on the PDMS. This epoxy reactive intermediate product can then be transformed into a range of anionic, cationic and amphoteric materials with unique properties. The cationic compounds are of particular interest to the finish formulator for preparation of pseudo ionic delivery systems. They have much higher substantivity for textile substrates than fully organic materials and form more tenacious films. The overall preparation of ionic organopolysiloxanes is shown in Scheme 7.11.

These examples illustrate the symphonic complexity of silicone chemistry, which has a largely untapped potential to produce many interesting products for textile finishing.

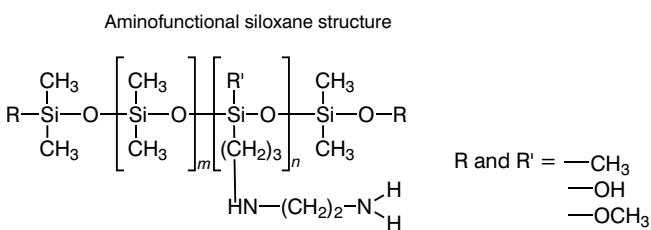
7.9.4 Aminofunctional siloxanes

Aminofunctional siloxanes represent the most active growth area in finishes since the 1980s. Products in this category include microemulsions and supersofteners. Their usefulness extends to every conceivable type of textile substrate, reflecting the diversity of properties and their pleasing tactile effects. They represent the best balance between organic and silicone chemistry yet produced and bring out the best characteristics of both. The basic building block is

Preparation of ionic organopolysiloxanes



Scheme 7.11



polydimethylsiloxane with aminoethylaminopropyl side-groups. Structure 7.30 [74] is by far the most common base for amino silicone finishes [108,109].

This structure lends itself to wide variation. The PDMS fraction, m , is usually in the range 50 to 2000 units. The amino-containing portion is usually in the range 1 to 20 units. Terminal groups on the PDMS can be $-\text{CH}_3$, $-\text{OH}$ or $-\text{OCH}_3$. Aminofunctional siloxanes as such lie within these bounds.

The outstanding softening properties of the aminofunctional siloxanes can in part be explained by the presence of the amine functionality. The polymer is cationic and is therefore strongly oriented at the fibre surface. This more ordered deposition coupled with the characteristics of the silicone leads to supersoftening effects. This type of handle is not defined – however, it is recognised as having the softness of the most effective cationics but with added bulk and resilience. Although these products can be applied from mild alkaline baths, they are normally applied at pH 6 or below. If the acidity is reduced towards pH 4 the amino groups become more strongly positively charged and the rate of exhaustion increases. The adhesion to the fibre also increases giving good durability.

Aminofunctional polysiloxanes can be applied by pad or exhaust methods. They are usually supplied as microemulsions and therefore have excellent stability to shear, temperature and water hardness. They also have good compatibility with easy-care resin/catalyst baths. Microemulsions have a much lower tendency to deposit on machine parts and shear breakdown on padding rollers is negligible. Typical application levels of aminofunctional siloxanes range from 0.25% to 1% based on the weight of fabric.

Microemulsions of aminofunctional polysiloxanes are particularly effective on microfibre [110]. The fine particle size allows the emulsion to penetrate into the closely packed yarn structure giving internal lubrication and softening [111–113]. This is illustrated in Figure 7.7, where a small section of a 76 dtex 144 filament yarn is shown. Each filament is 0.53 dtex and 7 µm in diameter.

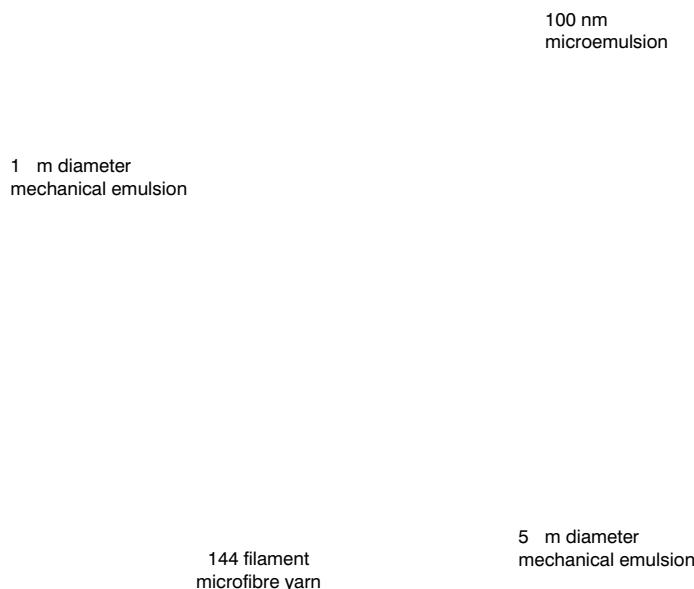


Figure 7.7 Microemulsion penetration into 76 dtex 144 filament microfibre polyesters yarn

The improved distribution on the true fibre surface results in easily demonstrated improvements in the properties of microfibre fabrics [114]. Microfibres are found in diverse markets and aminofunctional silicones can be selected which optimise the often conflicting requirements of different end-uses (Table 7.12).

Microfibre yarns contain many filaments and consequently have a much larger surface area than conventional yarns. Filament denier ranges from 1 denier to less than 0.5 denier for normal fabrics, but very fine fibres – as fine as 0.01 denier – are used in special non-wovens [114–118]. Abrasion resistance and tear strength are improved by epoxy reactive silicones. Wrinkle recovery is optimised with low amino content silicones in combination with more strongly crosslinking types. Softness is undoubtedly optimised with high amino content products but yellowing and water control may be compromised. Absorbency can be maximised with polyether modified silicones, whereas water-repellency is improved with strongly reactive silicones [119–123].

Aminofunctional polysiloxanes, which produce the greatest softening effects, have a tendency to cause yellowing as the amino content increases [93,94,98,108]. Good whiteness can be achieved by careful selection of a polymer with a maximum amine value consistent with an acceptable degree of yellowing. The yellowing behaviour is a result of the nitrogen's ability to form coloured azo and azoxy compounds. The presence of metal catalysts and prolonged exposure to high

Table 7.12 Finishing demands on microfibre fabrics

End-use	Garment types	Finish requirements
Outerwear	Slacks, dresses, shirts, blouses, skirts, jackets	Supersoft, excellent drape, easy-care, light-weight, dimensional stability, comfort
Sportswear	Raincoats, anoraks, ski jackets sailing wear track suits, sweat suits	Water-repellent, air-permeable, wind-tight, light-weight, soft, easy-care, dimensional stability
Technical	Sleeping bags, tents, shades, workwear, filters, car upholstery	Softness, dye fastness, light fastness, drape, easy-care, low soil, low fogging

temperature are the major factors. Aminofunctional silicones for use with easy-care resins should therefore be selected with care. For exhaust application followed by a normal drying regime, particularly on coloureds, a full supersoft finish can be easily achieved. On brilliant white fabrics there is a possibility of high-amine-value, strongly cationic finishes causing yellowing of the fluorescent whiteners, particularly at very low pH. The relationship between amine value, aminoethylaminopropyl content and yellowing is shown in Figure 7.8, for typical aminofunctional siloxanes. The amine value is determined by titration and is quoted as millilitres of molar hydrochloric acid required to neutralise the amine contained in one gram of silicone polymer.

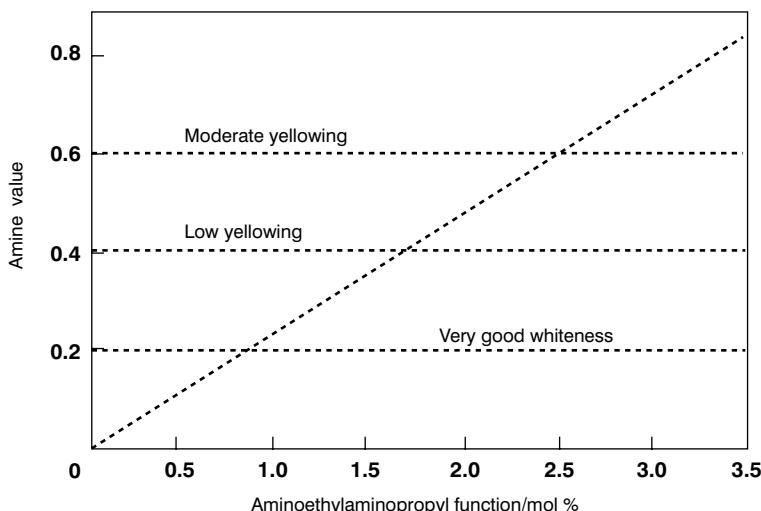
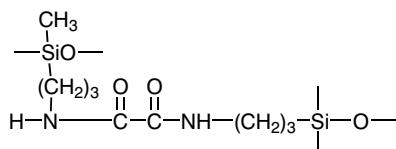


Figure 7.8 Relationship between amine value and aminoethylaminopropyl content and tendency to cause yellowing

Attempts to further improve aminofunctional polysiloxane technology have led to new products with useful attributes – in particular, lower yellowing. These are variants based on the aminofunctional siloxanes where the amine groups are further reacted – for example, by acylation of a portion of the nitrogen atoms to produce an amide (Structure 7.31).

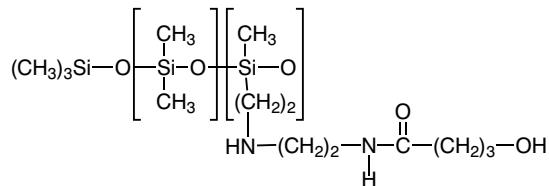
Other derivatives – for example, cyclohexylamine as a secondary amine and piperazine as tertiary amines – certainly give lower yellowing. However, there is some loss in softening effect and a change in the type of handle. Hydroxy amido functional siloxanes reduce the yellowing effect and improve hydrophilicity (Structure 7.32).

Amide modification of aminofunctional siloxane



7.31

Hydroxyamido polysiloxane derivative



7.32

Attempts to improve the soiling behaviour of silicones have led to work with combinations of polyether and amine functional siloxanes. These have improved anti-soiling and soil-release properties. High amine content gives good softness and poor hydrophilicity whereas high polyether content reduces softness. The nexus between hydrophobicity and softness remains difficult to break.

7.10 ENVIRONMENTAL ASPECTS OF CHEMICAL SOFTENERS

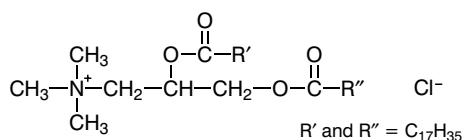
Chemical soft finishes are difficult to categorise in terms of environmental behaviour because of the great diversity in chemical types used. In recent years, numerous additions and changes to the laws and guidelines regulating the disposal of material into the environment have been published [124–127].

The regulations cover discharge of substances by all routes, such as in waste water, as sludge, as chemicals for disposal and as volatiles venting to the atmosphere. All chemical types must be assessed for compliance before use. Many softening materials are benign – for example, hydrocarbon waxes, fatty esters and sorbitan ethoxylates. Unfortunately, many softeners are based on nitrogen compounds that have a higher tendency to be physiologically active [128–131]. Certain starting materials used by softener manufacturers carry the greatest risks. Raw materials such as fatty acids, fatty alcohols, triglycerides and long-chain fatty amines are low risk components. Alkylamines are strong bases, often volatile and foul smelling and are difficult to handle. Another risk from alkylamines is their potential to form nitrosamines, which are carcinogens. They can be explosive and combustible and extremely irritant. Alkylating agents, dimethyl sulphate and epichlorohydrin – used to quaternise the nitrogen atoms in a softener, to

make them strongly cationic – represent an even greater risk and are subject to strict regulations. These materials are carcinogens, toxic, capable of absorption through the skin, mutagenic, explosive, combustible and strongly basic. Any manufacturer using such materials should be well aware of the appropriate regulations.

Luckily, once these raw materials have been converted to soft finishes the dangers are largely depleted. Softeners made from such materials are usually amine salts or quaternary ammonium compounds. Both types are relatively benign compared to the starting materials but are more hazardous than other types of softener. The amine salts are surface-active and have the usual risks of foaming and increasing the BOD and COD of the effluent. The quaternary ammonium compounds, however, have a degree of fish toxicity and retard biological effluent treating systems. It should be pointed out that only low concentrations of free DSDMAC actually reach the effluent system and have not caused adverse effects over many years of use. The newer esterquats are nonetheless far safer in the aquatic environment. A commercially successful esterquat is the di-tallow ester of 2,3-dihydroxypropanetriethyl ammonium chloride (Structure 7.33). This is particularly important in domestic rinse conditioners.

A diester quaternary (DEQ) as used in rinse conditioners



7.33

The material shown in Structure 7.33 hydrolyses easily in the environment via the 3-monoester to the very soluble diol quaternary ammonium compound, which is readily biodegradable. The DEQ has a low solubility of $2.8 \mu\text{g l}^{-1}$ and hence low bioavailability and low toxicity to sewage bacteria and aquatic organisms. Its use level is about 0.2 g l^{-1} in a domestic wash and it will usually be discharged with an excess of anionic carryover from the wash stage. DEQ is readily and ultimately biodegradable on an OECD (Organisation for Economic Co-operation and Development) (sturm) test [132–134] giving 80% of its potential CO_2 compared to less than 20% for DSDMAC. In this test a pass level is 60% CO_2 evolution.

7.10.1 Silicones in the environment

The silicones are much more easily dealt with in terms of environmental behaviour. The overall inertness and low physiological activity of silicones is well known, so it is not surprising that in environmental terms they have no known ill effects. Silicones enter the waste water from fabric manufacturers' losses in padding and exhaust treatments. Repeated domestic laundering also removes silicones, particularly point-of-sale finishes, and they eventually reach sewage plants. A considerable amount of silicone from antifoams eventually reaches the sewerage system also.

Various investigations [135] have shown that even high levels of silicone in waste water have no adverse effects on activated sludge processes. Silicones combine with particulate matter and are therefore removed and treated as part of the sludge. Concentrations in the treated water are not detectable. In the sludge they remain well behaved also. If disposed of as landfill, the silicone is slowly mineralised [136,137] by, initially, non-biological catalysis and finally by biological degradation. Incineration simply results in finely divided silica, which is no more innocuous than fine sand.

7.11 MEASUREMENT OF SOFTNESS

Many attempts have been made to correlate basic physical measurements with the sensation of softness, and to rate and record softness as perceived by touch. However, softness – though clearly associated with many fundamental physical properties – must remain highly subjective [138–143] because many important parameters in any grand combining formula are themselves not measurable, such as the mood and tactile sensitivity of the assessor [144,145].

If a soft finish is required to impart, say, stitch lubricity to aid making-up, then measurement of friction would be appropriate [146–151]. Similarly, if a lofty handle is required then load and compression characteristics could be measured and optimised. The final manual test by the customer at the point of sale would still be the most important [152–158]. Objective tests also depend on a complex interplay of forces, so that the friction coefficient, for example, depends on the temperature, humidity, phase structure of the lubricant layer and history of the sample. Results obtained by separate laboratories or instruments will therefore only agree up to a point. ‘Softness’ is only one aspect of a general descriptor of any material that can be referred to as its ‘hand’, a term attributed to F T Pierce in 1930. In measuring softness, our ideal aim is therefore to measure several properties and combine them in such a way as to produce a single figure that describes the handle as experienced by a human assessor. This has not yet been achieved except perhaps under strictly limited conditions used by Kawabata [159–163].

For general softness measurement on the very wide range of fabric types encountered in practice, the practitioner will often rely on a combination of a few simple traditional objective and subjective tests. For research and more advanced quality control purposes, several complex schemes have been developed including the Kawabata Evaluation System (KES) and the Fabric Assurance by Simple Testing (FAST) methods.

Simple tests that relate to the handle of a fabric are useful for comparing finish cost-effectiveness, for optimising the application level, or for selection of finishes with particular attributes. Apparatus for simple objective fabric measurement is widely available at low cost. Such tests include frictional properties, bending length and flexural rigidity, crease recovery and drape. Simple subjective tests are even lower in cost. The simplest and undoubtedly the most widely used test involves the ‘expert’ finisher picking up a newly treated swatch and by handling it, making a judgement on whether it is soft enough for the customer. Sometimes a reference standard will be available for comparison. For more accurate work, the somewhat more elaborate paired comparison method is used [164–168].

7.11.1 Traditional softness-related tests

The frictional properties of a fabric are closely related to its final overall hand. Here we are concerned with the fibre-to-fibre friction of the fibres within the yarns that make up the fabric. This is difficult to determine directly but is responsible for the flexibility and strength of the yarns. The yarn-to-yarn friction of adjacent warp threads or knitted loops is equally important. Finally, the fabric-to-fabric or surface friction of adjacent folds of the fabric is obviously intimately related to the perceived softness, drape and smoothness of touch. Many methods have been derived to measure fabric surface friction. The sledge method is useful for research and is simple to set up using a universal tester (Figure 7.9).

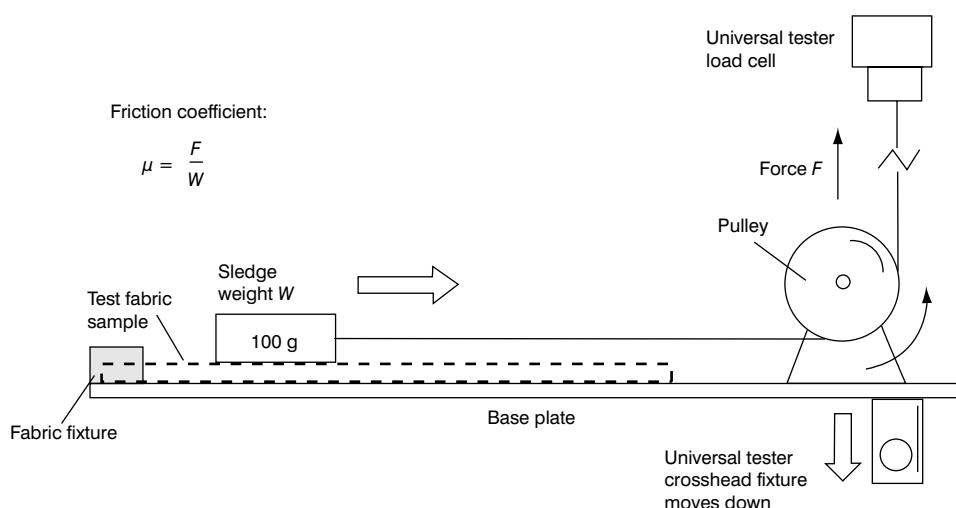


Figure 7.9 The sledge method for measuring friction coefficient

In a typical setup, the block weight is 100 g and a force measuring unit reading up to 100 g is required. A means of altering the speed from 0 to 50 cm sec⁻¹ is essential. The simple relationship due to Amontons ($F = \mu W$), gives the friction coefficient, which ranges from 0 to 1 (Eqn 7.1). This is adequate for comparison of finishes but far more complex treatments of friction and tribology exist for more detailed study.

$$\text{coefficient of friction } (\mu) = \text{force to pull sledge } (F) / \text{weight of sledge } (W) \quad (7.1)$$

If the pulling force is increased gradually until the block just begins to move, the static friction can be calculated. As the speed is increased the friction value will change, usually to a lower value. This is the dynamic friction and it usually levels out under 1 cm sec⁻¹. The ratio of dynamic to static friction is a good indicator of the type of hand. If the static friction is high and

the dynamic friction is low, a characteristic ‘scroopy’ handle will be perceived. Low static and low dynamic friction are associated with a more greasy handle. Finishes that impart a more bulky handle often have similar static and dynamic friction coefficients.

The ability of a fabric to bend under its own weight has obvious aesthetic and comfort connotations and is determined by the internal friction between component fibres, fabric construction and weight [169–171]. The bending length is the simplest measure of fabric drape and is the length of fabric required to bend to a specific angle under its own weight (Figure 7.10).

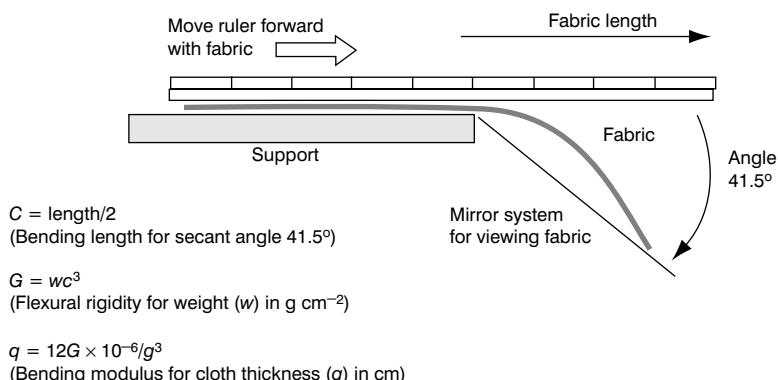


Figure 7.10 Measurement of fabric bending length

Fabrics of differing weight can drape to the same extent because they have differing stiffness. This can be resolved by measuring the fabric weight per cm² (*w*) and with this figure the ‘flexural rigidity’ (*G*) can be calculated from the bending length (*c*) (Eqn 7.2).

$$G = w \times c^3 \quad (7.2)$$

‘Resonant length’ [148,150] has been proposed as a measure of fabric rigidity but it remains of more interest as a research tool. A short length of fabric is firmly supported with one end free to oscillate. The rigidity, *R* (mN m) is calculated from the length (*L*) and the specimen weight, *F* (g m⁻²) (Eqn 7.3).

$$R = 20L^4 \times F \times 10^{-10} \quad (7.3)$$

The crease recovery angle is also simple to measure and is important for assessing the effects of easy-care and durable press finishes. It is often used to evaluate the effects of resin-softener mixtures and correlates with softness. Here, a small sample of fabric (5 cm × 2.5 cm) is folded to form a crease, which is compressed for several minutes under a 1 kg weight. When the sample is

removed, there is a tendency for the crease to open to some extent – this is the crease recovery angle.

In the drape test a circular specimen of fabric is placed on a central support with its edges allowed to drape freely. A light source projects the shadow onto a paper screen. The shadow area expressed as a percentage of the undraped area and gives the drape coefficient.

The most basic method of assessing softness is to simply handle the piece of fabric to obtain an overall impression of its softness. This method is used by expert finishers who soon develop handling techniques and expertise on quality assessment. Many adjectives are used by those involved with fabric handle. These would be difficult to define but the reader will immediately recognise several of them as useful for describing types of handle or for describing differences such as 'more scoopy' or 'more greasy'.

Table 7.13 Some common terms used to describe the feel of textile materials

boardy	kind	sheer
bristly	light	silky
bulky	limp	sleazy
clammy	lively	slippery
coarse	lofty	smooth
cold	loose	snagging
comfortable	lumpy	soft
compliant	mushy	springy
cool	oily	sticky
crisp	papery	stiff
dead	puffy	supple
dry	resilient	textured
even	rich	thready
flannelly	rough	velvety
furry	rubbery	warm
fuzzy	sandy	waxy
harsh	scratchy	wiry
irregular	scoopy	woolly

The appearance of a fabric is also important and visual descriptors are used to convey aesthetic impressions. Adjectives such as 'even', 'lustrous', 'sheer', 'shiny', 'sleazy', 'smooth', 'streaky', 'velvety', 'well covered' and 'wrinkling' have strong visual connotations.

Manual assessment can be made far more objective by using panel testing methods. The simple panel method consists of asking each member to rate each sample against a standard, giving a score. Totalling the scores will quickly reveal any order of preference. Alternatively, each member is asked to place all test samples in the order of softness and again trends are easily seen. Care is needed because not all observers can perceive worthwhile differences or indeed assess the same property. Some guidance on what is sought can help – for example, in the assessment of 'maximum bulk' or 'the most greasy handle'. Operator fatigue is a problem with all subjective methods where large numbers of samples have to be assessed.

A useful ‘one-man’ method of comparing several samples is based on the method of paired comparison. This consists of picking two fabrics at random from a test set, judging which is the best and entering the result in a table, as in Table 7.14. The table may be completed in two halves so that each pair is compared twice – for example, D is compared with E and E is compared with D. Alternatively, sample A is compared with all other samples and a ‘1’ recorded when it is preferred. Sample B is then evaluated in the same way, and so on, until all the samples have been evaluated.

Table 7.14 Typical matrix resulting from a paired comparison test

	A	B	C	D	E	F	G	Row sum
A	0	1	1	0	1	1	1	4
B	0	0	0	1	0	1	1	3
C	0	1	0	0	0	1	1	2
D	1	0	1		1	1	1	5
E	1	0	1	0		1	1	4
F	0	1	1	0	0		1	3
G	0	0	0	0	0	0		0

The total number of times a sample is judged better than the others is its rank score obtained from the row sum. Because of the double comparison a measure of consistency can be obtained. This method can be elaborated considerably and sensible statistics can be applied.

7.11.2 Objective systems for hand measurement

The basic physical properties of fabrics were determined by early workers in the 1920s and 1930s. Several attempts have been made to combine basic physical properties such as friction, compressibility, bending resistance and so on, in such a way as to produce a totally objective measure of fabric hand. Specialised instruments have been proposed that subject the fabric to a single test. However, the most successful approach has been to develop a set of specialised instruments to measure hand-related parameters. The Kawabata KES system and much simpler FAST system (CSIRO) are well known and widely used in research. Nevertheless it must be said that it is the instruments themselves that are of the most interest and a total hand value is rarely determined. Workers more often measure one or more parameters that are relevant to a particular project.

Kawabata recognised the existence of a two-stage process for arriving at a total hand and his system is based on how experts judge hand. This can be summarised as shown in Table 7.15.

Kawabata’s system showed that it is possible to map out a purely instrumental process for getting to a total hand value. Six types of measurement are required, four of which are done on KES-FB instruments. In all, sixteen parameters are produced so that some are derived from others. The basic parameters are listed in Table 7.16.

Table 7.15 Derivation of total hand value

Detect basic properties by handling the fabric	Tensile, Bending, Shear, etc.
Convert to primary hand values (PHVs) in the hand	Koshi (stiffness), Numeri (smoothness), Fukurami (fullness)
Combine PHVs to total hand value (THV) in the mind	'Total hand'

Table 7.16 The 16 Kawabata parameters

I Tensile	1. LT	Linearity of load-extension curve
	2. WT	Tensile energy (gf cm cm^{-2})
	3. RT	Tensile resilience (%)
II Shear	4. G	Shear rigidity (gf cm degree)
	5. 2HG	Hysteresis of shear force at 0.50 shear angle (gf cm^{-1})
	6. 2HG5	Hysteresis of shear at 50 (gf cm^{-1})
III Bending	7. B	Bending rigidity ($\text{gf cm}^2 \text{cm}^{-1}$)
	8. 2HB	Hysteresis of bending moment (gf cm cm^{-1})
IV Compression	9. LC	Linearity of compression-thickness curve
	10. WC	Compressional energy (gf cm cm^{-2})
	11. RC	Compressional resilience (%)
V Surface properties	12. MIU	Coefficient of friction
	13. MMD	Mean deviation of MIU
	14. SMD	Geometrical roughness (μm)
VI Fabric construction	15. W	Fabric weight/area (mg cm^{-2})
	16. T	Fabric thickness (mm)

Having collected the sixteen measurements of the fundamental parameters, translation I is done. This involves correlation of each to primary hand values (PHVs) using a large number of fabric samples (200 samples). The best correlation is found using statistical techniques such as Spearman's rank and so on. The resulting correlation coefficients are summed into the translation process (Eqn 7.4):

$$\text{PHV} = C_o + \sum_{i=1}^{i=16} C_i K_i \quad (7.4)$$

where C_o , C_i and K_i are constant coefficients for a particular fabric [157]. Translation II uses a similar process to convert primary hand values to total hand value. Computer assistance is useful at all stages.

The original work was limited to worsted suiting fabrics so that new correlation equations would be needed for other fabric types. THV seems to be of limited use to research and quality control. Most laboratories with the KES testing equipment limit its use to correlation of measurements of selective properties with subjective assessments. Shear hysteresis, for example, correlates well with the softness of woven cotton towelling treated with cationic softeners (Figure 7.11).

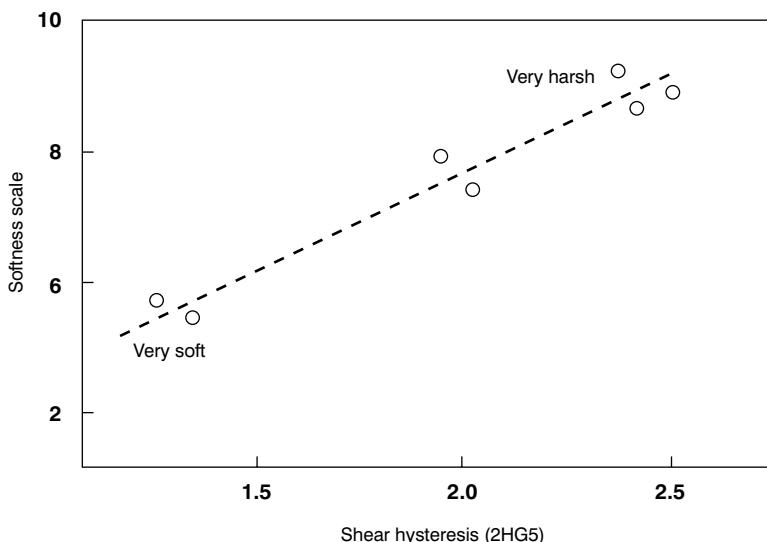


Figure 7.11 Typical correlation of perceived softness with 2HG5 shear hysteresis

The FAST (Fabric Assurance by Simple Testing) system is aimed at affordable quality control. It is very simple and quick to perform. Three custom-made instruments and a test method produce the required results, which relate simply to appearance, handle and performance. The tests are given in Table 7.17.

Table 7.17 FAST parameters which describe fabric quality adequately

FAST 1	Compression	Thickness at load
FAST 2	Bending	Bending length
FAST 3	Extension	Extension at load
FAST 4	Dimensional stability	Relaxation shrinkage

With this system meaningful results can be obtained in about one hour. The set of parameters are the most critical to the overall quality of a fabric for making-up into a final garment and its wear characteristics. Hand, and in particular softness, is only one part of the specification but compression, bending and extension will all correlate usefully with perceived softness. This is

therefore a useful set of data for work on soft finish development and quality control of hand. In a production environment the figures can be plotted on the familiar quality control (snake) charts to give a fabric 'fingerprint' (Figure 7.12).

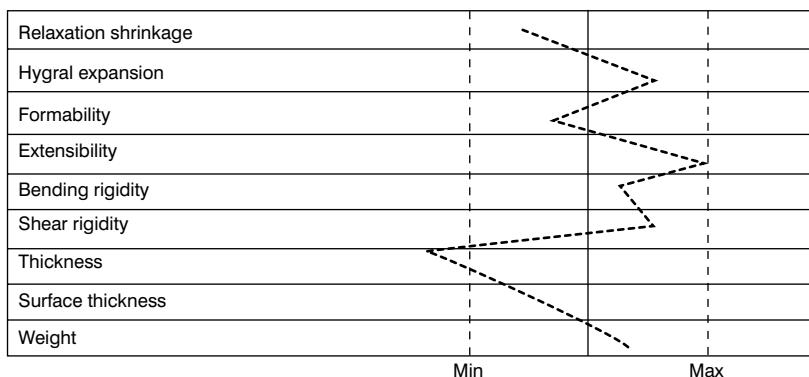


Figure 7.12 A typical FAST control chart

The ubiquitous universal tester, such as the Instron, is still regarded as a necessity in a textile research laboratory. Certain workers [151] have shown that all of the sixteen Kawabata parameters can be measured on an Instron with the appropriate attachments. The approach with recent test regimes is to subject fabrics to more realistic levels of stress akin to the forces encountered in the wear life of the garment and the gentle action of assessing softness by hand. This means operating at much lower forces than are required to rupture the fabric. The Instron tester can cope with this degree of sensitivity as well as tensile breaking strength and other high stress tests. However, it should be pointed out that such forces are approaching the sensitivity and response limit of this type of instrument.

The sixteen Kawabata parameters contain a degree of overlap such that some of the parameters are superfluous. The nine essential parameters derived from five measurements on the universal tester, which will fully describe a fabric, are summarised in Table 7.18.

Table 7.18 Measuring the nine essential parameters on a universal tester

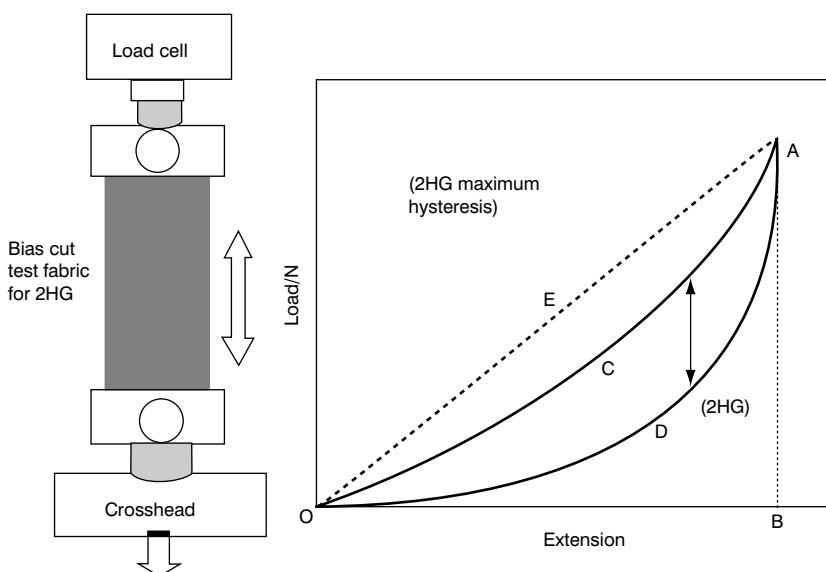
Test	Derived parameters	Method
Tensile	LT WT RT	Plot load against extension
Bending	2HB	Compress a cylinder of fabric
Shear	HG	As tensile but 45° to warp
Compression	RC T	Compress fabric face to face
Friction	MIU SMD	Sledge test static and dynamic

To measure these parameters, the universal tester must be used at low stress settings, which will give results similar to those obtained with the KES instruments. Suitable universal tester settings taken from the same source are given in Table 7.19.

Table 7.19 Low stress settings for the Instron or testometric type of universal tester

	Test				
	Tensile	Bending	Shearing	Compression	Friction
Length (cm)	15	6.35	15	6.35	20
Width (cm)	1.27	3.81	1.27	6.35	10
Speed (mm min ⁻¹)	1	10	1	0.5	10
Chart (mm min ⁻¹)	50	50	50	50	50
Displacement (mm)	2	2#	2	2.5 (g cm ⁻²)	40

In all cases the force (y-axis) is plotted against the displacement (x-axis) giving a typical hysteresis curve from which the parameters can be obtained in the same manner as when using the KES instrument. For example, in the derived tensile test as shown in Figure 7.13, where WT is the area OCABO, LT is WT/area OEABO and RT is the area ODABO/WT as a percentage.

**Figure 7.13** Derived tensile test for WT, LT and RT; 2HG is obtained from a bias tensile test as indicated

It is a simple matter to automate the calculation since most machines are now computer controlled. Visually presented data is easier to assimilate and the nine parameters can be plotted to give a fingerprint of the fabric under test. A circular plot with nine radii is most useful as the example in Figure 7.14 shows.

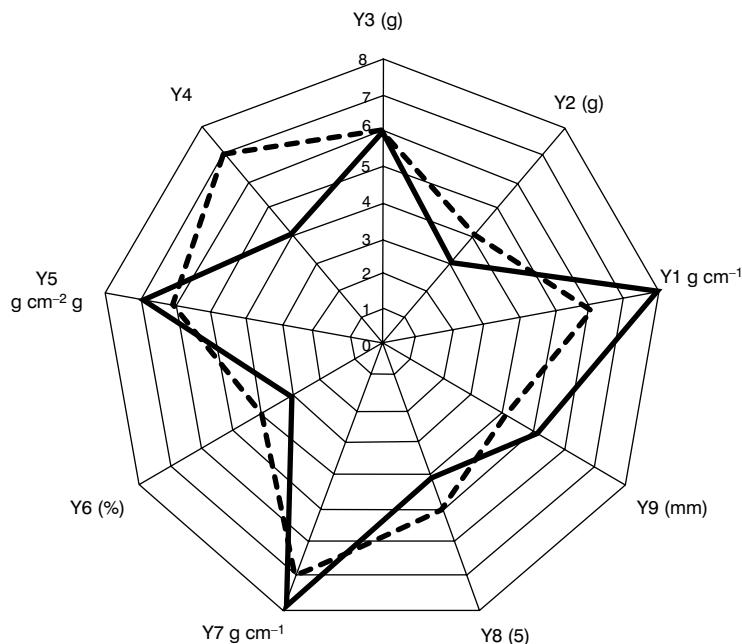


Figure 7.14 Radar plot of measurements taken with the universal tester

More detailed information on all the methods described can be gleaned from the literature, British Standard methods and instrument manufacturers. The test conditions can be easily adapted for different fabric types.

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CHAPTER 8

Antistatic and soil-release finishes

M Pailthorpe and S K David

8.1 ANTISTATIC FINISHES

8.1.1 Introduction

Static electricity is a natural phenomenon and is ever present in the everyday environment. In most circumstances the effects of static electricity may go largely unnoticed either because the build of static charge is too small or because the static charge leaks away rapidly. A gross example of static electricity would be lightning while a lesser, yet very annoying, example would be the clinging of garments. It may well be that life on Earth began as the direct result of a static discharge when a bolt of lightning initiated the formation of the amino acid glycine from ammonia, carbon dioxide and water vapour.

For the most part, the effects of static electricity may be only of nuisance value. Situations do exist, however, where the energy of the static charge stored in the human body might be sufficient to ignite flammable gases, detonate explosives, or damage electronic components.

8.1.2 Generation of static electricity

Static electricity can be generated in a multitude of ways; however, most static generation originates from triboelectric charge generation. In general, the generation of static electricity requires the following conditions:

- (1) contact between two different solid materials;
- (2) separation of those materials.

When two materials come into contact, for thermodynamic reasons there is a redistribution of electric charges at each surface. When equilibrium has been reached, the available electron levels in both materials are balanced. Such an equilibrium can only be achieved when electrical charges move from one material to another. Rubbing, which is referred to as frictional charging, is not necessary but will generally increase charge transfer.

When the two materials are subsequently separated the charge transfer becomes apparent as the electrostatic build-up in the two materials.

Various materials have been ranked in order of their ability to produce a static charge [1–4]. Such rankings produce the so-called triboelectric series, an example of which is given in

Table 8.1 The triboelectric series [1]

Air	+	
Hands	+	
Asbestos	+	
Glass	+	
Mica	+	
Human hair	+	
Nylon	+	
Wool	+	
Lead	+	
Aluminium	+	
Paper	+	
Cotton	+	
Steel	+	
Wood	+	
	-	Rubber
	-	Nickel
	-	Copper
	-	Brass
	-	Silver
	-	Gold
	-	Acetate
	-	Polyester
	-	Celluloid
	-	Orlon
	-	Polyurethane
	-	PVC
	-	Kel-F
	-	Silicon
	-	Teflon

Table 8.1. When a material selected from the top of the table – for example, glass – is brought into contact with a material selected from the bottom of the table – for example, Orlon (Du Pont) – the glass will acquire a positive charge while the Orlon will acquire a negative charge. In this example, some electrons in the glass are at a higher energy level than vacant energy levels in the Orlon. Thus electrons will flow from the glass to the Orlon until equilibrium is reached.

Conservation of charge requires that equal levels of charge are acquired by each material. The further the two materials are separated in the triboelectric series, then the greater will be the magnitude of the electrostatic charge when the two materials are brought into contact and subsequently separated.

The separated surfaces will become either positively or negatively charged depending upon their relative position in the triboelectric series. The polarity of the charge is of little practical importance when considering the safety aspects of static discharges. Obviously, this is because the amount of energy involved in the discharge is the same whether the discharge is from a positively or a negatively charged object. From the point of view of human comfort, however, it is generally found that persons feel more comfortable when their bodies are negatively charged while they may feel nauseous when positively charged. Therefore, when a small build-up of

static charge is expected on the human body, it is best if it is a negative charge. In buildings where the carpets cause the occupants to become positively charged, and those persons feel 'sick', the carpet may have contributed to the 'sick building syndrome'.

The electrical resistances of the contacting surfaces play a very important role in regulating the amount of static charge build-up. Low electrical resistances will allow the charges to run back along the separating surfaces to the point of contact, where they will neutralise each other. On the other hand, when the electrical resistances of the materials are high, the charge is not able to run back along the separating surfaces within the time of separation. In such cases, electrostatic charge generation will be high.

8.1.3 Problems caused by static electricity

Static electricity causes many problems [5–6], some of which can be life-threatening. Normal daily activities, such as walking over a carpet, rising from a chair, removing outer garments, and so on, cause the generation of static electricity.

In the textile industry, especially in dry (low humidity) atmospheres, electrostatic charge generation may cause:

- (1) fibres to be repelled from each other in charged slivers;
- (2) fibres to lap around rollers;
- (3) yarns to 'balloon' and catch on adjacent machinery;
- (4) fabrics to attract lint and dust.

These production-type problems are normally managed in the textile industry by controlling the relative humidity and by the addition of lubricants and antistatic agents, usually in the form of processing oils or dressings.

The adult human body has an electrical capacitance (C) of about 200–300 pF (picofarads) and can be charged to electrostatic voltages (V) as high as 25 kV (kilovolts). The energy, E , stored in a capacitor is given by Eqn 8.1:

$$E = \frac{1}{2}CV^2 \quad (8.1)$$

A simple calculation shows that the human body is capable of storing a static charge equivalent to an energy of about 90 mJ (millijoules). Since the human body is a conductor, the whole of this stored charge may be passed by a spark to a suitable earth.

This amount of energy is capable of giving the person concerned a very painful electrostatic shock when they touch a conductor – such as a metal filing cabinet or door handle – but it is not capable of causing any pathophysiological harm to the person. It has been shown [7] that, for direct currents (DC) up to 50 mA (milliamps) there is usually no pathophysiological dangerous effect. Currents of the order of 300 mA are required for a 50% chance of fibrillation of the heart. From the data provided in Table 8.2 it can be seen that the threshold for shock perception for the average person is about 2.8 kV while painful shocks occur above 10 kV.

Table 8.2 Energy stored in the human body (body capacitance 200 pF)

Electrostatic voltage (kV)	Energy stored in body (mJ)	Comments
0.5	0.025	No noticeable effect
1.0	0.100	No noticeable effect
2.0	0.400	No noticeable effect
2.8	0.784	Threshold of shock perception
5.0	2.500	Noticeable shock
10.0	10.000	Uncomfortable shock
20.0	40.000	Painful shock

Table 8.3 Minimum ignition energy for explosive materials and gases [8]

Material	Ignition energy (mJ)	Reference
Hydrocarbon/air mixture	0.25	[9]
Hydrogen/air mixture	0.02	[9]
Ether/air mixture	0.20	[9]
Lead azide	0.004	[10]
Lead styphnate	0.003	[10]

The real life-threatening danger from static discharges is the possibility that the spark produced may have sufficient energy to ignite explosive materials and gases, even though the person concerned may not sense the electrostatic discharge. Some typical values for the ignition energies of selected explosive materials and gases are given in Table 8.3. By comparing the data provided in Tables 8.2 and 8.3 it can be readily seen that all five explosive materials and gases could be ignited by body energies achieved below the threshold of shock perception.

Fortunately there are two mediating factors that substantially decrease the risk involved, namely:

- (1) from observations of spark profiles it has been found that static discharges from the human body to an earthed conductor consist of a series of sparks – the first spark is, by far, the most energetic and there is strong evidence to suggest that this first spark initiates combustion [11];
- (2) there is a relatively low probability that stoichiometric mixtures of gases and air will be achieved in the workplace.

Wilson [12], in his work for the British Ministry of Defence, examined the ignition of gases with electrostatic discharges through the finger. Wilson chose the correct gas/air mixtures for minimum ignition energies. The published ignition energies for coal gas/air and natural gas/air are 0.03 mJ and 0.3 mJ, respectively [13]. Wilson's results are given in Table 8.4, wherein it can be seen that the minimum *practical* energy required for ignition is substantially higher than the published values. The values of 3.4 mJ for coal gas/air and 18.6 mJ for natural gas/air are respectively 113 and 62 times higher than the published values.

Table 8.4 Ignition of gas/air mixtures with discharges through the finger [12]

Mixture	Body voltage (kV)	Number of trials	Number of ignitions	Energy* (mJ)
Coal gas/air	5.0	100	None	2.7
	5.5	100	None	3.3
	5.6	100	1	3.4
	6.0	60	3	4.0
	7.0	10	2	5.4
Natural gas/air	5.0	100	None	2.8
	7.0	100	None	5.4
	9.0	100	None	8.9
	12.0	100	None	15.8
	13.0	100	2	18.6

* The capacitance of the test subject was 220 pF

With the increasing use of computers, both in the workplace and at home, it is important to realise that computers, and their components, are highly susceptible to electrostatic discharges. The data provided in Table 8.5 clearly shows just how sensitive electronic components are to the effects of static electricity. Again, when one compares the data provided in Tables 8.2 and 8.5, it can be readily seen that a computer operator could accidentally damage the machine without realising that they were electrostatically charged. As shown in Figure 8.1, the electrostatic field strength surrounding an electrostatically charged person can, itself, be sufficient to damage electronic components. For these reasons, computer manufacturers place very strict limits on the levels of static electricity permissible in computer rooms.

Since static electricity can have such a major impact on all aspects of modern life, 'Codes of Practice for the Control of Undesirable Static Electricity' have been established in most countries – for example, in Great Britain [14–15] and Australia [5].

Table 8.5 Reported susceptibility ranges of various devices exposed to electrostatic discharge from a person or electronic equivalent [1]

Device type	Range of ESD susceptibility (V)
VMOS	30–1800
MOSFET	100–200
GaAsFET	100–300
EPROM	100
JFET	140–7000
SAW	150–500
OP-AMP	190–2500
CMOS	250–3000
Schottky diodes	300–2500
Film resistors (thick, thin)	300–3000
Bipolar transistors	380–7000
ECL	500–1500
SCR	680–1000
Schottky TTL	1000–2500

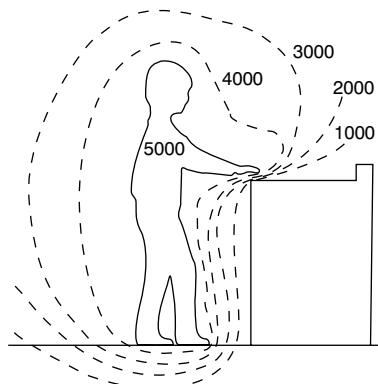


Figure 8.1 ‘Typical’ electric field surrounding a statically charged person; note the concentration of the field lines around the fingertips [1]

8.1.4 Measurement of electrostatic propensity

There is a large variety of test methods employed world-wide for the measurement of electrostatic propensity. These methods may be divided into three main categories:

- (1) measurement of cling time;
- (2) measurement of electrostatic voltage or charge;
- (3) measurement of electrical resistance or resistivity.

There is no doubt that the electrical resistance methods are the most reliable and reproducible and hence are the most commonly used methods.

Cling time

Cling time measurements attempt to duplicate the clinging behaviour of clothing on the human body. Most people agree that clinging garments are uncomfortable to wear because they may ride up the body. In addition, the clinging of undergarments spoils the drape of other clothing worn over them [16].

There are several methods for testing the clinging behaviour of fabrics. These methods make use of the principle of induction wherein a charged insulating material is attracted to a conducting (metal) surface. The methods do, however, employ different methods of charging the samples.

A widely used example of such a test is the AATCC Test Method 115 – 1989, Electrostatic Cling of Fabrics: Fabric-to-Metal Test [17], which integrates the effects of fabric weight, stiffness, construction, surface character and antistatic finish application on the tendency of fabrics to cling.

In this test, the fabric specimen is first charged in a standardised manner while resting on a polished stainless steel plate. The plate is then inclined at 70° to the horizontal and earthed. The strip is pulled away from the metal plate after each 30 s period and the total time that elapses

before the fabric ceases to cling to the metal plate is recorded. Testing is discontinued if the clinging time exceeds 10 min.

The metal plate is used to simulate the problems of clinging between charged garments and the human body. Fabric-to-metal clinging times, however, cannot be related directly to fabric-to-body clinging times for different individuals [17].

Electrostatic voltage/charge build-up and decay

Test procedures for both fabrics and carpets have been devised that measure the generation of electrostatic charge either on the textile or on the test subject. The time for the electrostatic charge to decay may also be measured. The time of decay is usually expressed as the half-life because the decay profile for electrostatic charge is generally exponential.

The electrostatic voltage or charge on a material or person may be measured using an electrostatic voltmeter or Coulomb meter. The best known test of this type [18] determines the electrostatic propensity of carpets by measuring the electrostatic potential on a test subject walking on carpets under a specified set of conditions.

In the case of carpets, the pass/fail criteria will depend upon the application. If the requirement is for 'human comfort' then an electrostatic potential of less than 2.8 kV on the test subject (Table 8.2) should ensure that persons walking over the carpet will not experience discomfort. However, if the carpet is to be in a computer room then much stricter criteria apply (Table 8.5) and an electrostatic potential of less than 1 kV might be specified.

Electrical resistance/resistivity

The measurement of electrical resistance/resistivity is the most objective way of determining the electrostatic properties of textile materials. Two measures of electrical resistance can be made, namely:

- (1) the surface resistance;
- (2) the bulk (or through) resistance.

Surface resistance is measured between two electrodes placed a specified distance apart on the same surface, while the bulk resistance is measured between two electrodes placed on the face and back of the material. Most standards require that the electrical resistance should be measured under an applied voltage of 500 V using an Ohm meter or electrometer with an input impedance of not less than $10^{14} \Omega$ [19–20].

Electrode geometries are essentially of three types, being rectangular [21], circular [22–23] and circular/annular [14–15,19]. In the latter case, the surface resistivity is calculated using the equation:

$$\rho = \frac{2\pi R}{\ln(r_2/r_1)} \quad (8.2)$$

where R = measured resistance (in Ω)

r_1 = radius of the inner electrode (in mm)

r_2 = inner radius of the outer electrode (in mm)

The pass/fail criteria depend upon the area of application. Some typical pass/fail criteria are:

- (1) domestic clothing (prevent clinging): $R < 1.0 \times 10^{12} \Omega$ [21]
- (2) industrial clothing (hazardous areas): $R < 5.0 \times 10^{10} \Omega$ [14–15]
- (3) computer room floors: $5.0 \times 10^5 \Omega < R < 2.0 \times 10^{10} \Omega$ [23–25].

The lower limit of $5.0 \times 10^5 \Omega$ for computer rooms is to protect the operators from accidental fatal electrical shock.

Wilson [26] studied the static behaviour of some 27 carpets under various atmospheric conditions and reported reasonable correlations between $\log(\text{bulk resistance})$ and $\log(\text{surface resistance})$ whereas the correlations between $\log(\text{bulk resistance})$ and body voltage were poor.

Later, Pailthorpe [27] re-examined the correlation between body voltage results and electrical resistance results for over 180 carpets. Figure 8.2 shows the correlation between $\log(\text{electrostatic propensity})$ and $\log(\text{bulk resistance})$ for a wide range of carpets. It can readily be seen that, while a trend exists, the correlation is poor. Pailthorpe [27] concluded that, for the time being, the recommended upper limit of $2 \times 10^{10} \Omega$ appears to be a suitable compromise for practical implementation with a satisfactory safety margin.

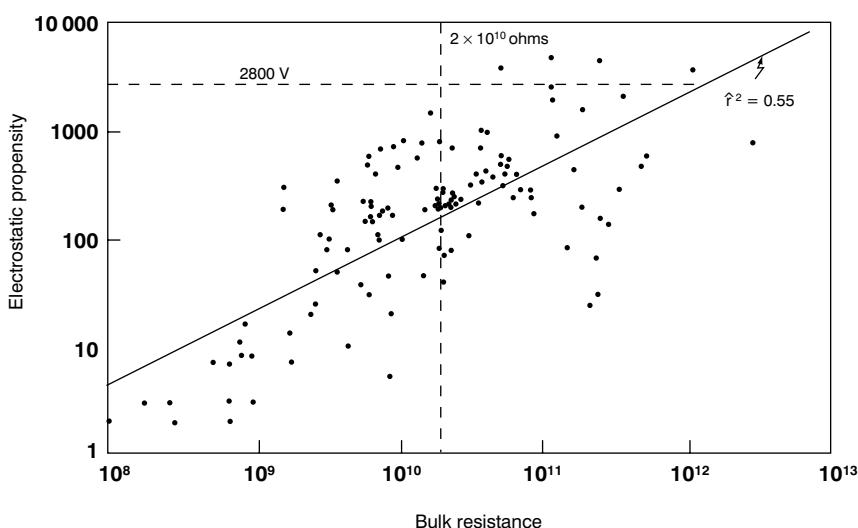


Figure 8.2 Log(electrostatic propensity) versus log(bulk resistance) for the AATCC 134-1975 walk test in leather-soled shoes [18]

8.1.5 Methods for the control of static electricity

Effect of moisture

It is well known in the textile industry that the relative humidity, and hence the moisture regain (content) of textile fibres plays a very important role in the reduction of static electricity. Temperature plays a less important role. Virtually all textile fibres (with the obvious exception of metal and carbon fibres), when completely dry, have very high electrical resistances. However, as the relative humidity increases, the fibres absorb moisture and their electrical resistance decreases [28] with a consequent reduction in electrostatic charge generation [29].

Synthetic fibres

The manufacturers of synthetic fibres are able to incorporate antistatic agents into the spinning dope or polymer melt prior to the extrusion and drawing of the filaments. The ranges of internal antistatic agents suitable for this purpose have been reviewed by Nahta [30] and Brown and Pailthorpe [31]. Antistatic fibres and filaments prepared in this way have the advantage that their antistatic properties have good fastness to washing and rubbing.

Fibres with internal antistatic additives are believed to function by providing a conducting layer in the form of moisture and ions at the fibre surface by the slow diffusion of the antistatic agent to the surface [5].

Blending with conductive fibres

Conductive fibres, such as metal (stainless steel, aluminium, and so on) and carbon fibres, can be blended with natural and synthetic fibres, before spinning, to produce an antistatic yarn. For most applications, satisfactory effects can be achieved with about 0.5–2.0% wt/wt of conductive fibre in the blend.

Antistatic finishes

The electrical conductivity of textile fibres, yarns and fabrics can be substantially increased by the application of many classes of chemical compounds. The general requirements for antistatic finishes are as listed below. The antistatic agent must:

- (1) be easy to apply – for ease of application the antistatic compounds must be readily dilutable in water and suitable for normal aqueous application procedures such as exhaustion, spraying, kiss-roller application and padding;
- (2) have no effect on the dyeing – in particular, the antistatic compound must not affect dye fastness or the intended colour;
- (3) not decompose, vaporise or diffuse into the interior of the fibre during processes such as drying, curing or setting;
- (4) have low toxicity;
- (5) not cause yellowing;

- (6) not cause an increase in soiling;
- (7) have good wash fastness and abrasion resistance.

Table 8.6 gives a number of examples of the chemical classes that are suitable for use as antistatic agents. Even though this list was first produced in 1975 [32], variants of the same chemical classes are still currently used as antistatic agents.

It can be readily seen from an examination of the chemical structures provided in Table 8.6 that the compounds can be divided into two broad classes, namely polyglycol derivatives and ionic compounds.

Garvanska and coworkers [33] have shown experimentally that an ion-transport mechanism is responsible for the transfer of electrical charges in polyglycol compounds. They further showed that aromatic groups in polyglycol compounds markedly increase the antistatic effect of the polyglycol moiety while increasing the number of ethoxy groups, and the presence of alkyl groups at the nucleus decreases the antistatic effect.

Lewis and Pailthorpe [34] examined the electrical resistance of wool treated with a range of polyethylene glycols (PEGs) of varying molecular weight. It was found that polyethylene glycols had a significant effect on the electrical resistance of wool, especially for PEGs of molecular weight 600. Furthermore, combinations of PEGs with cationic compounds, whether in mixtures or chemically combined, were especially effective in reducing the electrical resistance of wool.

The most widely used class of compounds for temporary antistatic finishes are the quaternary ammonium derivatives of fatty compounds [35]. Quaternary ammonium compounds normally impart very good antistatic protection at levels as low as 0.25% on weight of fibre. When one or more of the alkyl groups present on the quaternary nitrogen atom is substituted with a poly(oxyethylene) group, the water solubility of the antistatic compound is improved.

Anionic compounds are also used as antistatic agents, especially in 'spin-finishes'. Some typical examples of anionics used are mixtures of mono- and diesters of phosphoric acid, and semiester salts of alkylphosphonic acids [35].

Cellulosic materials: Cellulosic materials are generally considered to have a low static propensity and hence fabrics such as cotton are the preferred materials for use in applications where electrostatic discharges must be avoided – for example, for armourers, refuellers, and so on.

Cotton fabrics have a low surface resistance at 65% relative humidity (r.h.), being in the range 10^9 – 10^{10} ohms per square [12] increasing to 10^{12} – 10^{13} ohms per square at 20% r.h. Hence, for the processing of cotton, antistatic agents are rarely used because humidity control is usually sufficient. Antistatic agents have been used in the ginning of cotton [36] while alkylolated polyurethane resin compounds [37] have been applied as antistatic agents to cotton fabrics.

Protein materials: Provided the relative humidity remains above 50%, protein materials can be considered to exhibit 'low static' for normal domestic and commercial use. For specialised applications, where static build-up must be controlled, protein materials require an antistatic treatment.

In spite of their high moisture regain, wool fabrics have a high surface resistance even at 65%

Table 8.6 Chemical classes of antistatic finishes [32]

Chemical type	Indicative formula
Polyglycols	$H-(CH_2CH_2O)_xH$
Fatty polyglycol esters	$R-C(=O)-O-(CH_2CH_2O)_xH$
Fatty amide polyglycol ethers	$R-C(=O)-NH-(CH_2CH_2O)_xH$
Ethoxylated amines	$R-N(H)-(CH_2CH_2O)_xH$
Amine oxides	$\begin{array}{c} R_1 \\ \\ R_2-N \rightarrow O \\ \\ R_3 \end{array}$
Ammonium salts	$\left[\begin{array}{c} R_1 \\ \\ R_2-N-R_4 \\ \\ R_3 \end{array} \right]^+ X^-$
Quaternary ethoxylated amines	$\left[\begin{array}{c} R_1 \\ \\ R_2-N-(CH_2CH_2O)_xH \\ \\ R_3 \end{array} \right]^+ X^-$
Quaternary fatty amide amines	$\left[\begin{array}{c} O \\ \\ R_1-C-NH-R_2-N(R_4)R_3 \\ \\ R_5 \end{array} \right]^+ X^-$
Alkyl polyglycol sulphates	$R-O-(CH_2CH_2O)_xSO_3^-M^+$
Phosphoric esters	$O=P\equiv(OR)_3$
Phosphoric esters of ethoxylated alcohols	$O=P\equiv[O-(CH_2CH_2O)_xR]_3$
Ammonium salts of phosphoric esters	$\left[O=P(O-R_1)(O-R_2) \right]^- \left[H_2=N(R_1)R_2 \right]^+$
Quaternary polymers	e.g. vinyl pyridine
Quaternary copolymers	e.g. vinyl pyridine and vinyl pyrrolidone

r.h. Lewis and coworkers [25] have reported values of $6.0 \times 10^{12} \Omega$ while Brown and coworkers [38] reported resistances in the range $10^{13}\text{--}10^{14} \Omega$ depending upon the wool and fabric type. At low relative humidities (20–25%) it is not uncommon to measure negative body voltages of 10.0–17.0 kV in AATCC Test Method 134 [39].

Aliquot 336 (trioctylmethylammonium chloride) has been shown to be very effective [40–42] in decreasing the electrostatic charge build-up caused by walking on wool carpets. Since Aliquot 336 is insoluble in water, it has been marketed as a dispersion under the trade name Disperstat W (Stevenson Bros Ltd.) [43]. Treatment levels of 0.8–1.2% w/w reduce body voltages to zero; however, further addition of Aliquot 336 causes the body voltage to increase to +3.0 kV. This result suggests an overall triboelectric effect that varies with the extent of masking of the wool surface [39]. This proposal is supported by the fact that the application of Disperstat W to wool fabrics does not significantly decrease the electrical resistance of wool [25].

The International Wool Secretariat has outlined the range of antistatic agents available for wool yarns, fabrics and carpets [44]. Brown and Pailthorpe [38] have shown that quaternised ethoxylated amines with polyethylene oxide chain lengths of molecular weight 600 are very effective in decreasing the electrical resistance of wool fabrics.

Silk fibres can be made antistatic by grafting the fibres with glycidyl methacrylate, styrene and methyl methacrylate [45]. After degumming, silk treated with 6% alkyl trimethyl ammonium chloride for 30 min at 40–45 °C attains antistatic properties [46].

Acrylic materials: Acrylic tow can be made antistatic by treatment with an antistatic agent based upon ethoxylated diethylene triamine [47]. Antistatic agents based upon cationic agents [48] or compositions of polymeric cationic agents combined with anionic surfactants [49] are suitable for the processing of acrylics.

Polyamide materials: Polyamide fibres/filaments can be made antistatic by the application of antistatic agents based upon ammonium salts, quaternary ethoxylated amines and quaternary fatty amide amines. More permanent antistatic effects have been achieved with a variety of treatments including silver coating [50–51], grafting with polyacrylic acid followed by conversion to the sodium salt [52] and applying a block copolymer of poly(ethylene oxide) and poly(methyl methacrylate) [53].

Polyester materials: Sodium hydroxide (caustic soda) treatments, which are normally employed in the de-weighting of polyester fabric, and to modify the handle after heat setting, are claimed to decrease the static problems on polyester [54–57]. After the sodium hydroxide treatment, the polyester can be treated with a solution of a reactive polyethylene glycol of molecular weight around 1000 to achieve an antistatic finish that is fast to 30 washings [58].

Quaternary ammonium salts significantly decrease the surface resistance of polyester [59]. Quaternary ammonium functional silicon compounds [60] also provide significant reductions in surface resistance. Other antistatic agents for polyester that have been claimed to achieve wash-fast antistatic properties include block copolymers containing a polyester segment and a polyoxyalkylene segment [61–62], esteramides [63] and various acrylic derivatives [64–67].

8.1.6 Application methods

In general, there are two principal methods for the application of antistatic agents to textile

materials. During the processing of fibres, slivers, rovings, and so on, antistatic agents are applied by spray application of an aqueous solution. Spray application techniques can be used for the *in situ* treatment of carpets, though antistatic agents can also be applied to carpets *in situ* using conventional carpet cleaning/shampooing equipment.

Fabrics are generally treated with antistatic agents by padding the fabric with an aqueous solution of the selected antistatic agent, followed by drying in a stenter or other suitable oven.

8.2 SOIL-RELEASE FINISHES

8.2.1 Introduction

The purpose of soil-release finishing for textiles is to facilitate the removal of soiling matter during laundering of the item. With the advent of special fluorocarbon finishes for textiles, a soil-repellent property has also been introduced into this class of finishing treatments. A detailed review on this subject has been presented by Kissa [68] and summarised by Cooke [69]. This section therefore serves to provide an overview and update of the current literature.

Soil deposits on textile materials are usually of complex composition, containing both oily and particulate matter. Particulate soil may be clay, soot or metal oxides. Street dirt, for instance, contains several components such as peat moss, cement, silica, Raolin clay, mineral oil, carbon black and iron oxide [70]. Oily soils are typically fatty materials secreted by the body. Most common within this category is shirt collar dirt consisting of skin cells, sebum and eccrine sweat. Various other substances that contribute to the soiling of textiles include stains from oily liquids and food residues.

The mechanism of soiling is influenced by various factors associated with the transport and adsorption of soil onto a textile. Electrostatic attractive forces are primarily responsible for the deposition of air-borne particulate soil onto curtains or upholstery. In contrast, shoe dirt ground into a carpet surface, or soiling of a shirt collar or sofa by oily soil, arises from direct contact, exacerbated by rubbing action. Finally, cross transfer of soil or redeposition on the same fabric may take place during laundering of textile items. This last mechanism of soil transfer is referred to as 'wet soiling' (Section 8.2.4).

Irrespective of the method of soil transfer onto a textile, the main cause of soiling is considered to be due to subsequent adhesion of the soil onto the fibre surface [68]. This is effected mostly by van der Waals forces, which operate only over very short distances. The strength of this interactive force will depend on the nature of the soil and of the substrate, and the area of contact between the two. Kissa [71] has shown that iron oxide adsorption on polyester and cotton fabric increases with greater applied pressure; the soil particle is considered to deform under pressure and conform to the shape of the textile surface.

8.2.2 Detergency

The success of any soil-release treatment is intimately associated with the removal of soil by detergent action. A brief outline of the principles of detergency is therefore warranted here.

Detergency refers to the physico-chemical action of cleaning a solid surface by an aqueous solution of surfactant(s). It is accomplished by a combination of effects involving the alteration of interfacial tensions and emulsification of the removed soil. Oily and particulate soils, being quite different in their physical and chemical characteristics, are considered to be removed by entirely different mechanisms, as outlined below.

Removal of particulate soil

The removal of particulate soil is initiated by intimate contact between the detergent liquid (L) and fibre (F) and soil (S). The work required to cause removal of the soil from the substrate may be defined as:

$$W_{FS} = \gamma_{LF} + \gamma_{LS} - \gamma_{SF} \quad (8.3)$$

where γ_{LF} = interfacial tension between liquid and fibre

γ_{LS} = interfacial tension between liquid and soil

γ_{SF} = interfacial tension between soil and fibre

The adsorption of surfactant at the liquid–fibre (LF) and liquid–soil (LS) interfaces, in decreasing γ_{LF} and γ_{LS} , will consequently decrease the work (W_{FS}) required to cause removal of the soil from the fibre.

Hence, effective solvation of the fibre and soil particle surfaces by the surfactant solution facilitates separation of the soil from the fibre. The dislodged soil particle is then able to move freely into the bulk phase of the wash liquor, aided by mechanical action. The kinetics of particulate soil removal, which is considered to be essentially first order, is discussed in detail by Kissa [68].

Removal of oily soil

The removal of oily (liquid) soils is considered to occur via the roll-up mechanism [72]. The force responsible for the roll-up of oil is defined as the resultant, R , of the interfacial tensions (Figure 8.3):

$$R = \gamma_{SF} - \gamma_{LF} + \gamma_{LS}\cos\theta_d \quad (8.4)$$

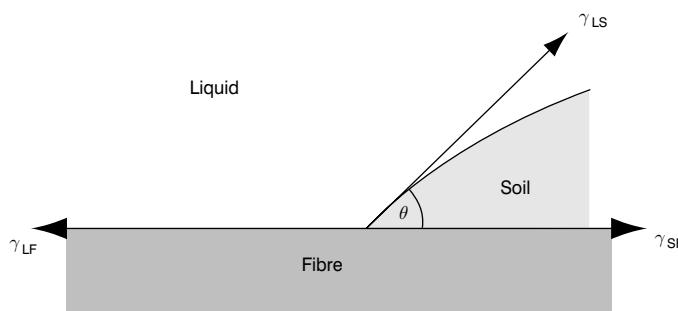


Figure 8.3 Water and fibre interfaces of oily soil (adapted from [68])

This mechanism is facilitated by preferential wetting of the fibre by the detergent liquid. As the dynamic contact angle, θ_d , approaches 180° , $\cos\theta_d$ approaches -1 , and the oily soil is thus rolled-up into a spherical ball, which is readily detached from the substrate (Figure 8.4), aided by mechanical agitation.

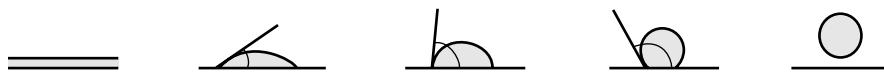


Figure 8.4 Roll-up mechanism

Kissa [73] has investigated the rate of oily soil release under conditions that promote spontaneous roll-up, and found that three consecutive steps are clearly definable. Initially, an induction period exists during which detergent solution diffuses to the soil–fibre interface. Separation of the soil from the fabric then takes place, followed by a final period during which further soil removal is very slow. The induction period and the extent of oily soil removed can vary greatly depending on the type of oily soil and substrate, as depicted in Figure 8.5.

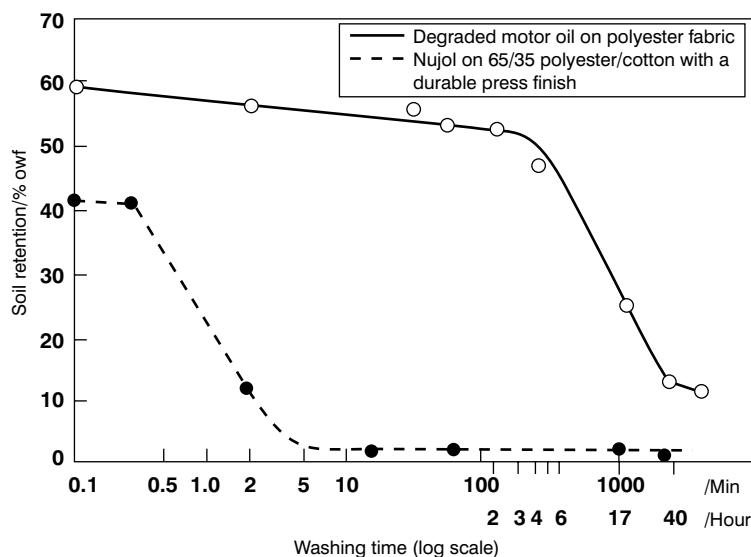


Figure 8.5 Release of oily soil under conditions emphasising spontaneous release [73]

Soil redeposition

During laundering, soil dislodged from a fabric may be redeposited on the same fabric or a different fabric via the detergent solution. The extent to which this occurs is determined by complex interactions between all the variables involved – for example, washing conditions, detergent solution, soil type, fibre type and fabric geometry [68]. The prevention of soil redeposition, or effective suspension of soil in the detergent solution, is an essential part of the overall detergency process. One of the most commonly used anti-redeposition agents in

commercial detergent formulations is sodium carboxymethylcellulose (SCMC). Prevention of soil redeposition is considered to involve the formation of electrical double layers of the negatively charged fibres coated with SCMC and detergent-coated soil particles, which results in electrostatic repulsion between the two. This reagent is reasonably effective for the laundering of cotton fabrics, whereas cellulose ethers are better utilised for synthetic textiles.

8.2.3 Factors affecting soiling and soil release

Nature of the soil

One of the most frequently encountered soils requiring removal during laundering is sebum (shirt collar soil). This soil type contains mostly fatty acids, triglycerides and fatty alcohols, which are predominantly removed at wash temperatures below 50 °C. However, if allowed to remain on the fabric for some time, the fatty acid component has a tendency to oxidise (or age), forming substances of higher viscosity that require higher temperatures for effective removal. Oxidised sebum remaining on the fabric during laundering can then exacerbate soiling by entrapping particulate soil from wash liquors or during fabric use.

Kissa [71] quantitatively assessed the effect of a liquid film on the removal of particulate soil from polyester and cotton fabrics. Liquids of varying viscosity and dielectric constant were selected in order to simulate various components of oily soil. It was found that soiling increased with the ratio of viscosity over the dielectric constant of the liquid film (Table 8.7).

Table 8.7 The effect of liquid coatings on the adsorption of soil on fabrics^a

Liquid on the fabric	Fe_2O_3 Cotton PET ^b		Viscosity (η)	Surface tension (γ)	Dielectric constant (ϵ)	η/ϵ
Nujol	2.90	3.19	167.7	31.0	2.10	79.8
Oleic acid	2.66	2.93	32.8	32.2	2.46	13.3
Glycerol	1.86	2.54	356.0	63.9	42.5	8.4
Dimethyl phthalate	1.52	2.46	11.3	41.4	8.5	1.3
None	1.53	2.15				

a Fabrics coated with a liquid film (2% o/wf), rotated with 5% owf iron oxide in an Accelerotor at 1500 rpm for 30 seconds (adapted from [71])

b Polyester

A similar trend was observed where both hydrophobic (polyester) and hydrophilic (cotton) fibres were examined, using iron oxide or synthetic soil as the particulate matter. The viscosity is considered to affect the resistance of the composite oil-particle to removal by shear stress, while the effect of the dielectric constant on soil adhesion is unclear. Kissa [71] further stated that when a particle is forced into a liquid film, wettability of the particle by the liquid is apparently not a prerequisite for adhesion.

Obendorf [74] has qualitatively examined the effect of multi-component soiling on cotton/polyester fabrics using electron microscopy as a means of detection. Irrespective of the soiling sequence (oil followed by clay particles, or in the reverse order) X-ray maps of the washed fabric specimens, tagged with osmium tetroxide (OsO_4), indicated that particulate soil was entrapped within sheaths of oil, resulting in a composite soil tenaciously bound to the fibre. This type of multi-component soil was removed less effectively from cotton/polyester blends than either clay or oil alone.

Nature of the substrate

It is well known that soil removal is far more difficult from hydrophobic synthetic fibres such as polyester than from hydrophilic natural fibres. Kissa [68] has reviewed the early literature that led to the understanding that hydrophobic finishes such as durable press (DP) treatments, silicone and conventional fluorocarbon finishes on cotton fabrics all result in greater soil retention during washing than in the case of untreated cotton fabric. In general, fabrics with low moisture regain, or treatments that decrease fibre regain, increase the tendency for soil retention [75]. Conversely, the ease of soil removal improves as the hydrophilic nature of a fabric (or moisture regain) is increased.

The extent of soiling is also heavily dependent on the area of contact between the soil and the substrate. Hence, fibre geometry and yarn and fabric parameters play a major role in the soil-release behaviour of any given fabric. Electron microscopy techniques [74,76] have shown oily soil to be located within the interfibre capillaries of yarns, on the surface of the yarn and embedded in crevices formed between adjacent fibres within the yarn. Additionally, with cotton fibres soil may be located within the lumen, crenulations and secondary wall of the fibre. Particularly in the case of damaged cotton, it is known that through repeated laundering and wear cycles sebum can wick rapidly into the fine capillaries of the fibre and into the cotton lumen. This degree of soiling, as found on shirt collars for instance, is especially difficult to remove during laundering.

Tomasino and Joyce [77] have investigated the role of yarn capillaries on the 'release point' of oily soil from polyester fabrics. The release point was recorded as the detergent surface tension required to release soil droplets spontaneously from a laboratory soiled fabric. The droplet release was observed under the microscope in solutions of varying surface tension. Highly bulked and stretched yarn samples finished and soiled to the same extent were compared; while the finished bulked (or relaxed) yarn released soil at approximately 43 dynes cm^{-1} , no release was observed for the finished stretched (or flat) yarn even in solutions of surface tension as low as 15 dynes cm^{-1} . Furthermore, the hydrophilicity of the finish used did not seem to affect the release point results significantly. These workers attributed this difference to the smaller size of the void spaces in the stretched yarn sample. This reasoning was also supported by the observed size of the released oil droplets from a textured yarn knitted fabric, which were larger than those from fabrics knitted or woven from flat or spun yarn. This evidence therefore helps to explain why soil-release treatments on fabrics made from unbulked, continuous flat or spun polyester staple yarns do not

perform as well as on textured knitted fabrics. Oily soil residing in the smaller capillaries of the stretched samples is considered to be more difficult to displace, due to the inability of detergent solution to successfully penetrate the small capillaries, and the higher capillary pressure involved in transporting the oil droplet to the yarn surface. Similarly, the degree of yarn twist within a fabric construction directly affects the interfibre distance and will consequently determine the rate at which a liquid will be transported by capillary action to the fabric surface.

Effect of fabric finishing

Extensive work carried out on the effect of various finishing treatments and soil characteristics on the wet soiling behaviour of fabrics has been detailed by Kissa [68]. Wet soiling is the process of soil deposition onto fabrics from aqueous media.

Berch and coworkers [78] examined the extent of wet soiling with both oily (carbon black/oleic acid) and hydrophilic (iron oxide) soils, on finished cotton. They found a linear correlation between the extent of soiling by the oily soil and the hydrophobicity of the fabric. (The extent of soiling was determined by the K/S value, and the cosine of the contact angle of oleic acid on a film of finish in water was used as a measure of the hydrophobic properties of the finish.) The extent of soiling by the hydrophilic soil, iron oxide, on the other hand, was observed to be relatively constant regardless of the hydrophobicity of the finish. These researchers also showed that wet soiling values decrease with increasing hardness of the finish [79].

Durable press cotton fabrics generally show a greater propensity towards soiling than untreated cotton. Fiebig and Rezk [80] have investigated the extent of soiling with increasing amounts of crosslinking N-methylol finishes such as dimethylolethyleneurea (DMEU). They found that soiling clearly increased with decreasing moisture regain of the treated cotton, particularly in the region from 5 to 4.3%. This corresponded with a nitrogen content increase, from the crosslinked finish, of 1.6 to 3.4% owf, respectively.

Hebeish and coworkers [81] have also summarised the main factors concerning durable press finishing on the soiling and soil-release characteristics of cotton fabric. These workers found that the finishing treatments significantly decreased the ability of cotton fabric to resist both aqueous and oily soiling, the diminished soil-release behaviour being more pronounced in the latter case. Increasing the concentration of the durable press finish was found to increase soiling and to decrease the soil release for both aqueous and oily soil systems. The type and concentration of catalyst, the softening agent and the curing temperature were further found to affect the degree of soil release, without affecting the degree of soiling. The nature and concentration of the catalyst, as well as the curing temperature, undoubtedly affect the harshness of the finish, while the softener coating might be expected to impede soil removal by entrapping soil particles and/or reducing the tendency of water to diffuse adequately into the fabric interior.

8.2.4 Soil-release finishing treatments

Soil-release treatments are generally polymeric finishes topically applied to fibres, yarns or fabrics

for the purpose of increasing their hydrophilic character. Soil deposition by electrostatic attraction is thereby minimised and soil release during laundering of the item is improved. Additionally, other treatments – such as alkaline etching of polyester and, more recently, plasma treatment – have also been investigated for their anti-soiling advantages.

Soil-release finishes are generally amphiphilic polymers, containing both hydrophilic and lipophilic groups. The hydrophilic/lipophilic balance is critical in terms of achieving appropriate soil-release activity. Other factors – such as water solubility of the finish, spreading on the fibre surface and hardness versus pliability of the finish – also determine overall performance.

These finishes may be conveniently classified [68] according to the hydrophilic component within the polymer, generally composed of carboxyl, hydroxyl or oxyethylene groups. Alkyl or aryl groups linked via ester or ether bonds along the polymer backbone constitute the lipophilic component. Additionally, reactive groups may also be incorporated in order to render the finish more permanent, by forming crosslinks, or pendent lipophilic groups may serve to anchor the soil-release polymer to the surface of thermoplastic fibres when softened by heat.

Carboxyl group polymers

Soil-release polymers in this class are commercially applied in conjunction with durable press treatments on cotton and cotton/polyester blend fabrics. Typically, they are copolymers of acrylic (or methacrylic) acid and ethyl acrylate as shown in Figure 8.6.

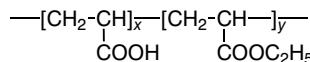


Figure 8.6 Acrylic acid–ethyl acrylate copolymer

The acrylic acid component must be maintained above 15% for adequate hydrophilic character and no greater than 25% to ensure durability to washing. The polymer molecular weight desired is approximately 100 000, also for adequate durability to washing, and about 2.5% polymer solids (owf) is required for optimum soil-release performance [82]. The soil-release properties of these acrylic polymers are related to their anionic character in aqueous alkaline detergent. Formation of the carboxylate anion under alkaline conditions imparts a negative surface charge thus decreasing the extent of wet soiling by negatively charged soil particles in the detergent solution. Additionally, their tendency to swell in alkaline media has been postulated as a mechanism for soil release [83]. The various factors affecting soil-release performance during the combined application of soil-release and durable press treatments are discussed in Section 8.2.5.

Oxyethylene or hydroxyl group polymers

Non-ionic oxyethylene adducts of polyesters, polyamides, polyurethanes, polyepoxides and polyacetals are important soil-release finishes for synthetic fabrics, particularly polyester. They

may be applied in a similar way as disperse dyes to polyester, although requiring lower temperature conditions. The effect of varying the length of the polyoxyethylene (hydrophilic) component within the polymer was investigated by Kissa and Dettre [84]. Initially, soil retention was found to drop substantially as the hydrophile/lipophile balance (HLB) value increased with increasing hydrophilic character. Eventually, however, this improvement in soil release levels off as a result of decreased sorption by the fibre, with higher polyoxyethylene content (Figure 8.7). Kissa and Dettre have emphasised the importance of an appropriate HLB in order to achieve optimum soil-release behaviour with these polymer systems.

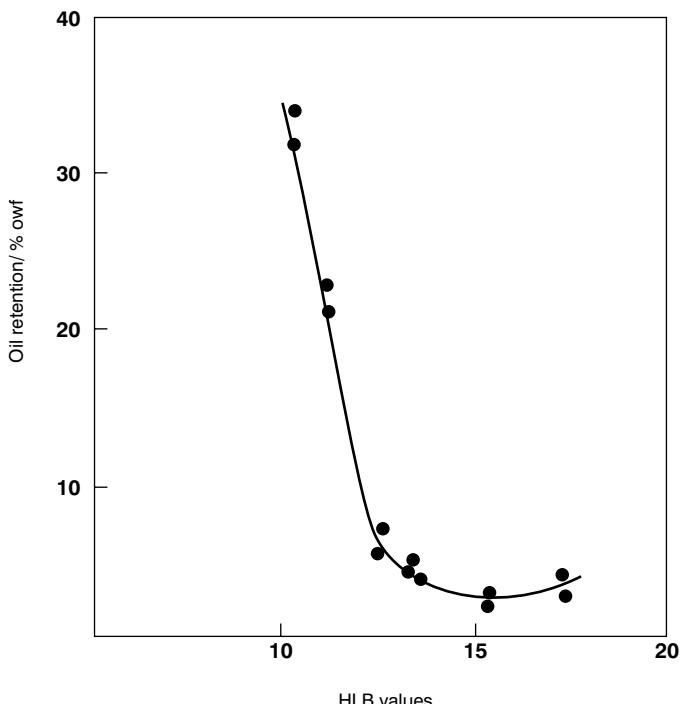


Figure 8.7 Oily soil retention as a function of the HLB values of nonylphenol-polyoxyethylene condensate sorbed on polyester fabric [84]

The earliest soil-release finishes were hydroxyl-containing water-soluble polymers such as starch, carboxymethylcellulose (CMC) and polyvinyl alcohol (PVA). Their function was to form a protective coating over the fabric, which was subsequently removed along with any soil during laundering. Those polymers used commercially, however, contain combinations of ethylene oxide, hydroxyl and carboxyl groups and are applied in conjunction with formaldehyde reactants for durable press/soil-release finishing [68].

Hybrid-fluorocarbon polymers

Conventional fluorocarbon finishes are known for their extremely low surface energy, which imparts the property of oil repellency in a dry state. In an aqueous environment, however, an oil

droplet is preferentially attracted to the oily fluorocarbon finish rather than to the surrounding hydrophilic environment, such that the droplet remains bound to the fabric surface during washing [85]. Hence, for both soil-repellent and soil-release properties, Smith and coworkers [85] have postulated that the following factors are necessary:

- (1) substantial reduction in surface irregularities;
- (2) reduction in surface energy of the fibre (to prevent spreading of oily soils in the dry state);
- (3) increase in surface hydrophilicity of the fibre (to facilitate release of oily stains in the wet state).

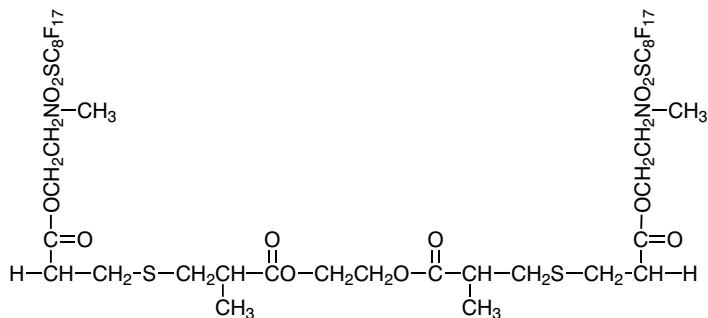


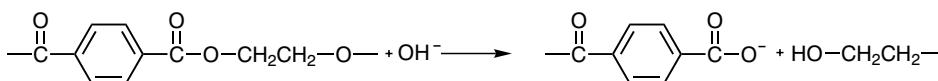
Figure 8.8 Average structure of F-H-F block copolymer [85]

In order to satisfy these apparently contradictory criteria specific hybrid-fluorocarbon soil-release agents have been developed, possessing a block copolymer structure, as exemplified in Figure 8.8 [85]. These polymers are capable of performing a dual function as a result of the different orientation of the lipophilic and hydrophilic segments of the polymer in air and in water. In the dry state, the polyoxyethylene segments remain coiled and the fluorocarbon moieties dominate the surface, ensuring the property of low surface energy, similar to a conventional fluorocarbon finish. In water, however, the oxyethylene segments swell with hydration, and thus impart a hydrophilic surface, essential for soil release during laundering.

While the presence of the fluorocarbon finish does not allow oily soil to penetrate via wicking into fibre capillaries, a disadvantage of this surface effect is that the oily soil remains concentrated over a smaller fabric area, such that after washing the soiled area may appear to contain no less residual soil than similar untreated fabrics. The application of this type of finish alone and in conjunction with durable press finishes is discussed in Section 8.2.5.

Non-polymer treatments

Alkali treatment of polyester: Alkaline hydrolysis of polyester is a well established treatment for the purpose of softening polyester and producing a silk-like handle [86]. As a result of attack by hydroxide ions, the surface of polyester is rendered more hydrophilic by the generation of hydroxyl and carboxylate end groups as shown in Scheme 8.1.

**Scheme 8.1**

A further consequence of this treatment is that a significant improvement in soil-release behaviour also results. Treatment with aqueous sodium hydroxide (10%) is reported to result in polyester fibres with excellent soil-release properties, equivalent to those of conventional soil-release finishes for polyester, and superior with respect to durability to repeated washing [87]. Relevant patents in this area have been summarised by Kissa [68]. Although the attack is predominantly limited to the fibre surface, leading to surface pitting, over-treatment can lead to excessive weight and strength loss of the fibre.

Dave and coworkers [88] have reported that, while the contact angle does decrease with increasing alkali concentration, the soil-release property of the treated fabric does not progressively improve (Table 8.8).

Table 8.8 Properties of sodium-hydroxide-treated polyester fabric [88]

Concentration ^a of NaOH release (molarity)	Weight loss (%)	Strength loss (%)	Contact angle (°)	Soil ^b (%)
0	—	—	82	73
1	2.3	3.8	80	92
2.5	7.0	6.4	79	92
4	14.7	13.3	76	92
5	24.0	24.4	72	94

a 100 °C, 5 min

b Lubricating oil applied in an Accelerotor; washing carried out in a Terg-o-tometer using a 1 g l⁻¹ sodium dodecyl sulphate solution at 50 °C

Plasma treatment of polyester: The modification of polyester fabric by plasma irradiation has been found to increase surface hydrophilicity of the fabric [89]. The advantage of this technology is that chemical changes are confined to the polymer surface and therefore the bulk properties of the fibre are generally not affected. In one recent study, plasma-treated polyester fabric samples were agitated in laboratory-formulated oily soil for 1 min and then gently blotted and air dried [90]. The extent of soil repellency was determined by reflectance measurement. This work showed that DC plasma treatment significantly improved the soil repellency, from approximately 30% to 68%, reaching a steady state over an irradiation time of 15 to 120 s.

Summary of patent literature

The earlier patent literature on soil-release polymers has been reviewed by Kissa [68]. An outline of the more recent patent claims [91–106] is given in Table 8.9.

Table 8.9 Summary of patent claims

Year	Polymer or formulation	Reference
1984	Aqueous emulsion of a softening agent/soil-release composition, imparting a smooth soft handle and superior soil release	[91]
1984	A combination of dispersions of organo-siloxanes and organic polymeric resins containing perfluoroalkyl groups imparting soil-, oil- and water-repellency	[92]
1984	Polyurethanes containing perfluorinated alkyl groups suitable for soil-, oil- and water-repellency	[93]
1986	Phenylene mono- and diester peracid precursors providing mixed hydrophobic/hydrophilic peracid generation to oxidise both hydrophobic and hydrophilic soils	[95]
1986	Family of silicone polymers for soil-resistant finishing	[96]
1986	Soil-release polymer based on caprolactam	[97]
1987	Polyorganosiloxane-polyoxyalkylene copolymers applied from aqueous or alcoholic solutions, imparting soil-release and softening properties	[100]
1987	Polyurethane containing amide linkages and two polyfluoroalkyl terminal groups imparting soil-, oil- and water-repellency	[101]
1988	Copolymer of polyethylene terephthalate and polyoxyethylene terephthalate applied as a soil-release finish for oily stains from polyester fabrics at low and high washing temperatures	[102]
1992	Lipase enzyme immobilised on the fibre surface for oil removal	[105]

Several patents claim excellent soil release in combination with either oil- and water-repellency or enhanced softening. The latter property is imparted by the combined application of organo-siloxane polymers. One exception to the various categories of polymers already described involves the anchoring of a lipase enzyme to the fabric surface for the purpose of achieving soil release [105].

8.2.5 Application of soil-release agents

Non-ionic soil-release agents

As mentioned previously, soil-release polymers in this category are mostly applied to 100% polyester fabric. Application may be via padding, in continuous or semi-continuous processes, or by exhaustion during dyeing or scouring. A crosslinking agent is generally added in order to insolubilise the polymer on the fabric surface. The fabrics are dried and then may be heat-set, if desired.

In the padding operation, wetting of the fibre surface by the soil-release agent, followed by adequate surface coverage of all fibre areas is essential for successful treatment. Spreading of

the soil-release agent may be facilitated by melting onto the heated fabric prior to sorptive bonding. The degree of sorptive bonding is then determined by the solubility of the soil-release (lipophilic) component in the polyester fibre. Kissa and Dettre [84] have studied the effect of cure temperature on the soil-release performance of fabrics treated via a pad–heat process. Soil retention after laundering was observed to drop markedly once the temperature exceeded that required for sorptive bonding of the polymer to the polyester substrate (Figure 8.9).

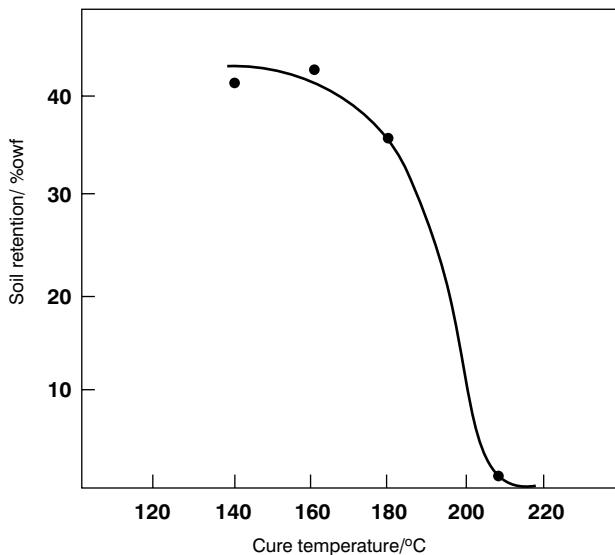


Figure 8.9 Effect of cure temperature on soil (Nujol) retention on polyester fabric treated with a nonylphenol-ethylene oxide condensate; fabric washed before soiling; heating time 2 min [84]

Kissa [68] has emphasised that the main problem in exhaust application relates to sufficient transfer and deposition of the predominantly hydrophilic soil-release agent from aqueous media onto the hydrophobic fibre surface. Non-ionic soil-release agents are suited to this application process. Binding and insolubilisation of the soil-release agent on the fibre then determines durability. Finally, for both padding and exhaust procedures, hydration of the hydrophilic component of the anchored soil-release agent determines its performance.

Fluorocarbon soil-release agents

Hybrid-fluorocarbon polymers can potentially be applied to any fibre type, predominantly by pad–dry–cure or spray procedures [107]. Both techniques ensure even application controlled by either nip-roll or spray-pressure, respectively. A curing stage is necessary to ensure correct orientation of the fluorocarbon polymer and improve bonding between polymer and fabric. This may be carried out in conjunction with heat setting for synthetic polymers (2–10 min at 150–190 °C). Other finishes for softening, flame retardancy, and so on, are also entirely compatible with the fluorocarbon finishing treatments.

Other claims include the application of a fluorocarbon anti-soiling agent as a spin finish for nylon carpet yarn [108]. The finish was found to be adequately durable during further fibre processing. A fluorocarbon agent has also been applied during the melt spinning process of nylon filaments [109]. The freshly solidified filaments are cured with the soil-release polymer, a lubricant and an epoxy resin.

Soil-release and durable press finishing

Soil-release agents belonging to the carboxylic acid class are commonly applied in combination with durable press finishes on cotton and cotton/polyester blends. The dual application may be carried out in a one-bath or two-bath process. While the single bath process is more durable to washing, the high temperatures required for curing (up to 170 °C) can substantially diminish the soil-release effect. The top-applied (or two-bath) process, however, provides good soil release regardless of curing temperature within the range 120–170 °C [68].

Warburton and coworkers [110] have postulated that a high curing temperature during co-application leads to the soil-release polymer becoming embedded in the crosslinked system of the durable press finishing agent. This would inevitably interfere with the swellability and hydrophilic character of the soil-release agent and thus decrease its soil-release performance.

Hybrid-fluorocarbon polymers provide the most convenient option for application in conjunction with durable press treatments [68]. The advantages are as follows: a lower treatment level is required (1.5% owf) compared with the acrylic acid polymer (10% owf) for the same degree of soil release; the single bath treatment in this case does not result in temperature-sensitive soil-release behaviour, and the additional property of oily soil repellency is also imparted. The main drawback is that the fluorocarbon treatment is more expensive. Hence, it is more often practical to apply mixtures of hybrid-fluorocarbon and acrylic acid soil-release polymers.

8.2.6 Methods of testing

Testing involves assessment of the degree of soiling prior to and/or after washing of the textile item. The form of mechanical application selected depends on the type of soil and substrate. The soiled sample is then subjected to a standard laundering procedure and then examined by either visual or instrumental measurement.

Soil application and laundering

For oily soil, AATCC Test Method 130 [111] has been widely used: 5 drops of Nujol are pressed onto the substrate using glassine paper and a 5 lb weight for 1 min. In the case of particulate soil, a mechanical device such as an Accelerotor (a cylinder fitted with a rotating blade) is used for application in order to maintain uniformity [68]. These methods involve direct soiling of the substrate. Alternatively, foam or felt cubes may be soiled initially and then allowed to contact

the textile substrate by systematic rotation within cylinders [112–114]. The advantage of this technique is that oily, particulate or composite soils may be used on fabrics samples.

Laundering is carried out in a Launder-Ometer or Terg-o-tometer under specified conditions of time, temperature and detergent solution. Given the complexity of domestic laundry products, a standard surfactant solution is generally used as specified in AATCC Test Method 130.

Evaluation of soiling

The degree of soiling may be evaluated either visually by comparison with photographic standards (1 for poor stain removal, up to 5 for best stain removal) [114], or by a variety of instrumental techniques. Unfortunately, no individual method of measurement is entirely satisfactory because the degree of apparent soiling depends on the optical properties of the fibre.

Reflectance data using the Kubelka-Munk equation have been frequently used as an objective method of assessing the degree of soiling. Kissa [68] has pointed out, however, that while the reflectance data do correlate with the actual oily soil content of the fabric, the data do not provide an accurate evaluation of residual particulate soil. The reasoning suggested is that particulate soil tends to become buried within the fabric and is thus shielded from the light path.

In one study the extent of ageing of oily soils on cotton and wool fabric was assessed [115]. Thiobarbituric acid (TBA) was found to be a sensitive colorimetric indicator, where highly coloured products were formed with the unsaturated systems of oxidised soil on the textile. After fabric cleaning, an evaluation of stain removal was compared using the Kubelka-Munk relationship and Stain Removal Index (SRI). The SRI method uses CIE L , a , b data, and the effectiveness of stain removal is calculated in terms of the contrast between samples before staining and after stain removal:

$$\text{contrast} = \left[(L_c - L_w)^2 + (a_c - a_w)^2 + (b_c - b_w)^2 \right]^{\frac{1}{2}} \quad (8.5)$$

where c = clean sample before staining

w = stained and washed sample

Differences in evaluation from these two measurement indices were found to be significantly influenced by the presence of dye on the textile. The SRI system was concluded to be a more reliable evaluation of total colour change since measurements are carried out at all wavelengths, while the Kubelka-Munk relationship uses a single wavelength for obtaining reflectance data.

Electron microscopy [74] has been successfully utilised for the detection of oily and multi-component soils from unwashed and washed cotton and polyester fabrics. The analysis was extended further to qualitatively assess a variety of laundry product formulations for their soil removal capabilities; the effect of durable press and soil-release finishing on cotton and cotton/

polyester blends was also qualitatively examined. This method of detection revealed soil distribution as mentioned in Section 8.2.3, and the presence of clay and/or oil in multi-component soils could also be distinguished.

Differential scanning calorimetry [116] has recently been shown to be a rapid, quantitative method of assessing the extent of soil release on cotton fabric. Single components of oily soil were applied and the fabric sample heated from room temperature to 80 °C at 5 °C min⁻¹, in a helium atmosphere. An unoiled sample was used as a reference. The heating curves obtained showed characteristic solid phase transition and melting peaks, where the peak area corresponded to the amount of soil present on the fabric sample. The thermograms were reproducible in repeated heating/cooling cycles. Each analysis required approximately 10 min, and drying after washing of the fabric sample was unnecessary.

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CHAPTER 9

Easy-care finishing of cellulosics

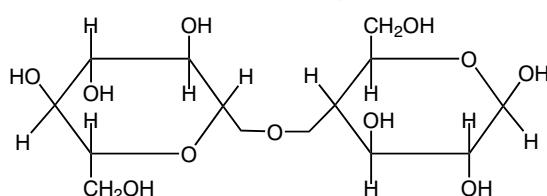
G Sharpe and P Mallinson

9.1 INTRODUCTION

Cellulosics dominate the apparel industry, with King Cotton taking centre stage. They are the fibres of choice because of their relatively high aqueous absorption, strength and resistance to abrasion – properties that yield comfortable, robust garments at competitive prices. Their inherent tendency towards creasing in wear and shrinkage on laundering constitute their principal disadvantages, which, although often improved by fabric or garment construction, are increasingly conquered by topical chemical treatment. The goal is ‘easy-care’ clothing that may be washed with minimal creasing and shrinkage and, depending on construction, then requires no or very little ironing to restore a pristine appearance – in short, apparel to suit the aspirational lifestyle that has been described as ‘wash, dry and go’ [1].

Cellulose fibres are polymeric. The polymer chain consists of condensed β -glucose molecules (Structure 9.1), the structure being a repeating pair of spatially opposed glucose units (a cellobiose unit). The degree of polymerisation of cellulose fibres depends on origin – approximately 3000 for cotton ($n = 1500$), and just 250–700 for viscose (regenerated cellulose) [2]. The cellulose polymer chains are held together in bundles by hydrogen bonds and van der Waals forces, to form individual fibres, the chains running parallel to the fibre axis in a typically crystalline structure, although around 30% of cotton and 60% of viscose is amorphous. Note the high density of hydroxyl groups – they are the key to cellulosic hydrophilicity; indeed, aqueous solubility is probably only prevented by strong hydrogen bonding in the crystalline regions, preventing ingress by water molecules. It is in the amorphous regions, however, that the chemistry of easy-care finishing takes place. Chemical finishing agents are able to penetrate the fibres, but do not enter the crystalline zones [3].

Structure of cellulose polymer chain



9.1

The shrinkage of cellulosic fabrics is a consequence of the relatively inelastic nature of the fibre and the dimensional changes that occur in the fibre during the transition from the dry to wet to dry state – effectively the ‘repacking’ of the structure, which has been disrupted when aqueous. The creasing of cellulosic fabrics depends again on fibre structure – on a molecular level, a schematic representation of creasing and crease resistance shows that an unstable polymeric structure may not hold firm on deformation, so that the structure fails to recover and creasing results when the load is removed [2]. For the same reason, moistening of cellulosic fabrics, prior to ironing, allows the cellulose to regain its original configuration or for it to be persuaded to adopt another one (for example, a crease or pleat).

The last 75 years have witnessed the evolution of a series of topical treatments, broadly termed ‘resin-finishes’, which have produced dramatic improvements in the after-wash performance of cellulosic fabrics. This chapter provides an overview of this development and describes the current state of the art.

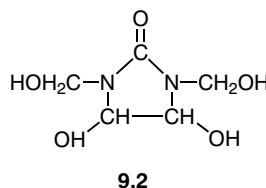
9.2 HISTORICAL REVIEW

So, how can shrinkage be reduced and crease recovery improved by topical chemical treatment? The approach has been to ‘set’ the fabric by the application of a crosslinking polymer. This was initially achieved by introducing a resin into the cellulose fibre that auto-condensed to produce a network within the fibre – see early work by Tootal Broadhurst Lee Co. Ltd. [4], who developed a process in 1926 for the production of a crease-resist fabric using urea formaldehyde precondensate where the resin was formed within the cellulose fibres. Many other similar thermosetting resins were developed that followed the same auto-condensation principle and some, based on urea formaldehyde and melamine formaldehyde (the detail is beyond the scope of this chapter, but is summarised in Section 9.7 [5]), continue to be widely used for handle modification and surface glazing. However, for easy-care the auto-condensing resins have been totally displaced by reactive crosslinking agents typically based on cyclic ureas. These agents react directly with the hydroxyl groups on the cellulose to form crosslinks that act to lock the structure together and resist shrinkage and deformation, conferring an improved degree of elasticity to the fibre structure.

True semantic accuracy suggests these products should not be termed resins – since they do not polymerise – but in spite of this they are widely referred to as reactant resins. They are bifunctional and, therefore, unable to form the three dimensional structures typical of the urea and melamine formaldehyde true resins. Early products were based on ethylene urea with a number of variations, all virtually superseded by reactants based on dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) (Structure 9.2). DMDHEU resins are based on a reaction of glyoxal, urea and formaldehyde and react with the cellulose by etherifying the all-important hydroxyl groups in the amorphous phase. The reaction is catalysed by a variety of acid or latent acid agents.

The moisture content of the fibre at the time of the crosslinking reaction has been studied extensively and found to be of major importance. The impregnate–dry–cure procedure

Structure of DMDHEU



(described later) is the only known commercial route and it implies that the onset of the crosslinking reaction follows the drying step and that crosslinking occurs in the absence of water, while the fibres are in the collapsed state. This may be termed 'dry crosslinking'. Much research has been carried out into the effect on fabric performance of crosslinking carried out when the fibres were swollen or partially swollen with water. This may be termed 'wet crosslinking'. It has been demonstrated [3] that very different properties are achieved by the two regimes, a phenomenon that is attributed to the possibility of crosslinks being formed at differing fibre sites – depending on availability, as dictated by moisture content. At the time of writing, however, dry crosslinking dominates the easy-care industry – it appears that viable, cost effective wet crosslinking processes have not been fully developed.

9.3 EASY-CARE PROPERTIES

9.3.1 Defining 'easy-care'

A 'wish list' for the easy-care finisher might be as follows:

- (1) high 'durable press' rating [6], high dry and wet crease recovery angles [7];
- (2) minimal shrinkage, abrasion loss, tensile/tear strength loss;
- (3) little effect on shade and fastness of dyed fabrics or yellowing of whites;
- (4) good absorbency;
- (5) low or zero formaldehyde levels;
- (6) good pilling resistance;
- (7) desirable handle.

Although some of these concepts are self-evident, others may require some explanation. Inevitably, the result of resination is a compromise, with the finishing technician balancing a number of closely inter-relating factors, all of which are affected by resination to some degree, depending on the chemical and physical route chosen for processing. This section attempts to give an insight into the complicated nature of these dependencies. Petersen [2] describes a statistical approach which, under specific test conditions, demonstrated that quantitative correlations exist between the finishing conditions employed and the main properties of resin-finished cotton fabrics.

9.3.2 Durable press

The durable press (DP) rating quantifies the after-wash appearance of fabrics by comparing the resulting surface appearance of washed, dried (flat, line or tumble, depending on the test protocol) and conditioned samples with that of a standard set of plastic replicas and assigning a numerical value to them. If AATCC Test Method 124 is adopted [6], a 'DP' rating of 3.5 or above is usually considered the pass level for an easy-care finish.

9.3.3 Wet and dry crease recovery

Wet and dry crease recovery angles represent a protocol whereby the 'wrinkle recovery' (that property of a fabric which enables it to recover from deformation) is measured. A test specimen, creased and compressed under controlled conditions (in either the wet or dry state) is suspended in a specially designed test instrument for a known period, after which the recovery angle (that is, the angle of fold remaining) is measured. Although the between-laboratory precision is poor, within-laboratory precision can be good. The principle appears to have logical merit and the test is widely used as a comparative research tool. Obviously the greater the recovery angle the greater the ability of the fabric to recover from accidental creasing – either in wear (dry crease recovery) or on washing (wet crease recovery).

9.3.4 Effect of easy-care finishing on fabric properties

Quantification of the relationship between the degree of crosslinking and changes in the mechanical properties of treated fabrics has been attempted. The matter is complicated by the dependence on fabric construction of tensile, tear and abrasion performance. Nevertheless, it is apparent that crosslinking impacts negatively on all mechanical properties and that the damage may be readily reversed by carefully breaking the crosslinks – for example, by acid hydrolysis. The literature also recognises the possibility of permanent damage – caused by some loss of the degree of polymerisation of the cellulose caused during the curing step. The 'degree of cure' of a resin finish attempts to quantify the percentage of resin on the fabric that has crosslinked, using an analytical technique. It may be readily observed that, as the degree of cure increases, so the mechanical properties degrade and any change of shade or yellowing will become more pronounced. In all cases, the magnitude of the effect depends on the specific chemicals and processing conditions used.

The fibre embrittlement brought about by resination, may, under certain circumstances, be beneficial. Pilling of fabrics occurs when mechanical abrasion or laundering allows fibre mobility and, consequently, small balls or 'pills' of agglomerated fibre appear on the fabric surface. The effect is particularly noticeable on fibre blends and, if one component of the blend is a relatively strong fibre, such as polyester, there is usually no tendency for the pills to wear off, because the strength of the fibre anchors the pill to the fabric surface. It has been observed that the resination of cotton/polyester blends dramatically reduces 'permanent' pilling, since the weakened cellulosic component encourages pill detachment. This effect has been used to

improve the wash/use performance of easy-care bed linen. A similar technique has been employed on knitted 100% viscose fabrics destined for apparel end-uses, also to improve pilling performance.

Resination of both white and coloured fabrics usually affects the shade to some degree. Typically the effect is a yellowing of the shade, the effect increasing with cure temperature. Techniques have been developed using spectrophotometry that allow compensation for possible shade changes to be made via the dye recipe itself. In other words, the dye recipe can be adjusted to make allowance for the shade change anticipated on resination.

9.3.5 Formaldehyde: hazards, sources and detection

The chemistry of the resination of fabrics with DMDHEU-type reactant resins is inextricably linked with that of formaldehyde (Section 9.7) some of which appears on the treated fabric in either a free or bound form. Increasing consumer concerns over the possible health risks associated with exposure to formaldehyde thus complicate possible routes to easy-care.

As an important metabolic intermediate in living organisms, formaldehyde may be detected in every human cell and, in fact, it is easily metabolised in our bodies to form essential amino acids. Its known hazards to health are its potential to irritate (especially the eyes and respiratory tract) and the ability to trigger skin allergy in susceptible individuals. Although, to date, there is no evidence to suggest that formaldehyde has caused cancer in humans, some evidence exists to demonstrate carcinogenicity in animals and, because of this, solutions of formaldehyde in water above 1% concentration are labelled with the risk phrase R40 'possible risk of irreversible effects' [8]. At much lower concentrations (above 0.2%) such solutions carry the R43 label ('may cause sensitisation by skin contact') [8]. The consequences of this are that restrictions are placed on the concentration of formaldehyde in fabrics for certain end-uses, particularly the Oeko-Tex Standard 100 [9]. This standard is a European-wide labelling scheme intended to offer consumers assurances that the textiles around them contain no substances harmful to health. It defines detailed analytical procedures for measuring levels of certain substances in textiles (including formaldehyde) and sets appropriate levels for these substances, depending on end-use. The current standards for maximum fabric concentrations of formaldehyde for Oeko-Tex Standard 100 are measured according to Japanese Law 112 (see below) in ppm and are as follows:

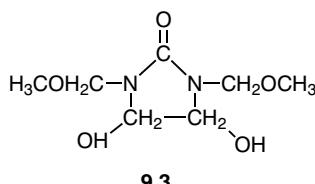
- (1) for furnishing fabrics – 300 ppm;
- (2) for adult clothing and other skin contact items – 75 ppm;
- (3) for children's items – 20 ppm.

As reactant resin systems develop, it has become increasingly easy to meet the 75 ppm standard after easy-care – many modified DMDHEU resins (described as low or ultra-low formaldehyde products) currently on the market may be used. The 20 ppm standard is somewhat more difficult to achieve, even with state of the art reactants, especially if it is unacceptable to give the fabric a wash-off after processing to remove much of the unassociated formaldehyde. For

this reason, zero add-on formaldehyde resins are gaining some credence, in spite of generally lower reactivity and higher cost; these are discussed in Section 9.5.2.

The sources of formaldehyde in treated fabrics are various. It is not possible to prepare an aqueous solution of a DMDHEU-type resin without the presence of its equilibrium partner, formaldehyde. In addition, the crosslinks formed between resin and cellulose may be back-hydrolysed under favourable conditions to release formaldehyde. It is therefore easy to see that the finishing conditions must be carefully optimised to minimise the potential for formaldehyde generation. The resin itself may be modified. Low formaldehyde crosslinking agents were developed based on methylated or glycolated DMDHEU, which has improved stability with respect to its precursor. Methylated DHDMEU (Structure 9.3) results when methanol is used to replace two or four of the hydroxyl groups with methoxy groups, while glycolated DHDMEU can be formed by reacting two moles of diethylene glycol with the subject compound. The end-caps of these products effectively prevent formaldehyde evolution. Such products, which may also be used in conjunction with a formaldehyde acceptor (but without reaction) such as diethylene glycol (again) or urea, can be used to generate even lower formaldehyde levels on resinated fabric. These products are, generally, not as good DP boosters as their precursors.

Structure of methylated DMDHEU



Test protocols for determining formaldehyde levels vary. At the time of writing, two methods dominate the UK finishing industry; they do not appear to cross correlate [10]. Results from both regimes are expressed as ppm on air-dried fabric weight.

- (1) The first test method relates to British Standard BS 6806 Part 2 (free formaldehyde) and Part 3 (released formaldehyde). Part 2 (free formaldehyde) uses a mild aqueous extraction procedure to remove any unreacted crosslinking agents, which may then be hydrolysed by strong acid to release the component formaldehyde – this is measured colorimetrically. Inadequate curing of the resin system can lead to residual water-soluble formaldehyde derivatives left on the fabric after processing. These residues may be regarded as potential skin irritants, which may manifest during garment make-up. Levels of free formaldehyde in excess of 700 ppm are generally considered undesirable, although tighter standards may be applied.

Part 3 (released formaldehyde) measures formaldehyde that is released in a given period from fabric suspended over water in a sealed jar. It is considered an appropriate simulation

of the slow hydrolysis that takes place of the cured resin-crosslink system on fabric storage. The rate of such release will depend on the relative stability of the cured system as well as residual catalyst levels. Levels of released formaldehyde below 1000 ppm are often considered acceptable.

- (2) The second test method relates to Japanese Law 112 (1973), which measures the actual formaldehyde content of an aqueous extract after the extraction period. Any formaldehyde potentially arising from future hydrolysis (for example, water-soluble resin) will not be detected by this method. It is also considered to be a measure of the propensity of the fabric to cause skin irritation.

It should be noted that measurements obtained using the Japanese method are generally lower than the BS 6806 Part 2 results, but fabrics considered ‘acceptable’ and ‘non-acceptable’ according to the BS 6806 Part 2 method may both give similar results via the Japanese protocol.

A recent comparative evaluation of several methods for formaldehyde detection, including the two above, concluded that the results obtained using BS 6806 (also referred to as the Shirley method) differed decisively from other established methods (including Law 112), since fragments of crosslinking agent are split off due to the elevated reaction temperature and the use of concentrated acid [11].

9.4 EASY-CARE TECHNOLOGY

Easy-care finishing of celluloses is achieved using an aqueous, known add-on technique, followed by a drying and then curing (crosslinking) step. The procedure may be applied to fabrics using a pad mangle and stenter or to made-up garments via a hydro-extract, press and cure method. This latter method is often referred to as ‘garment dip’, an extension of which is known as the ‘metered addition’ method, whereby a spray system is used to deliver a precise amount of resin mix liquor to made-up garments. A third variation, known as ‘post-cure’, relates to the crosslinking in garment form of a fabric previously treated and dried in flat form.

In all cases the chemical bath is made up with resin (reactant), catalyst and a cocktail of softeners and stitch lubricants to enhance handle and performance. Compatible water- and stain-repellent finishes (such as fluorocarbon emulsions) may also be incorporated in the chemical mix, to further enhance the final fabric performance.

The incorporation of silicone elastomers into the pad mixture deserves special note. Direct evidence exists that a suitable self-crosslinking silicone elastomer can improve the DP rating of a resinated system, although no measurable effect on dimensional stability has been recorded.

The addition of softeners to improve abrasion performance is often questioned, since transfer of the softener from fabric to abrasive may give a falsely enhanced result. This said, however, water-based polyurethane emulsions can produce dramatic improvements on the Martindale Test – it is even possible to improve on the original value achieved on unresinated fabric. For example, an original figure of 20 000 may fall to 16 000 on resination, but rise to 24 000 if a suitable polyurethane is added to the resin finish.

9.4.1 Catalysis and curing

Most of the catalysts used in resin finishing are either acids or latent acids (the latter developing acidity only on heating). For DMDHEU reactants, the most popular catalyst is magnesium chloride – being neutral in aqueous solution at all temperatures and thus offering maximum bath stability. Such metal salt catalysts do not generate acid conditions until a relatively high temperature is reached. As commercial pressures have increased to reduce processing times, pad–dry–cure has often been abbreviated to one-step, pad–stenter–cure with very short cure times. Since very high fabric temperatures must be avoided to prevent fibre degradation, sharper more active catalysts have evolved known as metal salt complex/co-catalysts – for example, magnesium chloride/citric acid, magnesium chloride/aluminium hydroxylchloride and magnesium chloride/sodium fluoroborate, these latter often referred to as ‘flash catalysts’.

Several studies of the mechanism of catalysis have indicated that a complex intermediate is formed between the metal catalyst ion and the reactant alkoxy group. Catalyst choice must reflect closely the desired finishing temperatures, fabric speeds and acceptable residual formaldehyde levels, taking into account the deterioration in mechanical properties and shade that occur as the degree of cure increases.

Prior to pad–stenter–cure (otherwise referred to as ‘single pass’), the amount of liquor on the fabric should be kept as low as possible to minimise the energy required for processing. In some cases, resin migration to the surface of the fabric will occur if the water is driven off too swiftly in the earlier stages of drying, leading to a harsh handle and generally poor performance. This effect is especially noticeable on viscose and cotton fabrics, where, for example, when using a five-bay stenter the first compartment should be around 100–120 °C, the second at 130–140 °C, while the last bays are used to effect the final cure at 170–180 °C. This migration effect is barely significant in cotton/polyester fabric blends, thus allowing full use of the flash catalysts described above. Flash curing should be avoided in mechanical systems as it induces a degree of ‘pre-cure’ (low-temperature curing), which often translates into a poorer mechanical finish.

9.4.2 Typical recipes for resination

Table 9.1 outlines some practical resination routes covering various constructions and fibre blends. It must be appreciated, however, that process optimisation is possible only ‘in bulk’, in order to reflect possibly unique production arrangements and fabric properties.

For 100% cotton single jersey, application is via impregnation at a padding mangle or other suitable means. Drying may be carried out in the stenter or in a contemporary tensionless dryer. Single-stage drying–curing on the stenter may also be employed. Typical curing conditions are in the range 150 °C for 2–3 min to 180 °C for 30 s.

For 100% cotton woven shirting, once again, application is via impregnation at a pad mangle. Practical cure conditions for single-pass processing for this recipe are also 1.0–1.5 min at 170–190 °C.

In the case of cellulosic garment dip, the dry garments are tumbled at room temperature in a solution containing the recipe in Table 9.1, including a cocktail of suitable softeners (typically

Table 9.1 Typical recipes for resination using DMDHEU

	Pad-dry-cure of 100% cotton single jersey	Pad-dry-cure of 100% cotton woven shirting	Cellulosic garment dip
Concentrated DMDHEU resin ^a :	40 g l ⁻¹	80 g l ⁻¹	60 g l ⁻¹
Catalyst:	16 g l ⁻¹ MgCl ₂ solution (30% anh.)	12 g l ⁻¹ MgCl ₂ / citric acid combination	12 g l ⁻¹ MgCl ₂ solution (30% anh.)
Softener:	40 g l ⁻¹ silicone elastomer (30% solids)	20 g l ⁻¹ amino silicone (30% solids), 15 g l ⁻¹ polyethylene non-ionic emulsion	silicone and polyethylene emulsions/ mildly cationic fatty acid amide types/ polyurethanes
Water:	To one litre	To one litre	To one litre
Pick-up:	70%	60%	60%
Bake:	—	—	8–10 min 150–160 °C

a DMDHEU reactant resins are usually prepared to two typical strengths. By far the most popular strength is usually referred to as a 'concentrated resin' and has an active solids level of around 60–65%. A selection of contemporary, commercially available resins is given in Table 9.2

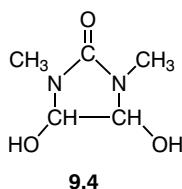
silicone and polyethylene emulsions as well as mildly cationic fatty acid amide types and, increasingly, polyurethanes) to confer specific handle characteristics and to improve some physical properties that are adversely affected by resination. After impregnation, the garments are centrifuged to 60–65% pick-up, and then dried to 6–10% residual moisture at around 75 °C, prior to pressing. This low-temperature drying step ensures there is no premature resin curing. After pressing, the garments are placed in a baking oven for 8–10 min at 150–160 °C, to effect the final cure.

9.5 FORMALDEHYDE-FREE EASY-CARE FINISHING

The concerns over residual formaldehyde levels in resinated fabrics have already been discussed. For many years now the search has been on for so-called 'zero formaldehyde add-on' resins that are cost effective and at least meet the performance standards of the formaldehyde derivatives. The number of effective cellulose crosslinking agents that are stable, water-soluble and non-volatile during heat-curing at 115–215 °C, using non-tendering, environmentally acceptable catalysts, appears to be relatively small. Still fewer carry a smaller risk to health or to the environment than the products currently in vogue.

The cyclic addition product of glyoxal with NN'dimethyl urea, namely DHDMI

Structure of DMDMI



(1,3-dimethyl-4,5-dihydroxyethyleneurea), has attracted much attention (Structure 9.4). The initial patent on DHDMI finishing was issued in 1963 and featured zinc fluoroborate as an especially effective catalyst. Indeed, kinetic studies of the reaction of DHDMI with cotton cellulose at relatively low curing temperatures indicated a first order reaction rate with respect to zinc, but zero order with respect to magnesium. In the interim, further progress has been made and products are now commercially available that may be satisfactorily catalysed using conventional magnesium chloride solutions.

Work in this area has shown that compounds of this general type produce a less uniform distribution of crosslinks in the cotton fibre than do conventional products such as DMDHEU [12]. Indeed, this uneven distribution of the crosslinks appears to have several consequences for fabric strength, colour, easy-care performance, moisture regain and dyestuff affinity. Suffice it to say that products like DHDMI find some commercial application to produce zero formaldehyde add-on easy-care finishes and some typical recipes are included in Section 9.5.2 (Table 9.2). They offer less than optimal performance and, at the time of writing, a higher cost base than the conventional, formaldehyde-containing types.

The ability of polycarboxylic acids, particularly citric acid, to act as crosslinking agents has been recognised for many years. Their major drawback is the accompanying dramatic tensile strength loss in the fabric, attributed to acid-catalysed cellulose chain cleavage. Advances were made by base-catalysing the crosslinking of polycarboxylic acids containing 4 to 6 carbonyl groups per molecule. The base (typically sodium carbonate or triethylamine) neutralised up to 50% of the carboxyl groups, the resulting salts acting as buffers that greatly reduced the acid-induced tendering. Further development work has been carried out using the more effective weakly basic catalysts – for example, alkali metal salts of phosphorous containing mineral acids – giving even better easy-care performance. The acid of choice appears to be 1,2,3,4-butanetetracarboxylic acid (BTCA), but, once again, cost appears to have precluded commercialisation. The possible combination of BTCA and citric acid (CA) may offer a cost-effective, environmentally acceptable finishing route, with only a mildly reduced performance compared with DMDHEU-type systems. A comparison of the performance of these three possible alternative crosslinkers with DMDHEU has been compiled by Welch [12], which clearly demonstrates the overall superiority of the DMDHEU finish, especially on the all-important DP rating – only BTCA appears to be able to offer a similar performance, but the

corresponding crease recovery angle is somewhat lower. The conclusion must be that only legislation will drive the change to ‘zero add-on’ finishes, while increased costs and lower performance continue to represent the current state of the art.

9.5.2 Typical recipes for zero formaldehyde add-on levels on fabric

DHDMI-type resins often exhibit a partial cure at typical fabric drying temperatures (say 110 °C). Since this could take place when the fabric is not presented at its optimum finishing tension, poor stability may result. As a consequence, the whole operation of dry-cure for 100% cotton single jersey should take place at around 170 °C with a cure time of around 45 s. Similar dry-cure conditions are suitable for 100% cotton woven shirting, following pad mangle application.

As outlined in Section 9.5.1, DHDMI-type resins generally demonstrate reduced performance when compared with the commonly employed DMDHEU-types. This is manifested in the increased resin levels required to achieve an acceptable performance (Table 9.2), and the consequential cost impact. Their poorer and more random crosslinking capability is not enhanced by the use of ‘sharper’ catalysts – indeed, attempts to improve their performance generally result in weaker, more yellow fabric (or other shade change). As a consequence, stability control, DP ratings and degrees of resin cure may be expected to be poorer in any comparative evaluation. This said, however, certain finishing circumstances dictate that no additional formaldehyde should be added to the fabric (for example, for baby-wear or skin contact items for possibly sensitised adults) and, in these cases, DHDMI-type products offer a commercial route to easy-care. Products marketed for such purposes must obviously be proven ‘hypo-allergenic’, since the elimination of formaldehyde does not, automatically, preclude the

Table 9.2 Typical recipes for zero formaldehyde add-on levels on fabric

	Pad-dry-cure of 100% cotton single jersey	Pad-dry-cure of 100% cotton woven shirting
DHDMI type resin ^a :	80 g l ⁻¹	200 g l ⁻¹
Catalyst:	24 g l ⁻¹ MgCl ₂ solution (30% anh.)	60 g l ⁻¹ MgCl ₂ solution (30% anh.)
Softener:	40 g l ⁻¹ silicone elastomer (30% solids)	40 g l ⁻¹ silicone elastomer (30% solids)
Water:	To one litre	–
Pick-up:	100%	–

^a DMDHI resins are usually prepared with an active solids level of around 30%

introduction of some other sensitising moiety or bi-product. Practical experience with some commercially available, so-called, 'zero' resins has identified considerable differences in the degree of yellowing/shade change occurring on resination, as well as the appearance of unpleasant odours (possibly pyridine) on the finished fabric.

9.6 CONCLUSIONS

At the time of writing there have been no major commercial developments in the chemistry of easy-care finishing in the last 10 years – indeed, the last episode of significant progress occurred with the advent of reactant resins in the late 1940s. It must be added, however, that the appearance of 'garment dipping' (Table 9.1) in the early 1990s has resulted in the development of innovative application technology.

Recent advances in the mechanical processing and handling of fabrics have revolutionised fabric stabilisation, especially on knits. In many cases, such treatment may eliminate the need for the application of resin to control shrinkage. Such regimes do not, of course, give any improvement in the associated easy-care properties of wet and dry crease recovery. Other topical treatments (for example, based on polyurethanes and other binder-type products) have been demonstrated to impact positively on these values, with the added advantage of offering a route (via careful chemical selection) to easy-care that is zero formaldehyde add-on, when used in conjunction with advanced mechanical finishing. Similarly, development work is ongoing to exploit the use of crosslinkable protein derivatives in this demanding field.

As with many areas involving the use of 'performance chemicals', increasing concerns over their environmental impact and any associated health hazards have served to require very careful screening of new candidate compounds and, inevitably, the filtering out some otherwise promising candidates. The development challenges are clear – to replace the conventional DMDHEU compounds with formaldehyde-free alternatives at acceptable cost and, if possible, to develop more reactive, controllable systems that are capable of giving robust, easy-care properties to challenging, relatively unstable substrates, such as weft knits. The ultimate judge of any topical treatment (no less true for easy-care than other areas of textile finishing) must be the unbiased consumer who demands 'value for money' rather than responding to the aesthetic appeal of some neat chemistry!

However, a compromise may be achieved, with ultra-low formaldehyde resin being produced on a large enough scale to give finishing costs around the same as those for conventional DMDHEU compounds.

9.7 APPENDIX – AUTO-CONDENSING TEXTILE RESINS

The predecessors of today's easy-care reactant resins are self-condensing, producing a polymeric structure within or upon the textile fibre itself, thus imparting stiffness and a degree of dimensional stability to the fibre and to the overlying fabric construction.

9.7.1 Urea formaldehyde resins (UF type)

The reaction of urea with one or two molecules of formaldehyde (to produce the mono-methylol and di-methylol derivatives, respectively) takes place at room temperature. The derivatives are also relatively unstable, which mitigates against their production at a remove site. Indeed, the reaction was often carried out *in situ* at the factory of use – with, inevitably, all the associated issues concerning the handling of formaldehyde. Their average molecular size is not stable – it increases with time. It can become so large that it is no longer soluble and falls out of solution, thus rendering the product unusable. All this said, such derivatives were once widely used to impart crease resistance to cotton and viscose fabrics.

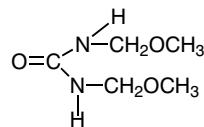
9.7.2 Highly condensed urea formaldehyde resins (condensed UF type)

Under the action of considerable heat and in acid conditions, the methylol ureas may be condensed to form three-dimensional structures, which are more stable than the simpler precursors, but which, because of their high molecular size, impart a stiffer handle to fabrics.

9.7.3 Methylated urea formaldehyde resins (methylated UF type)

Treatment of the methylol derivatives of urea with methanol results in the formation of an ether – a methoxy methyl urea (Structure 9.5). Once again, improved stability compared with the simpler starting materials results – this time the handle is somewhat less stiff than that associated with the condensed UFs. Excellent crease resistance of cellulosic substrates may be achieved as well as durable, stiff finishes for nylon and polyester. Furthermore, the addition of thiourea enables a degree of durable flame retardancy to be incorporated. It is believed that, in the case of cellulosic fibres, the resin enters the fibre and, when catalysed, produces a polymeric network that prevents the fibre from creasing and shrinking on washing. With nylon and polyester, the resin does not actually penetrate the fibre, but forms a durable and stiff external film, resulting in significant modification to handle.

Structure of methylated dimethylol urea



9.5

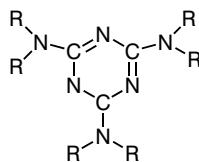
9.7.4 Melamine formaldehyde resins (MF type)

Melamine (2,4,6-triamino-1,3,5-triazine), just like urea, reacts with formaldehyde to give methylol derivatives (Structure 9.6). In theory, six derivatives are possible, although only the tri,

penta and hexa methylol derivatives have achieved commercial significance. Increasing degree of substitution may be associated with enhanced reactivity as well as cost. Stability of all forms may again be improved by etherification with methanol. For similar applications, the MF types give better storage stability and exhibit fewer problems with odour and chemical degradation (for example, during laundering) than the simpler UF resins. Four major markets for MF resins have been identified and they continue to be widely used in the following areas:

- (1) in the durable, mechanical finishing of cellulose (Schreinering, glazing, embossing, permanent pleating, and so on);
- (2) as crosslinkers for acrylic, polyvinyl acetate, polyurethane and other polymers – for example, pigment printing;
- (3) as stiffeners for polyester and nylon;
- (4) as handle builders, when used with other finishing products.

Structure of generic melamine formaldehyde



9.6

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CHAPTER 10

Anti-microbial, rotproofing and hygiene finishes

I Dring

10.1 INTRODUCTION

Although the history of many scientific discoveries and inventions can be accurately chronicled, there are others whose origins are lost in the mists of time. One such example is the wheel; another is biocides!

Of the basic organisms against which biocides are used – fungi, bacteria and algae – humankind has been aware of the first for thousands of years. Macro fungi can not only be seen but also eaten; micro fungi manifest themselves in the form of visible moulds and mildew; yeasts are responsible for fermentation and the production of wine. The deleterious effects of micro-organisms on food and clothing due to mould and rotting have also been obvious for a long time, but at what stage did people first realise that they could do something about it and go on to invent or develop biocides? Did Moses discover something that prevented the manna from rotting [1]? Who found out that salting meat prevented decay? Did an observant sailor note that rope that had picked up tar from caulked seams lasted longer than clean rope?

Today biocides are important in textile finishing in the area of anti-microbial finishes. These include material protection (rotproofing and preservation), aesthetic (prevention of staining) and hygiene finishes (control of the development of odour and bacteria). Such finishes must reach a range of performance criteria, and be practical and economic in terms of application as well as meeting modern environmental standards.

It is known that bacteria were first recognised and described in the late seventeenth century (Anton van Leeuwenhoek, 1632–1723) and by the middle of the eighteenth century the effectiveness of certain chemicals against bacteria was readily recognised with the use of the first antiseptics. Taking this concept through to the protection of materials, 8-hydroxyquinoline was sold as an antiseptic in 1895 [2] and was later used as a biocide on cellulosic materials.

On the practical side, it is known that the early fishermen of Norway soaked their nets in hot suspensions of bark and then treated them with wood smoke. This is akin to the tanning of leather, a trade going back hundreds of years, and involves the extraction of a tannic acid (for example, gallotannic acid, $C_{14}H_{10}O_9$) which has a preservative effect [3]. In more recent times, copper naphthenate was first investigated towards the end of the nineteenth century and marketable products were available from about 1912 onwards. However, it was not used

extensively until 1941 when the mass production and treatment of sandbags for civil defence purposes occurred in London and elsewhere [4]. Since then, many developments have occurred leading to today's biocides and their wide range of applications.

10.2 FIELD OF APPLICATION

Any textile finish that inhibits or kills micro-organisms can accurately be described as 'anti-microbial'. (A list of definitions is given in Table 10.1.) However, it is convenient to sub-divide this general type of finish into three main groups.

- (1) Rotproofing is an anti-microbial finish applied to give material protection, either long-term or short-term, against physical deterioration. For plastics, the term 'preservation' is used; it is also often used when referring to the short-term protection of textiles, either natural or synthetic, when mould growth can occur.
- (2) Hygiene finishes are concerned with the control of infection and unwanted bacteria; a specialised development is the prevention of dust mites.
- (3) Aesthetic finishes are used to control odour development and to prevent staining.

Table 10.1 Terms associated with the field of biocides

Term	Definitions
Anti-microbial	The effect, chemical or otherwise, of inhibiting the growth of or destroying a microscopic organism
Rotproofing	The treatment of a material to prevent decay due to bacterial or fungal action
Hygienic	Promoting health or cleanliness
Fungicide, bactericide, biocide	Substances capable of killing fungi, bacteria or living organisms, respectively
Fungistat, bacteriostat, biostat	Substances capable of inhibiting the growth of fungi, bacteria or living organisms, respectively
Bacteria (plural)	Unicellular micro-organisms
Fungi	A kingdom separate from bacteria, plants and animals. Fungi lack chlorophyll, leaves, true stems and roots, but their cell walls contain chitin, which is only found in the animal kingdom. Fungi reproduce by the production of spores.
Micro fungi	Fungi such as mould, mildew, yeasts and so on, not producing a macroscopic fruiting body like a mushroom
Enzyme	A protein produced by living cells to act as a catalyst in a specific biochemical reaction
Virus	A sub-microscopic entity capable of replication only within a living cell
Pathogen	An agent that can cause disease
Sterilisation	A process that kills living micro-organisms
Disinfection	The process of destroying, inhibiting or removing micro-organisms usually by chemical means
Antiseptic	Completely free of contamination by micro-organisms, or the chemical agent that attains this state

Some finishes fulfil two or even three of the above purposes – for example, cotton socks (prevent degradation, control dermatophytic fungi, inhibit odour development). Some examples of the uses of anti-microbial finishes are given in Table 10.2.

Table 10.2 Examples of uses of anti-microbial finishes

Finish type	Problem	Area of application
Material protection (rotproofing) – long-term	Loss of tensile strength in use	Tents, webbings, awnings
	Loss of tensile strength during storage	Storage of all cellulosic goods
Material protection (rotproofing) – short-term	Loss of tensile strength	Cotton, viscose, flax, jute and wool fabrics, fibres and yarns left wet between processing
Aesthetic	Odour Staining	Socks, underwear linings Shower curtains, roller blinds, garden furniture, curtains and curtain linings
	Staining, odour	Storage of fibres, yarns and fabrics with high humidities (climate or storage)
	Staining	Storage of packaged non-cellulosic textiles under fluctuating temperature conditions
	Staining	All textiles left wet between processing
Hygienic	Difficult to launder Dust mites	Bedding, mattresses, carpets Bedding, upholstery, carpets, mattresses
	Cross-infection	Protective clothing

Bacteria and fungi exist all around us and are essential in the cycle of nature for the decomposition of cellulosic materials such as plants and wood. Similarly, any textile made from cellulosic material – for example, cotton, viscose, jute, flax, hemp or blends of fibres containing these materials – can be degraded under appropriate conditions. Much work has concerned the study of the microbial decomposition of cellulose and this is well documented [5]. However, it is an indication of the complexity of the subject that the mechanism of breakdown is still not fully understood and research continues [6]. Another natural fibre, wool, breaks down under the influence of micro-organisms albeit more slowly than cotton. There are isolated claimed examples of microbiological attack of synthetic fibres [7], but in general the common ones – polypropylene, polyethylene, polyamide, acrylics and polyesters – are not subject to microbial attack [8,9], although residual monomers can provide a carbon source for micro-organisms. The exception to this general rule is polyurethane fibres.

There are often other chemicals present in yarns and fabrics that can provide a food source for micro-organisms, even if the fibre itself does not. These include spinning oils, lubricants and finishing aids, starch-based size, and fillers, finishes or coatings based on acrylics, polyvinyl alcohols, plasticised polyvinylchloride (PVC) and polyurethanes. Both PVC and polyurethanes are widely used as coatings in the textile industry. PVC itself is not attacked by micro-organisms [10] but plasticisers, fillers, pigments, stabilisers and lubricants are all susceptible. Some systems originally had some protection against biodegradation due to the use of heavy metal stabilisers such as lead and cadmium, but these have been largely phased out on environmental grounds. Many of the plasticisers are particularly susceptible and readily metabolised [11]. This degradation causes hardening, loss of tensile strength and eventual cracking of the PVC, as well as staining and the destruction of the appearance of the film due to surface growth. Table 10.3 lists plasticisers in descending order of susceptibility to microbial attack.

Table 10.3 Plasticisers susceptible to microbial attack

Highest susceptibility	Sebacates Epoxidised oils Polyethers Glycolates Adipates Azelates Pentaerythritol esters Phthalates Phosphates Chlorinated hydrocarbons Citrates
Lowest susceptibility	

Most plasticisers are esters and a number of fungi are capable of degrading them [12]:

- (1) *Aspergillus flavus*;
- (2) *Aureobasidium* sp;
- (3) *Fusarium* sp;
- (4) *Mucor* sp;
- (5) *Paecilomyces varioti*;
- (6) *Penicillium* sp;
- (7) *Gliocladium* sp. (*Trichoderma* sp.)

However, many bacterial species have also been isolated from degraded plastics and it is thought that the fungi act as primary colonisers, converting the plasticisers into simpler organic compounds, which are then available to both bacteria and fungi. Such bacteria include:

- (1) *Achromobacter* sp;
- (2) *Bacillus* sp;
- (3) *Brevibacterium* sp;
- (4) *Nocardia* sp;
- (5) *Pseudomonas* sp.

The pink stains often seen on PVC- or PU-coated fabrics are caused by the bacteria *Streptoverticillium waskmanii*. Typical end-uses requiring protection include shower curtains, tents and ground sheets, tarpaulins, pool liners, flooring, roof linings, wall coverings, waterproof and protective clothing, and agricultural films. With polyurethanes, the polymer itself is subject to biodegradation by a wide range of fungi [13] with polyester types being considerably more susceptible than polyether types. Fungi can produce extra-cellular enzymes capable of attacking part of the polyurethane molecule. These include proteases (capable of attacking amide groups), esterases (capable of attacking urethane and ester linkages) and ureases (capable of attacking urea linkages). This leads to splitting of the molecules and results in the cracking of polyurethane films without prior hardening or appreciable weight loss. Problems have occurred in a wide range of applications including protective clothing, shoe uppers and soles, foams and sheet materials. Staining and odour problems can also arise particularly with open-cell foam structures. Typical fungi associated with these problems are listed below, and bacteria such as *Streptomyces* are also involved:

- (1) *Aspergillus flavus*;
- (2) *Aspergillus terreus*;
- (3) *Chaetomium globosum*;
- (4) *Cladosporium cladosporioides*;
- (5) *Penicillium pinophilum*;
- (6) *Rhizopus stolonifer*;
- (7) *Gliocladium virens*.

Long-term protection is required for end-uses such as tents. There are other applications where short-term protection is needed irrespective of the end-use of the material because of problems such as mildew attack during processing. Under warm damp conditions, mould and mildew can develop in one to two days and this can result in actual spoilage of the material (loss of tensile strength), or staining (which may be very difficult or impossible to remove) and the characteristic musty smells associated with contaminated goods. It was estimated in 1983 that total losses (direct losses, replacement and reprocessing costs) due to biodeterioration in the UK wool industry alone amounted to between £8 million and £10 million per year [14]. In such instances a treatment with a biocide to give short term protection is desirable particularly if the goods have a high value – for example, mohair fabrics.

Another important field of application that applies to any type of material subject to microbiological attack, irrespective of its end-use, is in storage. Mould will develop when fabrics are damp even if the temperature is quite low. In apparently dry conditions it is possible for mould to develop in localised areas because the normal moisture regain held in fabrics can be transferred and concentrated under fluctuating temperatures. Impermeable packaging can exacerbate this problem.

During processing fabrics can be left wet over a weekend. In warm conditions mould growth can easily develop during this period. Lancashire became the home of the British cotton spinning industry in part because the climate in this location west of the Pennines meant

damper conditions, higher moisture retention in the cotton and fewer breakages. Some yarn processing today still requires higher than normal moisture content, in extreme cases up to 30%, and such yarns – even though they are synthetic – can develop mould growth under appropriate conditions.

Staining is a major problem in certain areas and may make a product aesthetically unacceptable even if physical properties are not impaired. This can happen irrespective of the type of fibre used, in applications such as shower curtains, garden furniture and curtains or curtain linings. The latter problem is due to curtains brushing against windows and absorbing condensation. Dirt, shampoo and soap deposits, and other finishing chemicals can all provide nutrients for fungi and bacteria.

Clothing worn close to the skin can absorb perspiration, which is then decomposed by micro-organisms producing unpleasant smells.

Hygiene finishes are important in a wide variety of applications where it is necessary to either control or prevent the development of micro-organisms that otherwise can produce undesirable effects such as cross-infection. A number of textile household goods may be difficult to clean or are only cleaned occasionally and will become reservoirs for micro-organisms unless hygienic finishes are applied. Some bacteria are not harmful in themselves (although they may be responsible for undesirable odours) but others are pathogenic and their control can help reduce infection or cross-infection in communal areas and hospitals.

The incidence of allergy problems has increased substantially in recent years. In part, this is due to changes in modern homes. Improved insulation and double-glazing cuts down air movement. A warmer and more moist microclimate assists the development of micro-organisms and also dust mites. The latter proliferate in bedding, mattresses and – to a lesser extent – upholstery and carpets. Their faeces contain the allergen DER P1, which is responsible for the symptoms of about 50% of asthma sufferers. In addition, about 5% of western populations have some type of mildew allergy. Dust mites feed primarily on skin scales. Everybody sheds these every day. Fungi also grow on the skin scales fulfilling a role as a type of pre-digester and also providing additional nutrients.

The maintenance of good hygienic conditions and the use of biocides can help substantially reduce or eliminate these problems. A good anti-fungal treatment will reduce dust mite numbers but for real protection a product is required that has a specific effect against the dust mite. In the UK and Europe, a range of products produced by Sanitized AG, Switzerland, and sold under the Actigard trade name, fulfils this function.

10.3 MODE OF ACTION

In order to live and multiply, micro-organisms need moisture, warmth and a food source. Therefore, if the micro-organisms can be deprived of any one of these, or if the micro-organism itself can be destroyed or prevented from multiplying, then it follows that an anti-microbial effect will be in force. For practical purposes, keeping material permanently dry or very cold is impossible although it is worth noting that degradation of materials in deserts or Polar Regions is

very slow. Normally micro-organisms are present all around us and, being airborne, are constantly landing on textiles and materials. Given an adequate food source they will then start to multiply, producing deleterious effects as described above. The food source may be the textile itself (for example, cellulose or polyurethanes) or another chemical present on the substrate (for example, spinning oils or soiling). The latter category includes dirt deposited from the atmosphere, perspiration, skin scales and soap residues. The level of soiling varies considerably depending on the environment; consider the difference between greasy deposits that accumulate near cooking areas and ordinary dust accumulation in a bedroom. The foodstuff may be in a form that is immediately useable by the micro-organism; an obvious example of this is the breakdown of sugars by yeast in the fermentation process. More usually, however, it is necessary for the micro-organism to break down more complicated molecules into a form that is accessible as food. To do this the micro-organism produces an enzyme that is a biocatalyst. A typical sequence in connection with the breakdown of cotton is shown in Figure 10.1.

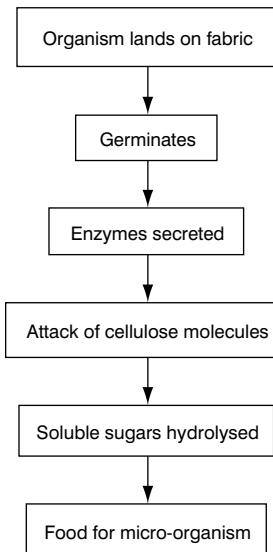


Figure 10.1 Degradation process (cotton)

It follows, therefore, that in order to prevent degradation of textile materials, four possibilities are available:

- (1) kill organism;
- (2) block enzyme;
- (3) insert a barrier (for example, coating);
- (4) modify fibre (top surface or whole).

Only the first option applies to hygiene and aesthetic finishes while all four options apply theoretically to a rotproofing finish designed to prevent breakdown of fibres.

The process of destroying a micro-organism is achieved with a biocide in one of two ways. There can be a chemical reaction with the cell membrane, which stops the metabolic process; for example, silver- and mercury-based biocides work by displacing hydrogen ions from bacteria with the relevant metallic ion. Alternatively, the biocide can penetrate the cell wall and poison the cell from within.

A second approach is to block the enzymes elucidated by the micro-organisms. This is an important consideration. The mechanism whereby the microbe recognises the presence of a food source and produces the relevant enzyme is still not understood. However, it is possible for enzymes to be produced that will break down a material even when it has been treated with a biocide. This is obvious when one considers a tent fabric. If buried in the ground these will eventually rot almost irrespective of what treatment is given to them, and before the biocide has leached out of the fabric. Many of the enzymes produced by micro-organisms have been identified, particularly those associated with the breakdown of cellulose but blocking these is not yet practical.

Some substrates can be protected by coating or impregnation. Such a process will substantially change the physical properties of the fabric but this may be desirable for other reasons. A coating may be required in order to give water-repellent or waterproof properties and this will lend a considerable degree of protection to the fabric against microbial attack, but it is usual to also include a biocide to give aesthetic protection and to prevent degradation of the coating material itself. The degree of protection will depend on how much strike there is of the coating into the substrate or whether the substrate is coated both sides.

The alternative barrier method is to use a treatment that gives the fabric direct surface contact activity against microbial growth. The only example of this to date is the use of an organo-silicon polymer that contains quaternary ammonium groups and forms a bio-barrier on the fabric. The chemical process involves a condensation reaction and needs available hydroxyl groups for permanent bonds to be formed. This is only available in cellulosic fibres and therefore has limited applicability.

The fourth approach is to modify a biodegradable fibre. In the case of cellulose this involves reacting a chemical with the appropriate site on the molecule so that the biochemical reaction carried out by the micro-organism, via its enzyme, can no longer take place. The earliest practical example of this was in 1920 when Doree discovered the resistance of cellulose acetate to micro-organisms [15]. Full acetylation to the diacetate or triacetate results effectively in new fibres with substantially different properties to cellulose [16] Partial acetylation still produces some loss of physical properties and because of other problems and high processing costs this route for producing a rotproof fabric has never become commercially viable.

To protect against rot-producing fungi, disease-causing bacteria or aesthetic-destroying microbes it is necessary to use an anti-microbial treatment. This can take several forms.

10.4 AFTER-TREATMENT

The most common, versatile and economic method for applying anti-microbial finishes is by padding, exhausting or spraying the finish onto fabric, fibres or finished articles. A wide range of products is available and the type and amounts used depend on the requirements of the finished product. In order to achieve good durability the anti-microbial product used should not be volatile and should be essentially insoluble so that it is durable to weathering and washing. However, the anti-bacterial or anti-fungal agent present must be released from the fabric at a sufficient rate to kill or inhibit the growth of bacteria and fungi. Therefore, what is effectively a 'controlled-release' mechanism is necessary either by a chemical or physical reaction with the textile. A specific, but not widely used, example of a chemical controlled-release mechanism is the modification of poly(vinyl alcohol) fibres with a 5-nitrofurylacrolein in the presence of an acid catalyst to form an acetal. This fibre, Letilan, reacts slowly in the presence of moisture to release the nitro compound and give anti-microbial activity. Another example is the Permax process, which involves the controlled release of zinc and peroxide after repeated laundering. A physical controlled release can be achieved, although no commercial methods are yet available, by micro-encapsulation. The biocide is enclosed within a plastic film through which controlled amounts can migrate. When washing or laundering removes the biocide from the plastic film it is replaced from the enclosed reservoir.

Many biocides are applied with other finishes – for example, a fluorocarbon. Such hydrophobic finishes affect a controlled release by reducing the wetting out of the fabric and thereby controlling the migration of the biocide.

The more common biocides used are discussed separately. There are in addition a number of exotic treatments that have been established at laboratory level, which give anti-microbial finishes to a range of fabrics and fibres, but because of limited application none have been introduced commercially.

10.5 TREATMENT OF FIBRES

Synthetic fibres can be treated during production in order to make them anti-microbial. This property is usually imparted by the addition of a biocide into the polymer solution before spinning. Potentially this route offers the great advantage of excellent durability because the biocide is distributed throughout the fibre and is very durable to washing and weathering. Care must be taken in the choice of biocide to ensure that, as appropriate, it does not react chemically with the fibre, thereby neutralising itself, or modify the properties of the fibre to an unacceptable degree. It must also withstand high processing temperatures, survive a chemically hostile dope solution or spinning bath, not contaminate the spin bath, not adversely affect subsequent dyeing and finishing of the fibre, and not be affected itself by such processes.

10.6 MATERIALS TO BE PROTECTED

As mentioned already (Section 10.2), cotton, wool, jute, flax, other cellulosic materials, and blends of these materials with other fibres, can all be physically degraded by microbial attack, leading to breakdown of the fibre, loss of tensile strength and premature failure of the finished product. The rate at which degradation takes place is dependent on a wide range of factors including the type of fibre used, construction of the material or goods, other chemical treatments applied, the end-use of the product and the climatic conditions under which the product is used. The latter is particularly important since under either very cold or very dry conditions degradation is minimal but where moisture and warmth combine, degradation can be rapid. Field trials with untreated sandbags showed that they could last for up to 6 weeks in the Dutch East Indies (where there is less than 10 inches of rain per year) [17] but only survived for 11 days in New Orleans in September, a period with a sub tropical climate [18]. Tents used at Milne Bay, New Guinea, where there is 100 inches of rainfall per year, leaked after 3 to 4 months and had to be discarded after 6 to 8 months. However, at Port Moresby, where the rainfall is only 40 inches per year the life of the tent was extended by one third as much again [19].

It might be supposed that the best way to overcome the rotting of fabrics and fibres would be to use other materials that are not subject to microbiological degradation. This has happened in certain areas – for instance, many ropes are now made from polypropylene or nylon instead of traditional hemp. However, in many situations the properties required in the finished fabric can only be achieved by using cellulosic-based fibres. Cotton fabrics used for tents, when dry, have the very desirable property of high water vapour permeability. This is an essential pre-requisite for living in tents. However, when cotton becomes wet it swells so that water penetration becomes very difficult. This is one of the reasons why when cotton tents are being used, localised pressure should not be applied to the tent fabric during rain since this stretching of the fabric can allow the ingress of water. Sandbags made from jute 'grip' well on each other so that stacking is easy but with some synthetic fibres the bags slip off each other with consummate ease. For a number of military applications it is essential to avoid the build-up of static and the risk of a static discharge causing a spark. For this reason cotton or other cellulosic fibres are preferred to synthetics.

In the area of clothing, comfort is possibly the most important factor. Cotton and viscose, because of their high moisture uptake and excellent water vapour permeability, are generally preferred for use in warm climates because of the comfort factor, while the natural properties of wool make it an excellent fibre for applications such as sweaters and carpets.

Lastly, but by no means least, economic factors play a very important part in fibre and fabric choice. Changes in oil prices, the failure or success of cotton crops and the demands of local economies all interact to change the supply and demand of different fibre types, but with natural and cellulosic fibres being based on 100% renewable sources it is probable that their share of the total world textile market is unlikely to decline much further in the foreseeable future. For this reason, biocides will continue to be in demand in order to give the necessary

protection to those natural fibres that would otherwise rot or decay, or enhance the properties of the fibres through the use of hygiene finishes.

10.7 PRACTICAL BIOCIDES

It is fairly easy to list the desirable properties of an 'ideal' biocide:

- (1) wide spectrum of effectiveness against both bacteria and fungi;
- (2) durable for the life of the product;
- (3) non-toxic to humans at concentrations used – safe to handle and use;
- (4) colourless and odourless;
- (5) reasonable cost, and effective at low concentrations;
- (6) resistant to leaching, weathering and sunlight;
- (7) no adverse effect on handle or other physical properties of the fabric;
- (8) compatible with water-repellent and flame-retardant finishes, dyes and other textile chemicals;
- (9) does not accelerate or catalyse other degenerative processes;
- (10) applicable using standard textile machinery;
- (11) withstands processing conditions and temperatures;
- (12) no environmental problems.

There is no one preservative that fulfils all these properties. Some biocides are very effective against bacteria but have little or no effect against fungi, and vice versa. Others may show a much better effect against Gram positive compared to Gram negative bacteria. Some comparative figures for minimum inhibitory concentrations (MIC) are given in Table 10.4. From this it can be seen that the use of more than one active compound in a biocide formulation can achieve effectiveness against a wide range of micro-organisms without having to use excessive applications levels.

Biocides must be durable; they must therefore be essentially non-volatile. Some finishing processes involve the formation of formaldehyde and small quantities may remain on the fabric, giving it an anti-microbial effect. However, this will be lost over time because of volatility. For some applications, durability can be improved by applying the biocide in conjunction with a binder or resin.

Hygiene finishes are applied to fabrics and goods that come into contact with the skin. It is essential therefore that biocidal finishes and treated goods are safe to handle and use, and are completely non-toxic and non-irritating to human beings. If the products are to be handled regularly by individuals, the finishes must be non-sensitising as well as non-irritating. Legislation exists describing safe handling and giving maximum exposure limits and occupational exposure standards for a wide range of chemicals, including several biocides [20]. The days when harmful solvents could be used in textile applications have long passed!

Many of the older biocides imparted colour to the treated material. For instance, organo

Table 10.4 Minimum inhibitory concentrations for some biocides

Biocide	Minimum inhibitory concentration (MIC) (ppm)		
	Bacteria	Fungi	Yeasts
Para chloro meta cresol	80–800	80–200	200
1,2-Benzisothiazolin-3-one	5–77	9–70	19–50
2,2'-Methylene bis (4-chlorophenol)	2–25	6–200	–
2-Bromo-2-nitropropane-1,3-diol	12–50	–	–

copper compounds give a green or yellow-green colour. While this may be acceptable for certain end-uses – for example, tents – it considerably limits their areas of application. A biocide that leaves an odour on the fabric is also unacceptable even if harmless.

Low add-ons of chemical finishing agents are always less likely to interfere with other properties or other finishes and therefore low concentrations of biocides are desirable. Costs should also be reasonable taking into account the chemical cost per treated kilogram of fabric, and application costs.

Many textiles treated with a biocide will be used in situations where they are subject to exposure to sunlight, leaching and weathering – for example, in tents and awnings. Hygiene finishes may be applied to products that are either washed or dry-cleaned. Any biocide used must be able to withstand these conditions and retain its effectiveness over a period of time.

Although not so important with technical textiles, the handle of many other fabrics is very important and therefore the addition of a biocide should not affect this, or other physical properties.

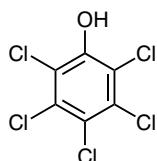
Biocides are often used in conjunction with other finishes and must be compatible with them. Original work done for the protection of polyurethane coatings used pentachlorophenyllaurate (PCPL). However, this reacted with the PU system in many cases, completely inactivating the biocide. Many biocides have very low solubility in water and therefore have to be applied using solvents or emulsifying agents. Some emulsifying agents also have a wetting effect and these would be unsuitable for use with a fluorocarbon or water-repellent finish. Some resins that might be used in order to give better durability could crosslink with a biocide, inactivating it. Some biocides are quite pH-sensitive; methylene bis thiocyanate (MBT) is gradually hydrolysed in solution. Its half-life at pH 5 is more than 30 days but at pH 9 is less than three hours.

Biocides must be capable of application using standard textile processing equipment. Most commonly, biocide finishes are padded on but there may be occasions when it is necessary to exhaust a finish (application to finished products such as hosiery) or use a spray (treatment of footwear or items *in situ*). Although there are a few textile finishes for which specialised equipment is used – for example, the Proban treatment – this is only economically viable if the quantities of fabric being treated are large and consistent. There have been a number of proposed biocide treatments for textiles that have given good results in laboratory trials but scaling up to full-scale production is uneconomic.

In addition to being capable of use with standard textile equipment, the biocide must also withstand processing. If the biocide is in the form of an emulsion this must be stable under processing temperatures and conditions and the biocide must be able to withstand drying temperatures of up to 180 °C or 190 °C depending on the fabric being treated.

Environmental considerations have been responsible for the major changes in textile biocides in recent years. The ‘cradle to the grave’ approach requires that due consideration be taken not only of the disposal of effluent at the manufacturing stage but also the eventual disposal of treated products. Various EC Directives and resultant UK legislation [21] have produced changes in chemicals that are acceptable in industry. There is now a more precautionary approach to the input of dangerous substances to the environment and a policy of reducing inputs of hazardous substances into the aquatic environment. By considering various chemical properties, such as persistence in water, acute and chronic toxicity, bioaccumulation and total production, a Red List of substances was drawn up (and can be added to) of substances that are effectively banned from discharge to water. This includes a number of very effective biocides including mercury and its compounds, triorganotin and its compounds, pentachlorophenol (PCP) (Structure 10.1) and its esters and salts.

Pentachlorophenol

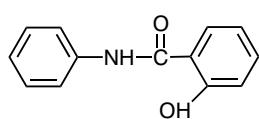


10.1

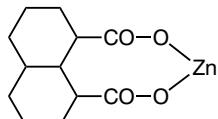
Consideration of the above requirements means that the trend over recent years has been, and will continue to be, towards more sophisticated biocides. An old rotproofing process could have involved using a water-insoluble copper compound (toxic but effective against a wide range of organisms), dissolving this in a harmful solvent (no longer acceptable), padding this onto fabric, drying (release of large quantities of organic volatiles is now illegal) and dropping any remaining bath down the drain (now banned!).

Today a biocide might well be a mixture of more than one active compound made into a stable water-based emulsion, which can be applied to a fabric by conventional padding, and dried without the release of harmful volatiles, any discarded spent liquor being sufficiently biodegradable to be accepted in a normal effluent treatment system. Examples of such products include the range of biocides produced by Sanitized AG and sold under the Actifresh and Sanitized trademarks.

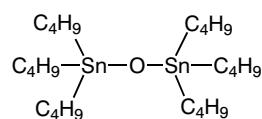
Changes in biocides are very well illustrated by comparing different editions of BS 2087: Preservative treatments for textiles [22]. The 1981 edition lists eleven products (excluding mothproofing chemicals) under Class A and three under Class B. The 1992 standard showed the deletion of three products from Class A (chrome tinting, salicylanilide (Structure 10.2) and tar oils) but with considerable limitations with the remainder. Only three could be used on white fabrics (zinc naphthenate (Structure 10.3), PCPL and dichlorophen). Of these, PCPL is banned on textiles in some countries, such as Germany, and is a Red List product, meaning that no water-based effluent containing it can be discharged. Dichlorophen is not recommended for apparel and decorative furnishings. Under Class B, tributyl tin oxide (TBTO) (Structure 10.4) and pentachlorophenol (PCP) had been deleted and 2-(thiocyanomethylthio) benzothiazole (TCMTB), zinc-2-pyridinethiol-N-oxide (zinc pyrion), and dichlorophen mixed ester had been added. With only a few biocides available that will meet BS 2087, there are moves to assess biocides on the basis of performance requirements and there is an intention to produce a BS 2087 Part 3, which will focus on assessing textile preservative treatments relative to performance criteria. This would then allow any biocide or combination of biocides to be used provided they met the necessary criteria. The Ministry of Defence has taken one step down this road by producing an Interim Defence Standard [23].

Salicylanilide (*N*-phenylsalicylamide)**10.2**

(Zinc naphthenate)

**10.3**

Tributyl tin oxide (TBTO)

**10.4**

10.8 MODERN BIOCIDES

Reference has already been made to the requirements of a modern biocide and restrictions on chemicals once widely used. The general trend is towards fully organic products with, depending on end-use, a good environmental and safety profile. There is, however, one metal that is in use and that is silver – or, more accurately, silver ions. The positively charged silver is used with a glass ceramic carrier. Although expensive, biocides of this type have the advantage of a very low toxicity profile and excellent heat stability. Typical biocides used today are shown in Table 10.5.

10.9 TEST METHODS AND ASSESSMENT

Testing anti-microbial finishes on textiles is more difficult and more complicated than many other tests. The two main difficulties are reproducibility of results and establishing a meaningful correlation between laboratory results and actual conditions in the field. The current British Standard on preservative textile treatments (BS 2087) is purely analytical in content. It is based on field experience over many years and does not have any references to anti-microbial tests! While in some ways this is an unbeatable approach, it provides no scope for swift development. Laboratory testing is essential to provide reasonably rapid screening of new preservatives and to check the effectiveness of existing preservatives under new conditions or when used in combination with other finishes. For example, the use of a melamine formaldehyde resin could result during curing in the crosslinking of not only the resin but the biocide present and its consequent inactivation.

There are four main test methods for evaluating anti-microbial finishes. They are summarised in Table 10.6 and a brief description of each method is given below. In all cases, controls as well as treated materials must be tested.

10.9.1 Agar plate method

In the agar plate method, a nutrient gel containing a micro-organism is poured into a plate and, when set, a piece of the fabric under examination is put on the surface of the gel and the whole plate is then incubated under conditions ideal for microbial growth. (Alternatively the inoculum is sprayed onto the sample after it has been placed on the agar plate.) For bacteria, this could be 18–24 hours at 37 °C; for fungi, 3–14 days at 28 °C, or up to 4 weeks for materials such as PVC-coated fabrics. At the end of the incubation period samples are assessed either visually or by performance loss. The visual assessment is normally a comparison between uninhibited growth of the micro-organism in the dish and the growth on, or in contact with, the sample. There may be a reduction in growth or a complete absence of growth on the sample. There may also be a zone of inhibition (or ‘halo’) around the sample where the biocide has diffused into the gel and prevented the micro-organisms from developing. Large zones of inhibition are not desirable; they

Table 10.5 Typical modern biocides

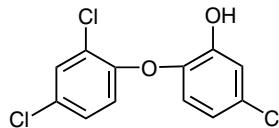
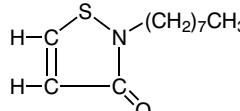
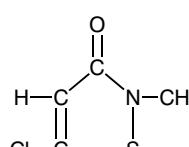
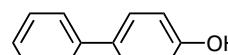
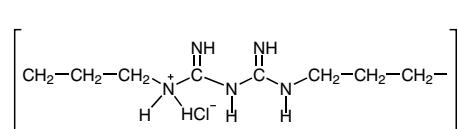
Name	Comments
2,4,4'-Trichloro-2'-hydroxy-diphenyl ether	Originally developed by Ciba
Triclosan 	Has a very good toxicity profile and is considered to be very safe; used in toothpastes as well as on textiles where skin contact is involved
2,2'-Dihydroxy-5,5'-dichloro-diphenyl methane	Effective biocide with good biodegradability
Dichlorophen	Suitable for many applications although not recommended for skin contact
Iothiazolones e.g. 1,2-Benzothiazolin-3-one (BIT) 2-n-Octyl-4-isothiazolin-3-one (Octhilinone)	These biocides are used in a wide range of applications from preservatives in aqueous latex systems and cosmetics to mildewcides, slimicides and textile uses
	
5-Chloro-2-methyl-4-isothiazolin-3-one 	
Ortho phenyl phenol 	
Poly hexa methylene biguanide (PHMB)	The structure of this molecule enables it to bond to cellulosic materials and give very good durability. It has a long history of safe use in applications such as swimming pools and cosmetics
 Average n = 12	

Table 10.6 Summary of microbiological test methods**(1) Agar plate test**

Procedure:	Sample is maintained on an agar already containing, or inoculated with, an organism for 18–24 hours (bacteria), or for up to 4 weeks (fungi). Agar normally contains a nutrient but samples can be tested with a nutrient-free agar to see if they are a viable carbon source.
Evaluation:	Visual (growth in contact area and halo).
Advantages:	Relatively quick. Can be used for testing with bacteria or fungi, or mixed spores. Can be modified to cope with different materials e.g. samples with low diffusion rates (plastics, textiles treated with hydrophobic chemicals) can be held on the agar for 24 hours prior to incubation to allow biocide to diffuse out.
Disadvantage:	Size of halo can indicate highly effective biocide or, more usually, high diffusion rate.
Accuracy:	Good (average of 4 samples); variation of more than 1 mm in halo size is significant. Ratings of growth on sample can be less accurate.

(2) Soil burial test

Procedure:	The most severe test. Samples are buried for up to 28 days (longer for plastics and coated materials).
Evaluation:	Measure loss of tensile strength or loss of weight. Control sample must rot completely in about 7 days.
Disadvantage:	Long, time-consuming and expensive.
Accuracy:	(Average of 9/10 samples) \pm 10%.

(3) Saturated atmosphere test

Procedure:	Usually used for examining effectiveness against fungi or yeasts. Sample is sprayed with a mixed spore suspension (fungi) and held over water for 14 days. Relative humidity is minimum 90%. In order to develop, organism must obtain its carbon from material under test.
Evaluation:	Visual assessment (including using a microscope).
Disadvantage:	Long time of incubation.
Accuracy:	\pm 10%

(4) Count test

Procedure:	Samples are inoculated with micro-organisms and left in contact for 0, 6, 12, 18 and 24 hours at 37 °C. Organisms are then extracted and counted.
Evaluation:	Number of colony forming units (cfu) counted after 24 hours and compared with the number at time 0 hours.
Advantages:	Relatively quick. Can distinguish between a biocide and a biostat.
Disadvantages:	Only suitable for bacteria. Time-consuming and expensive. With some fabrics, micro-organisms can 'hide' producing invalid results.
Accuracy:	(Average of 6 samples) \pm 30–40%.

indicate that either the material has been over-loaded with biocide or that the biocide is diffusing rapidly and easily into the gel, an indication that durability will not be good.

Because of possible variations, samples will always be tested at least in quadruplicate with controls to check the viability of the organism. Care must be taken to prevent contamination from outside bacteria or fungi.

The agar plate method provides a reasonably economical and swift method for assessing materials. The test method is flexible and many variants are possible:

- (1) the test can use single bacteria or fungi or mixed cultures;
- (2) a wide range of textiles both coated and non-coated and cellulosic and non-cellulosic can be tested;
- (3) a mineral salts agar can be used so that the only carbon source is the material under test and development of the micro-organism will indicate that degradation is taking place;
- (4) quite large numbers of samples can be handled so that it is possible to compare a range of treatments and their durability – for instance, leaching, washing, dry-cleaning and exposure to UV light.

Assessment by performance loss is done by measuring loss of tensile strength or weight loss but this type of assessment is not relevant to all materials. For instance, with a polyurethane-coated nylon fabric the nylon substrate may be completely unaffected by micro-organisms so that the tensile strength of the material is unaffected during tests and weight losses are minimal. However, fungal attack of the polyurethane can result in cracking and a loss of waterproofness.

The agar plate method, when used with bacteria, relies on the biocide on the material under test migrating or diffusing into the agar gel. If the diffusion rate is very low – for example, with certain coated materials or with water-repellent finishes – misleading results may be obtained particularly with bacteria with growth occurring before the biocide has had time to diffuse out. This problem can be partly overcome by holding a sample on the plate at 5 °C for 24 hours prior to incubation. The test organism does not develop during this period but the biocide on the material has more time to diffuse into the gel.

10.9.2 Soil burial test

The soil burial test is a relatively crude method for assessing anti-microbial finishes and is very severe. It is, however, particularly suitable for assessing products that come into direct contact with soil such as tents, tarpaulins and sandbags, or other applications that will be subject to exposure to micro-organisms. Strips of the material under test are buried in prepared soil for 7, 14, 21 or 28 days (or longer for plastics and coated fabrics) and after burial the samples are then tested for loss of tensile strength.

Different test standards require up to 20 of each sample to be tested so the method as a whole is time-consuming and expensive. It is essential to use a control material that must rot quickly to confirm the efficacy of the micro-organisms within the soil. There are a number of inevitable variants in this method – for example, the type of soil, moisture, pH, type and number of micro-organisms present. The most meaningful results come from assessment based on comparisons rather than looking for absolute standards.

The soil burial test cannot be used for assessing aesthetic anti-microbial finishes but if the fungicide performs well in this test it will almost certainly perform well in less severe procedures.

10.9.3 Saturated atmosphere test

This method is suitable for assessing fabrics that will come into contact with airborne micro-organisms but will not be in contact with the ground. The method consists of hanging the test specimens over water in a kilner-type jar, spraying the specimen with a single or mixed fungal spore suspension and then incubating for a minimum of 14 days at 28 °C. A visual assessment is made at the end of the test period.

This test method is suitable for assessing anti-microbial finishes intended for aesthetic purposes or those intended for use to prevent mould or mildew development during storage. It is fairly easy and economical to perform but is not as precise as the agar plate method.

10.9.4 Count test (bacterial challenge)

The previous test methods are all qualitative or at best semi-quantitative. In contrast, the count test is quantitative although its application is more limited.

The count test involves inoculating swatches of the test fabric with a bacterial culture containing typically 10^4 – 10^6 colony-forming units (cfu) per ml. An extraction is made at time zero to establish the number of cfu present, and then further counts are made after, say, 6, 12, 18 and 24 hour periods of incubation so that a pattern of growth is established. A control sample will show a large increase in the number of cfu after incubation (although there is normally an induction period and the rate of growth eventually plateaus); an ineffective biocide will also show an increase. If the cfu value is more or less the same after incubation then the anti-bacterial agent is bacteriostatic; if its value is significantly reduced then the agent is bacteriocidal. This is illustrated in Figure 10.2.

The count test is only suitable for testing hygienic finishes and cannot be used with fungi. It is the least severe of the four basic test methods described and, because of the time needed to make the individual counts, is expensive.

There are some limitations to this test method. In order to give valid results the biocide must be able to leach fairly readily into the aqueous medium. It is not, therefore, suitable for coated fabrics nor, often, for fabrics where other finishes have also been applied – for example, a fluorocarbon. Also, depending on the structure (physical and fibre) of the fabric, as well as factors such as soiling, bacteria can ‘hide’ in the fabric, so that the biocide appears to be ineffective particularly in the short term.

There are several variants on these test methods as well as variations in national standards. In the UK, BS 6085: 1992, Methods for determination of the resistance of textiles to microbiological deterioration [24], gives methods for three of the above tests but other countries have other standards. Details on test methods and standards are widely available [25,26].

It is important for exporters to be aware of these variations and to ensure that any textiles intended for overseas markets meet the required standard.

In addition to assessing the efficacy of biocide treatments, testing the durability of such finishes is also frequently required. This can be done via field trials but more practically in the laboratory.

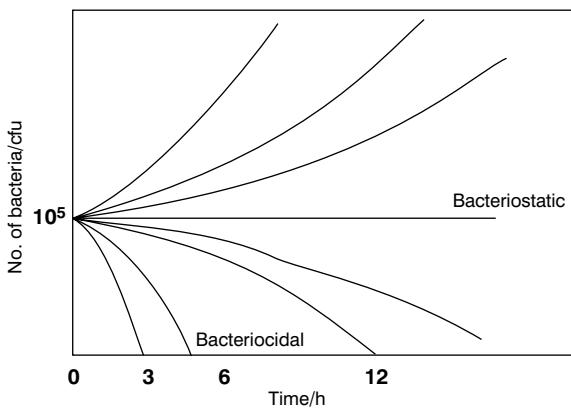


Figure 10.2 Graph to show possible results of count tests to measure the effectiveness of anti-bacterial agents

Samples are evaluated microbiologically before and after various treatments such as washing or leaching to check fastness, heating to ensure thermal stability, exposure to carbon arc or xenon lamp to evaluate susceptibility to actinic degradation, and Q panel to test weathering. The latter piece of equipment allows samples to be exposed to light (UVA or UVB), humidity and spraying with water, in different settings, combinations and cycles.

10.10 THE FUTURE

Perhaps the only certainty about the future is that there will be ongoing change. This will certainly apply to biocides. The Biocidal Products Directive is having a significant impact on the industry. The BPD came into force on 20 May 1999, and should have been fully implemented by 20 May 2001, but in some countries – for example, France and Germany – this has not yet happened. The BPD requires that each biocidal product will, in effect, have a full risk assessment carried out on it. Core data will be needed for each product with additional data needed depending on end-use. For instance, any biocide used for wood preservation will need full data on environmental aspects. An anti-microbial finish for textiles involving skin contact will need additional safety data concerning this aspect. For manufacturers with biocides with relatively low volumes the cost of generating the necessary data may make ongoing production uneconomical. Acute toxicity data is relatively cheap to generate but sub-acute and other long-term studies are very expensive. It is therefore likely that the number of biocides being produced in the future will diminish and bringing new products to market will be even more expensive. Avecia (formerly Zeneca) withdrew their product Densil (2,3,5,6-tetrachloro-4-(methylsulphonyl) pyridine) for these reasons.

A possible future development would be the micro-encapsulation of biocides. The potential is considerable if the correct performance and economics can be achieved. Benefits could include better durability and greater safety.

The search for more cost-effective testing methods will continue. The British Textile Technology Group pioneered the detection of micro-organisms on textiles using ATP

luminescence in the late 1980s. It is now possible to assess the growth of micro-organisms by the Firefly Bioluminescent Detection or the analysis of adenosine triphosphate (ATP) [26]. This is a much more rapid method than culturing samples onto an agar plate and waiting to see if growth develops. There will also be ongoing moves to standardise test methods. Within Europe there is the CEN / TC189 / WG5 Committee 'Determination of Resistance of Textiles to Microbiological Attack' which was set up in 1992. New standards will be produced in due course, which will replace national standards.

Overall the need for anti-microbial and hygiene finishes looks set to continue for the foreseeable future. Improving performance and cost-effectiveness, while meeting environmental and toxicity requirements, will continue to challenge those working in this field.

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CHAPTER 11

Wool finishes: the control of shrinkage

D L Connell

11.1 INTRODUCTION

Wool has been used in clothing for thousands of years, and presents considerable benefits to the wearer in terms of warmth and comfort. The main disadvantage of wool as a textile fibre in today's market lies in the tendency of wool to felt and shrink severely on washing. It is often underestimated how much a wool garment can shrink during modern household laundering processes: dimensional changes of more than 50% for untreated wool are not unusual. In addition, the handle and texture of the garment changes radically on felting.

Fortunately, techniques have existed for many years to enable the textile manufacturer to address this problem and produce garments with excellent wash and wear characteristics. There is therefore no need to limit the use of wool in the manufacture of garments, designed to be easy-care, on the basis of the tendency of untreated wool to shrink. This chapter addresses the science and technology that delivers this benefit to the consumer.

11.2 FIBRE STRUCTURE

Wool is an animal hair fibre, and shares many of the characteristics of this class of fibre. It is composed of an outer layer of overlapping scales (the cuticle) surrounding an internal core (the cortex) composed of numerous long, thin, spindle-shaped cells running axially within the fibre, and firmly cemented together. Cortical cells in turn contain long, thin bundles of microfibrils or filaments in an amorphous matrix (Figure 11.1). These structures are composed largely of keratin, a protein complex with a high sulphur content, containing a number of disulphide crosslink residues [1]. It is these residues that are believed to give wool its relatively high wet strength as well as its low lateral swelling and insolubility. They also play a key role in many shrink-resist systems.

In wool, the cuticle, or scale layer, is only one scale in thickness over most of its area, except where one scale ends and another commences. It is composed of a number of layers, principally the exocuticle, which is keratinous protein, and the endocuticle, which is mainly non-keratinous protein. There is an outer layer, which is revealed by the Allwörden reaction: if wool fibre is immersed in chlorine water, within 15–20 s it develops a series of blisters associated with the scales [2]. The scales all point in the same direction: outwards along the fibre towards the

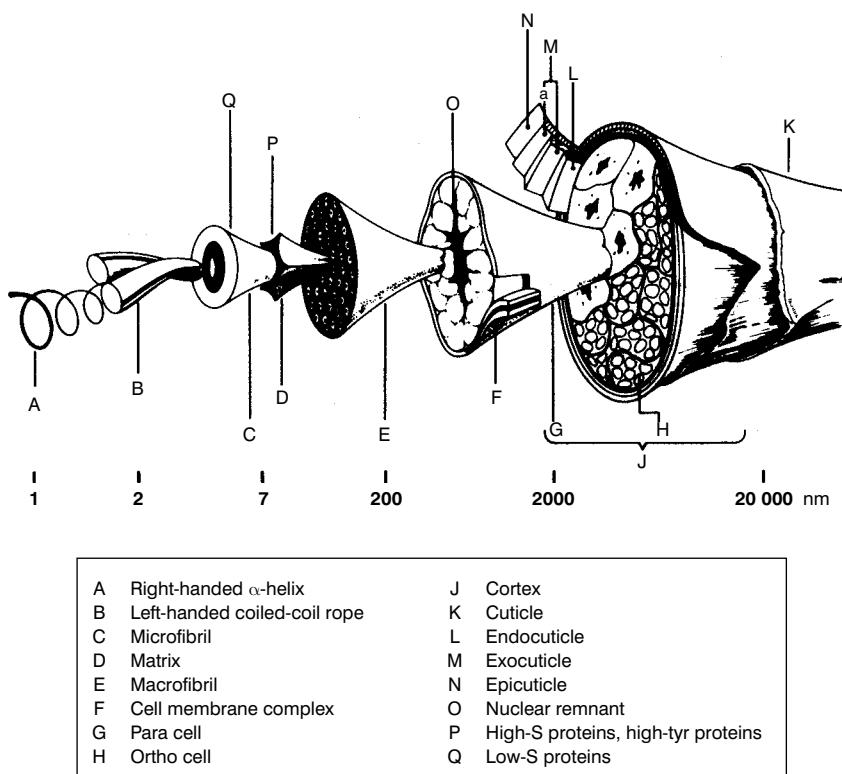


Figure 11.1 Structure of wool fibre (courtesy of Division of Protein Chemistry, CSIRO, Australia)

tip. The surface of a wool fibre is therefore serrated in appearance when examined under the microscope, as are most animal fibres, though the scale pattern can differ depending on the animal from which it derives. Scale patterns do not always differ significantly, however – so, for example, fine wool and cashmere are very similar in appearance, and differentiating between them by visual examination microscopically is a skilled task.

In the cortex, microscopic examination shows considerable fine detail, as the outline of the fibrils can easily be seen with proper staining [3]. The fine structure differs depending upon the type of animal fibre, and can also differ between different classes of wool fibre. Generally, in wool the cortex can be seen to be composed of two halves, called the orthocortex and the paracortex. The orthocortex, which contains cells of larger diameter, is more readily stained by acid and basic dyes and metal salts, and is located on the outside of the crimp, or curvature, of the fibre.

Wool fibres are also not usually straight, being more or less wrinkled, or crimped in appearance. This crimp is dependent on the breed of sheep from which the wool is taken, and the nature of the diet of the animal in question [4].

11.3 FELTING AND SHRINKAGE – THE DIMENSIONAL STABILITY PROBLEM

Wool fabrics can change in dimension during washing or laundering for two quite separate reasons: felting and relaxation. In order to understand the processing procedures necessary to produce dimensionally stable products, it is important to understand the different mechanisms involved.

11.3.1 Felting shrinkage

The major cause of shrinkage in wool is felting, in which the fibres become compacted or entangled with one another, which results in an overall contraction of the wool textile structure [5]. The underlying cause of the propensity to felt is the differential friction effect caused by the scales on the fibre surface. This effect can readily be demonstrated manually with a human hair: the hair is held firmly between thumb and finger in one hand, and then an attempt is made to pull it out of this grasp. If the pull is exerted at the tip end of the fibre, it will strongly resist the pull and be very difficult to withdraw. If the pull is exerted on the root end, the fibre is easily pulled from between thumb and finger. This differential friction effect arises from the ratchet-like nature of the fibre scales, with their sharp edges all pointing in the same direction towards the fibre tip. Movement of the fibres against any surface in the root-to-tip direction results in contact with the smooth surface of the scale sides and a low resistance to sliding. Movement in the opposite direction brings contact with the edges of the scales, which catch against any protrusions in the opposing surface and strongly resist movement.

This differential friction effect causes felting through a mechanism first identified by Shorter [6]. It is best illustrated by considering two cases (Figure 11.2). In the first case, a fibre is held at one point (X) by an entanglement of fibres such that it may not move readily against the other fibres in its axial direction, and at another point (A) such that it may move axially only away from the point at which it is fixed. Any mechanical agitation of the structure will cause the fibre to move so that the distance between the two points of entanglement is shortened. In the second case, the entanglement point (B) allows movement only towards the fixed point, and mechanical agitation results in an increase in the distance between the two entanglement points. The first situation will thus result in the production of tightly stretched fibres as the entanglement points are pulled together, and in the second case in the production of loops of fibre as the entanglement points are pushed apart. Felted wool structures can be seen to contain both these situations, and a moderately felted wool structure can be heard to crackle if it is pulled sharply between the hands while holding it against the ear as the tight fibres break due to the force of the pull.

For felting to take place, three main factors are involved: moisture, mechanical agitation and heat. Moisture causes wool fibres to swell, as wool is capable of absorbing up to 30–38% of its own weight in water, and this renders the wool fibre more flexible. The exact role of water in felting is the subject of a number of hypotheses [7], but the most probable explanation is that water increases the tendency of the scales to interact with rough areas on adjacent surfaces or scales on other wool fibres, causing an increase in the frictional differential between the with-scale

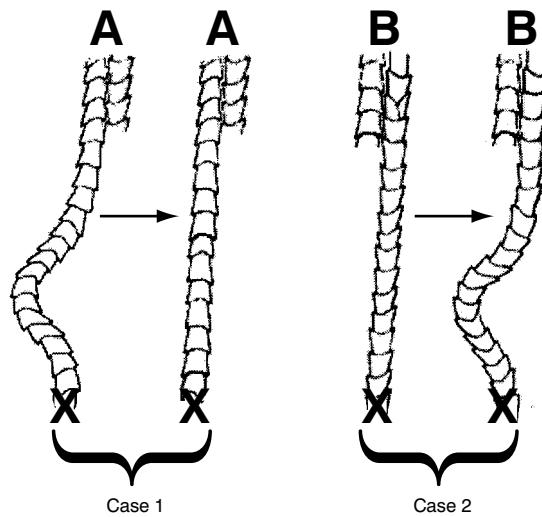


Figure 11.2 Shorter's mechanism for felting

and against-scale directions. This is probably coupled with a tendency of the wool fibres to collapse against one another when wet thus increasing the interaction and therefore the tendency to felt.

Mechanical action is very clearly needed to induce felting. The more vigorous the action, in general, the more quickly felting can be induced [8]. This has presented difficulties over the years as laundering habits have changed, and machinery with more severe mechanical action has been introduced onto the domestic market. Thus the early process standards (for example, those developed by Precision Processes Textiles under the Dylan trademark to meet the needs of a market that largely washed wool by hand) were not adequate as people began to launder wool in washing machines. This led to the introduction of the IWS Woolmark Superwash standard to meet the need for greater resistance to felting. In the late 1990s, a further and more severe standard was introduced to allow for the increasing use of tumble-dryers and the additional mechanical action so introduced into the home laundering process.

Temperature also has some effect on felting, but the relationship is not linear [9]. It would appear that felting reaches a maximum at temperatures in the range of 50–60 °C. Above this temperature there is no clear evidence that felting increases further. The choice of a laundering temperature of 40 °C for washing wool in most washing machines is therefore a compromise between the need to use heat to promote cleansing and lower temperatures to reduce felting.

11.3.2 Relaxation shrinkage

When any garment is immersed in water, the stresses and strains introduced into the structure by the various manufacturing and handling processes involved in its production are released. The garment dimensions therefore change. This change usually, but not necessarily, results in shrinkage, though it may be reversed by pressing out the garment and is therefore not

destructive. Mild agitation is sometimes necessary to fully release the potential dimensional change. In some cases, these stresses and strains are the result of deliberate 'setting out' of the garment or fabric in a drying or pressing process, where manufacturing or processing has resulted in undersized items. However, such stresses and strains are more usually introduced during production, and are a particular problem where the garment is not subsequently given a wet process or washing step during which they can be released. The problem for the garment producer is that when such garments are laundered for the first time, the dimensions change, and therefore so does the fit.

Relaxation and felting shrinkage are equally important, and indeed are indistinguishable, as far as the consumer is concerned, and both are therefore taken into account by retail organisations. However, the technologist needs to be able to discriminate between the two in order to diagnose problems.

11.4 MEASUREMENT OF SHRINKAGE – EQUIPMENT AND PROCEDURES

If an organisation is producing goods with a claim for shrink resistance on washing, a prerequisite is that the organisation must be able to test the claim against a predicted lifetime of washing and wearing by the consumer. The development of suitable methods that correlate to actual experience in wash and wear is imperative.

Shrinkage is measured in effect by measuring the amount of dimensional change induced by a controlled wet process. Precision Processes Textiles introduced one of the earliest methods on which their Dylan care label standards were based. Their Cubex machine [10] effectively consists of an insulated box rotating about an axis running through two diametrically opposed corners (Figure 11.3).



Figure 11.3 The Dylan Cubex (courtesy of Precision Processes Textiles)

The device is filled with a carefully measured quantity of water containing electrolyte buffer of known pH and temperature. The samples to be tested are then introduced together with a quantity of polyester squares to create a load of a specified weight. Before testing, the articles are marked with thread, indelible marker or some other means that will not move or become loose during testing. The dimensions between the marks are then carefully measured, the test conducted, and the test pieces dried either in an oven or by exposure to air. The distance between the markings is then measured again. The amount by which the dimensions have changed is expressed as a percentage of the original dimension.

Shrinkage is usually measured in two directions: along the warp and the weft for fabrics, and along courses and in the wales direction for knitted structures. Care must be taken when evaluating the results from shrinkage tests, as some organisations express shrinkage as a positive number and extension as a negative – that is, a negative shrinkage. More properly, the property should be referred to as ‘dimensional change’, and then negative numbers are used for shrinkage and positive ones for extension. Most commonly, area shrinkage is used to denote the overall shrinkage inherent in the garment, and is by convention generally calculated by adding together the percentage changes in the two dimensions. While this is not an entirely accurate technique, especially above shrinkages of 10% area, it forces the calculation of percentage change in both dimensions. Examination of these figures in turn can indicate problems associated with garments distorting during washing (that is, becoming longer and narrower, or vice versa).

During the late 1970s and early 1980s, the Dylan Cubex was displaced by the Electrolux Wascator as the test machine for felting shrinkage. This device (Figure 11.4) is based on the design of a small-scale commercial laundry machine, and is also programmed to fill and empty to duplicate rinse cycles as well as to use detergent powder during the main wash cycle. It is therefore regarded as more properly duplicating the mechanical action encountered in the domestic wash. Wash testing is otherwise conducted in much the same general manner as with a Cubex, with measurement marking and a fixed weight loading. To emulate the effect of multiple wash cycles, several test washes can be applied to a garment sequentially, with, in some cases, measurements being taken after each wash cycle [11].

By this means it is possible to evaluate the nature of the shrinkage that has occurred, either to provide evidence of incomplete anti-shrink treatment, or to predict the likely behaviour during consumer wear and therefore the likelihood of complaints. Some systems of evaluation also incorporate an initial extremely gentle wash cycle together with measurement in order to provide data on relaxation shrinkage. Although some authorities would argue, correctly, that the consumer does not differentiate between the forms of shrinkage, separation of the felting shrinkage from the relaxation shrinkage does give a more complete picture to the technologist and therefore assist with the diagnosis of problems.

Although this type of machine is much more flexible than the earlier method, care must be taken in its operation and maintenance. The volume of water present directly affects the severity of the mechanical action. A larger volume of water than that specified in the method will result in a more gentle action and a lower volume in a more severe one, thus distorting the



Figure 11.4 The Wascator (courtesy of James H Heal Ltd.)

results obtained. In the case of a badly maintained machine, this difference can be very significant. By the same token, care must be exercised when comparing results obtained using different test regimes in the Wascator. Different water volumes and agitation regimes can be used, and detergent may or may not be used. Detergent can noticeably influence the shrinkage, both by regulation of pH and also through suds production, which can reduce the mechanical action in the machine. Water quality, especially hardness, also plays a role, particularly in suds generation when testing with detergent present. While troubleshooting shrinkage problems, it is therefore prudent to ensure that the correct test regime has been applied.

In the later years of the twentieth century, further changes took place in the household laundering habits in the developed nations. Particularly in colder climates, tumble-dryers replaced air drying as the preferred option after laundering. This has further complicated the issue of wash testing, as the industry has had to develop standards for suitable machines and modified test regimes in order to attain reproducibility in testing [12].

A particular problem, which will arise with tumble-drying of wool garments, is that of water content. Wool will continue to felt if subjected to mechanical action while damp. The degree of moisture removal achieved by the washing machine in its last hydroextraction cycle is therefore significant, especially if it varies considerably from the norm. Again, good maintenance of machines is important to ensure consistency of results.

When evaluating the results of wash testing, the data generated by the test are of prime importance. However, wash tests are by their very nature prone to a degree of imprecision. It is

tempting to quote shrinkage results to an accuracy of one place of decimals or more and ignore that the error in the method will not permit that degree of accuracy in the results. Examination of the washed garments is therefore of prime importance, unless an unusually severe test regime has been used. The garments should be inspected for excessive surface fibre or 'face', 'beards' of fibre at the edges, or evidence of loss of clarity of the knitted structure. All of these are indicators of felting, and their absence would suggest that the garment is capable of better wash and wear performance than the numerical results allow. Commercial judgement has then to be used, and most standards systems allow for this situation.

Variants for evaluation of felting resistance have been introduced. The most important of these relates to woven fabric testing. The test pieces in this test are sewn over to represent edge seams and to reproduce the conditions for what is termed 'cuff edge' felting to occur [11]. In this situation, usually found with resin-only finish systems, the bulk of the fabric is perfectly acceptable, but at the edge where the fabric is held in a folded form, felting occurs along the line of the fold. (The author has seen an extreme example of this where a trouser had been heavily resinated and then pressed. The garment after wash appeared at first sight unchanged, but closer inspection showed that the creases in the front of the legs had turned into two lines of felted beading.) In these cases, measurements are taken along the edges as well as over the body of the fabric. These measurements are then compared with the dimensional change in the body of the fabric, and the cuff edge felting measured as a differential against this.

Methods of evaluation of the felting resistance of wool in loose stock form or top are also occasionally used, usually by companies engaged in applying various anti-shrink finishes at this stage in processing. Most commonly, the wool is sewn up in a muslin or polyester bag and tested in the same way as knitted fabric. The degree of felting is estimated by measuring between two ties placed at either end of the sample, or by evaluating the volume change that has taken place. Used with care, such methods can give an indication of resistance to felting, but are not sufficiently reliable to be taken as a replacement for testing of knitted panels produced from yarn spun in a sample spinning machine. An alternative to this approach is the Aachener Filtztest developed by Blankenburg and Zahn [13,14]. In this test, 1 g samples of wool fibre are shaken in a specially designed machine and turned into felted wool spheres. The size of sphere, and therefore its density (the quoted result) is related to the capability of the wool to resist felting. Again, the test must be used with care. Neither of these types of test has achieved widespread utility.

11.5 SHRINKAGE PREVENTION AND CONTROL

In any study of wool shrink-resist treatments, whether for research into new finishes, selection of finishes for commercial application, or simply to gain an understanding of the field, it is important to appreciate the factors that affect felting control, and how they interrelate. From this knowledge, various options emerge that can lead to a new line of investigation for the researcher, or towards a process for the commercial technologist. When evaluating these options, it is always important to bear in mind the relative strength of the effects being considered. Work

published prior to the 1970s, for example, may claim good shrinkage control, but will be referring to standards too low to be of utility in today's context. It is also important to avoid the acceptance of over-simplistic explanations for the effectiveness or otherwise of shrink-resist treatments. In reality, there may be a number of considerations to take into account to produce a coherent and comprehensive model.

11.5.1 The options – physical considerations

All shrinkage control processes seek to prevent selective fibre movement during washing resulting from the difference in friction between the with-scale and against-scale directions. This can be achieved either by reducing the frictional differential or by preventing the tendency of the fibres to move.

Friction control

Friction control is the most widely used approach to control of felting tendency [15,16]. The frictional difference can be eliminated either by raising the coefficient of friction in the with-scale direction, reducing friction in the against-scale direction, or modifying fibre geometry. If the coefficient of friction of the scale surfaces is increased sufficiently such that the with-scale coefficient of friction nears that of the against-scale direction, the remaining difference then becomes insufficient to generate felting except under conditions of more severe mechanical action than would be expected in home laundering. However, a side effect of such an approach is that the end-products may have a harsher handle, and therefore be commercially unacceptable. If attempts are made to moderate handle by using softening agents, these have the side effect of lowering the surface friction again, and thus recreating the frictional difference and therefore the tendency to felt.

The coefficient of friction in the against-scale direction can be modified in two ways: by modifying scale behaviour or by use of friction-reducing agents. The most successful approaches to commercially useful shrink-resist treatments are all based on modification of scale behaviour using some type of aggressive chemical treatment to attack the protein structure and render it more flexible when wet. With this approach it is important to ensure that as little commensurate damage as possible occurs to the cortical structure in order to maintain fibre strength. This type of treatment is accompanied by a certain amount of modification of the scale tip geometry, which will assist in reducing the against-scale frictional effect, but is not sufficient to be considered as scale removal (mentioned below).

The concept of reducing against-scale friction, and therefore felting tendency, by using friction-reducing agents uses the idea that agents with a sufficiently low frictional coefficient when applied to the wool fibre will reduce these effects in both directions. For this to be effective, the frictional effects must be reduced to such an extent that the difference between them becomes small enough to prevent the felting process from occurring easily. The only substances known to have such a significant effect on friction are polysiloxanes (silicones), and

fluorocarbons. In practice, neither type of material, nor any variant, has been found to be effective enough to be of practical value other than in specific cases, or as a component in a process.

The idea of modifying fibre geometry by removing the serrated scale tips and therefore eliminating felting has existed for a long time. Early studies on oxidative treatments claimed that they work by this mechanism, but later studies on more controlled processes cast doubt on this [17]. Scale removal has since been achieved in some commercial processes, and does indeed result in a fibre that strongly resists felting. The severity of the treatment needed to achieve this, and the subsequent weight loss and alteration of fibre properties involved, have greatly restricted its utility. A modern application of this mechanism results in the production of so-called 'lustre wool', where the drastic changes in physical properties of the fibre are exploited as a commercial differentiation [18].

This concept later re-emerged in the 'scale masking' hypothesis, which suggested that a sufficiently thick layer of polymer evenly applied to the fibre surface would even out the surface roughness associated with the scales and therefore reduce their effect [19]. A modified version has been advanced as the explanation for the mode of action of Hercosett polymer. This is applied at a rate that is insufficient to meet the needs of the hypothetical model, but swells in water to a thickness considered sufficient to satisfy the requirements. It is now generally accepted that this mechanism plays some part in shrinkage resistance as imparted by the chlorine-Hercosett and similar processes [20].

The 'spot welding' concept

As an alternative approach to friction control, it has been suggested that felting can be overcome by creating linkages between adjacent fibres within the textile structure. If sufficient linkages are formed and they are of appropriate strength, then movement of the fibres against one another is prevented and felting cannot occur. Such linkages must be created by the application of suitable polymers, which can be crosslinked to form bonds of sufficient strength to prevent fibre movement. The main problem associated with development of systems of this type is the practical one of depositing a polymer onto the textile assembly in such a way as to form linkages between fibres rather than an even coating of polymer over the surface of the fibre [21].

Some commercial processes exist in which this mechanism plays an important role. Most of these are processes for woven fabric, where it is possible to pad a solution of the polymer onto the fabric, and where the fibres are generally in very close proximity to one another, so facilitating the developments of the linkages or 'spot welds'. One major problem with this approach to felting control is that the linkages can restrict the fibre movement, and, especially if the polymer used is not soft and elastic enough, can cause the fabric to become much stiffer and lose its drape characteristics. It may also become harsher to the touch.

11.5.2 The options – chemical considerations

For a full understanding of the options available to the process technologist or researcher in the

field of shrink-resist treatments, there are two main chemical areas to consider: scale modification and fibre coating. In all successful processes, one of these effects is involved, and for most commercially important processes both come into play.

Scale modification

The vast majority of successful processes in the market have used some chemical means to modify the nature of the scales of the wool fibre. All the agents do so in broadly the same way by attacking various links in the protein structure and rupturing them, so making the protein more readily swollen on immersion in water, and the scales more flexible. Although there are a number of ways in which the keratin structure of the cuticle cells may be degraded, the most important is considered to be the severing of the cysteine disulphide bond between two protein chains, to produce two cysteic acid residues [22]. Not all disulphide bonds should be severed, however, as this would result in unacceptable degradation of the scales [23].

The choice of oxidant is also important to achieve maximum felting control for minimum collateral damage. There are surprisingly few oxidants that can be used to achieve a useful effect in a commercial process. The most common of these is chlorine, usually in aqueous solution, either as dissolved chlorine gas, or from the degradation of a compound that readily yields chlorine under mild conditions. Chlorine will rapidly attack wool proteins to oxidise the cysteine links, and has found the widest utility in industry. The main alternative to chlorine is permonosulphuric acid or its salts, particularly the potassium salt (K_2SO_5). This also modifies the keratin structure, but is more selective in its attack, and produces a characteristic striated look to the scales when these are examined under the microscope. The full effect of this oxidant is only produced if the fibre is subsequently treated with an aqueous solution of a sulphite, usually sodium sulphite [24].

Fibre coating

Alongside scale modification, fibre coating represents the second most important component of all successful shrink-resist treatments. The mechanisms of 'scale masking' and 'spot welding' cannot function without a surface coating, though not all polymers work through these mechanisms, as several clearly contribute to surface friction modification. For polymers that are claimed to work by either the 'scale masking' or 'spot welding' mechanisms, the manner in which the polymer is deposited is critical. In the first case the polymer must be evenly applied to the fibre; in the second case, it should be concentrated at points where fibres touch.

Many different chemical systems have been suggested as fibre coatings in wool treatments, but certain fundamental rules apply. Firstly, the coating must adhere to the fibre surface, even under extreme conditions such as dyeing at the boil, or reductive or oxidative bleaching. Secondly, where a scale masking or other overall effect is aimed for, the polymer must be capable of spreading evenly over the fibre surface. Thirdly, the polymer must crosslink after application to form a residue with sufficient mechanical strength to perform the function for

which it is being used – as an adhesive in the ‘spot welding’ system, for example. Fourthly, the polymer chemistry must lend itself to the preferred mode of application.

The main problem with fibre coating lies with the issue of surface spreading. In its untreated state, wool fibre has such a high surface tension that many materials do not wet it. Silicone polymers are the most significant group of materials found to be of value on untreated wool or wool treated in such a way that it retains its high surface tension. Other materials tend to ‘bead’ or form clumps on the fibre. This of course may be valuable if the intention is to ‘spot weld’ the fibres together. Fortunately, techniques exist for reducing the surface tension and making the fibre wettable by a wider range of materials. Of these, the most common is oxidation using a chlorine source [25]. Control of the physical properties and chemistry of the polymer employed can then meet the other requirements. It must also be understood that, for polymers to adhere to the wool fibre surface, the surface must be clean and free from dirt, oil, wax, softeners or other materials that form an interfering surface coating. The excessive use of polymeric, cationic dye fixatives in advance of shrink resistance is a typical example where shrink-resist treatments may be caused to fail through incorrect processing.

11.6 PROCESSING – THE ISSUES AND OPTIONS

Any shrink-resist process must be tailored to the nature of the goods to be treated, and the process route by which they are made. There are therefore a number of considerations to be taken into account in choosing the route or designing it.

11.6.1 Woollen and worsted routes for yarn production

Wool products produced from spun yarns are either woollen or worsted depending on the nature of the spinning route chosen for producing the yarn. There are many considerations lying behind the decision of which type of route is chosen, and the reader is referred to a suitable text on the subject for detail on these [26]. For the purpose of deciding on how to achieve a shrink-resist treatment, it is only necessary to know the different routes in outline.

All wool is first scoured in a loose form to remove dirt, wax, oil and other impurities. The cleaned wool is then carded to produce a continuous web of roughly parallel fibres. In woollen spinning this web is then split and used more or less directly to produce a spun yarn with a rather hairy appearance because many of the fibres are not fully parallelised in the carding process. In worsted spinning, more care is taken to produce a web with parallel fibres, and the web is then condensed into a sliver or top. The top is then processed by gilling to further blend and parallelise the fibres, and combed to remove short fibres and impurities. Worsted yarn is thus much smoother in appearance. Since the production of worsted yarn involves the extra step of wool top manufacture, a stage that is not needed in woollen spun yarn production, this provides an additional possibility for applying shrink-resist treatments.

There is a further distinction between the two types of yarn at the wet processing stage. Woollen articles, especially knitted items, are usually subjected to wet milling. This process

involves agitating the garments in water sometimes containing surfactants and other additives, so as to create an even mat of surface fibre or 'milled finish'. This gives the articles a softer and more even appearance. Worsted articles are not milled; in fact great care is usually taken in processing to avoid the creation of any loose fibre on the surface. Knitted garments produced from worsted yarn are usually given an anticockle treatment before any other wet finishing to remove the distortions and rippled or cockled appearance that often occur at the transition between rib and body knit structures, caused by stresses introduced when the garments are knitted.

There is another important distinction. Generally, knitted articles made from worsted yarns are harder to stabilise against felting than woollen goods.

11.6.2 The choice of where to treat in the production route

Shrink-resist treatments have been applied at all stages of production of wool articles. There are some basic constraints, which limit the usefulness of any process and therefore its application at particular points in the production route. These vary according to the type of process. Application of a 'spot welding' polymer must take place after the final assembly of fibres has been made, or subsequent processing would break the fibre–fibre bonds. Similarly, any process that relies on an even deposition or exposure of the fibres to a chemical finish will be more successful in situations where the fibres are in a state such that treatment liquor can circulate sufficiently around them.

Thought must also be given to the processing that must be applied to the wool as it progresses along the manufacturing route after the treatment has been applied. For example, woollen spun knitwear made from pretreated yarn is much more difficult to mill to the correct handle and texture. Although knitwear has been manufactured by this route, the achievement of a satisfactory finish has been found to be problematic. In some cases, such as with woollen garments, it has been found more convenient to apply the shrink-resist treatment at the same time as application of colour by garment dyeing. This combined process has been found to be very effective for several decades in the United Kingdom. It is ecologically more acceptable in energy usage than applying two separate wet processes in the production route and the consequent drying involved. The main drawback of this process route is that it does not allow the creation of ingrain effects in the garment, which are produced by the blending together, carding and spinning of different coloured wool fibres.

The question of where to treat the wool is therefore dictated by the requirements of the designer and by convenience or economics. This in turn dictates or limits the choice of process route for achievement of the desired level of shrink resistance. In general, it is the practice to treat worsted wool at the top stage, and woollen spun product at the garment stage, though there are many exceptions to this. 'Spot welding' resin processes are mainly used for woven fabric, and are the main route for this type of product.

11.6.3 Machinery and mechanical aspects

The form of the product to be treated and the degree of protection desired dictate the mechanical aspects of shrink-resist processing. Mild treatments can be achieved in a wider spectrum of processing conditions than those required for higher levels of protection, which are usually the goal for commercial processes today.

Fibre

The largest proportion of all shrink-resist treated wool product worldwide is manufactured by the top treatment route. Top may be conveniently processed as a web of parallel strands of wool top, approximately 1.0–1.5 m wide in most cases, through a multiple bowl backwasher (Figure 11.5). In each bowl, the web of slivers is fed into the bowl through a pair of rollers, and round a perforated drum, which serves to immerse the web in the process liquor. At the same time liquor is sucked out of the end of the drum and recirculated into the edges of the bowl creating a strong liquor exchange around the sliver web, as well as serving to press it against the drum. The wool then exits the bowl through a squeeze nip between two rollers to remove as much treatment liquor as possible. The suction drum backwasher usually comprises between five and seven of these bowls together with drying equipment of generally similar operating principles except that circulating hot air serves to hold the slivers on the perforated drums, and they are of much wider diameter. This machinery has proven very effective in achieving consistent and level treatments over a number of decades.

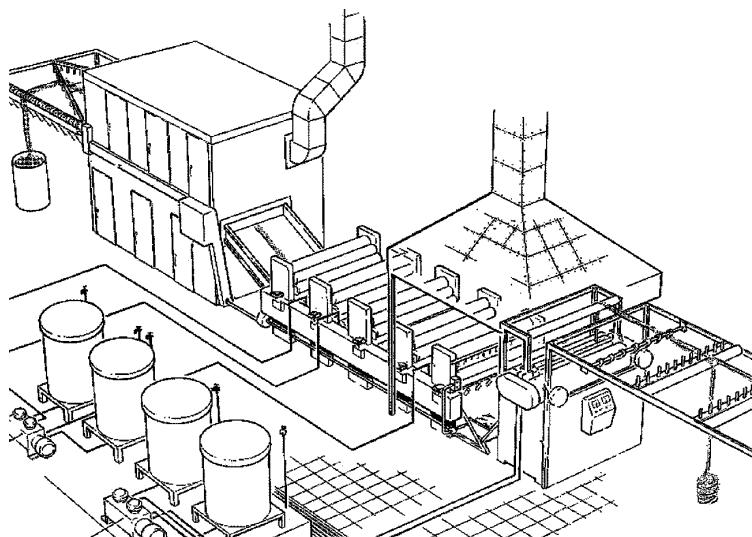


Figure 11.5 A backwasher plant (courtesy of The Woolmark Co.)

Attempts have been made from time to time to treat wool top in dyeing machines, with the wool wound in 'bump' form. No truly commercial process is known where the level of resistance is sufficiently high to be of widespread interest.

Yarn

Wool, both in woollen and worsted form, has been successfully treated in yarn form, but only to the author's knowledge in the form of hanks in suitably designed machinery where the liquor can be circulated in more than one direction, so as to achieve the maximum degree of evenness of treatment. Despite this, the process is only of value for yarns that have already been dyed, because the shrink-resist treatment is relatively unlevel and therefore subsequent level dyeing is extremely difficult. Dyeing may be carried out in the same overall wet process as the treatment with the shrink-resist chemicals, provided dyeing precedes shrink-resist treatment. It is theoretically possible with modern soft cone systems to envisage a similar process using yarn on cones in suitable machinery, but this is not usually attempted, and would be prone to the same limitations as hank treatment.

Fabric

Although many forms of equipment are available to wet process fabric, and therefore apply conventional oxidative shrink-resist processes, in fact these usually result in high levels of relaxation shrinkage due to the tensions induced by the processing and finishing machinery. The only process to achieve widespread commercial utility is the application of 'spot welding'-type polymers. This is a simple process using a vertical pad mangle to impregnate the fabric with a controlled amount of water containing the polymer in solution or suspension, followed by a drying and baking operation. More recent developments of this type of process have introduced a separation between the drying and baking steps, with baking sometimes being conducted after the garments have been made and pressed, thus producing permanent press effects as well.

Garments

Garment processing of wool knitwear, both woollen and worsted has been popular in the UK for several decades, but has not achieved world-wide popularity mainly due to the control needed to process garments so as to achieve level results, and the restrictions on dye fastness. In recent years, there has been an upsurge in popularity, and garments are processed in various countries around the world, especially in Hong Kong and southern China. This is in part due to the introduction of processes with greater controllability, but also to the development of better machinery for garment dyeing and wet processing. The oldest machines for garment processing are paddle machines in which the garments are treated in a bath of water, agitation being achieved by means of a rotating paddle wheel. The simplest type of machine is the overhead paddle, where circulation is from top to bottom of the bath. A better development of this is the

side paddle, where the garments are pushed around a toroidal channel by the paddle, which thus achieves a circulation from top to bottom and side to side (Figure 11.6).

The main problem with paddle machines is that the garments cannot be effectively drained of process liquor, necessitating multiple rinses and therefore prolonged process times. At the end of the process, the garments must be manhandled into a hydroextractor to remove the considerable amount of water held in the knit structures. Alternatives exist in the form of the modern rotary dyeing machines, broadly based on the design of front-loading washing machines, but obviously with much greater capacity and control facilities (Figure 11.7). These machines have the advantage that they can hydroextract the goods, rendering processing and garment handling easier. They also operate at lower liquor-to-goods ratios than paddle machines, and this has a number of advantages for the dyer. However, the design of machine makes anticockle treatment of worsted knitwear much more difficult, and the lower liquor ratio is a disadvantage when attempting to chlorinate the garments. The latest non-chlorine processes lend themselves much more readily to this type of machine.

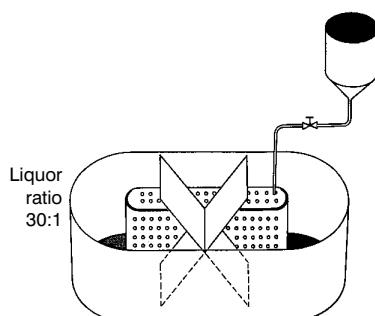


Figure 11.6 Schematic diagram of a side paddle

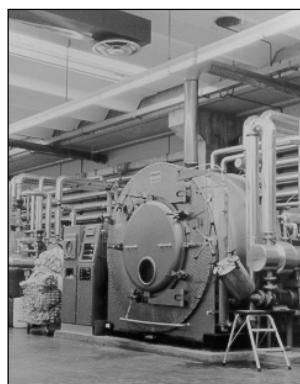


Figure 11.7 A rotary dyeing machine (courtesy of The Woolmark Co.)

11.7 ADDITIONAL ASPECTS

11.7.1 Aesthetics, comfort and handle

When evaluating any shrink-resist treatment, it is important to bear in mind that this property is only one of many considered by the consumer when choosing the product to purchase. In many cases, the alternative may well not be made from wool at all. The consumer is only concerned that the garment can be cleaned in a manner that is acceptable. Increasingly this means machine washable and tumble-dryable, hence the introduction of the Woolmark Total Easy-care Standard [12].

Of much greater concern to the consumer are the aesthetic considerations of style, colour and handle. The consumer will be evaluating the garment more from the point of view of its attractiveness. One key element of this is how comfortable it will be to wear. This can be considered to consist of two main elements: softness and prickle.

It is relatively easy to produce shrink resistance in a wool product provided handle is not a consideration. A number of processes have been introduced over the years that achieved shrink resistance but left the product with an unacceptable harsh handle. This cannot always be readily overcome, especially if the harsh handle is a result of a treatment that achieves shrink resistance by increasing fibre–fibre friction. Any attempt to soften the product could override the high fibre–fibre friction and neutralise the treatment [27].

The best treatments therefore seek to achieve the desired performance result and give at the same time the desired handle. Since handle is a very subjective matter, flexibility in the type of handle produced is valuable. Some specifiers, for example, do not like the particularly slick handle imparted by some silicone finishes. In this case, a treatment based on the known shrink-resist effects of silicones would not be commercially viable.

The ‘prickle effect’ is well known, and some consumers believe that all wool will be prickly when worn next to the skin [28]. This is a misconception, which has to be overcome in selling wool products to the consumer. In fact, wool underwear has been very popular in some countries for a considerable time, and fine Italian wool underwear is still popular, for example. Wool will feel prickly if the fibres are very rigid and the fibre diameter is relatively coarse. Prickle can be avoided by using wool of an average diameter of 21 µm or finer (provided that no very coarse fibres are present), or by using some treatment which reduces the effective fibre diameter or renders the fibre more flexible [29].

Some types of shrink-resist treatment fall into this category. For example, chlorination can be taken to such an extent that subsequent treatment with alkaline sulphite removes all or most of the cuticle and produces a smooth surface on the fibre, which has a smaller diameter than the untreated material. Recently there have been reports of the use of proteolytic enzymes being used to achieve greater fibre flexibility and hence reduced prickle effect [30].

11.7.2 Ecological and environmental issues

All production processes affect the environment in some way; thus there is no such thing as a completely environmentally neutral shrink-resist process [31]. That having been said, some of

the processes in current use are considered to be unacceptably harsh to the environment, and therefore new types of process are being constantly developed.

It is important to realise that there are various ways in which shrink-resist treated wool can affect the environment. Not to treat the wool is also no answer because the garments so produced have then to be either very carefully hand-washed or, more usually, dry-cleaned – a process that creates the risk of release of organic solvents into the atmosphere.

The main environmental impacts of shrink-resist treatments are related to the amount and type of effluent produced. Some of the effluent pollution is, however, related to the manner in which some yarn is produced. Woollen spun yarn can be manufactured with a very significant level of mineral oil lubricant – as much as 6–8%. When this is removed from the yarn during the shrink-resist treatment, it creates a process liquor with a very high biological and chemical oxygen demand, placing a significant strain on effluent treatment plants or local riverine ecosystems. In this case, no alteration to the process will remove the problem, which has to be solved by amending the yarn production route, using one of the more modern 'dry' spinning systems. Here, much lower levels of oil, usually of a more readily water-soluble and biodegradable nature, are used. In contrast, worsted yarns incorporate relatively little added oil and do not therefore give rise to this type of problem.

The use of chlorine as an oxidant in shrink-resist treatment also gives rise to a significant environmental problem. While the objective of using chlorine might be considered to be to oxidise the cystine links to cysteic acid groups, there are inevitably a considerable number of side reactions. Some of these reactions result in the production of chlorinated water-soluble protein residues. These are thought to be relatively poorly biodegradable and therefore potentially able to be accumulated in the food chain. The materials are measured as AOX, or absorbable organic halogen compounds [32]. In this test, process liquors are passed through a column containing carbon. The column is then heated to degrade the halogen compounds and the resulting halogen is measured. In a variant, extractable organic halogen (EOX) is measured by submitting the treated wool to an aqueous extraction step, and the AOX procedure applied to the extractant. This latter process is aimed at determining how much AOX may be produced by subsequent wet processing operations such as dyeing or domestic laundering.

11.8 COMMERCIAL PROCESS ROUTES

In this section, the main commercially important processes that are used to apply wool finishing in industry today will be discussed. This is not intended to be a comprehensive summary, and therefore it is possible that other processes may be encountered in practice.

11.8.1 Continuous fibre treatment

By far the largest quantity of wool treated world-wide is processed in a continuous treatment process. This is mainly wool in top form, destined for the worsted market, though some top is subsequently broken and spun into washable woollen spun yarn.

Wool top

The dominant technology in this area is the chlorine Hercosett process developed by McPhee [33,34], and named by reference to the trade name of the polymer originally used, which was produced by the Hercules Powder Company. In this process, wool is subjected to oxidation by chlorine in solution in water in a multiple suction drum backwasher (Table 11.1). The chlorine is generally produced by the action of acid on sodium hypochlorite and is carried out at an acid pH (usually 1.5) and at relatively low temperature. Other variants on this theme have emerged, of which the main one is the use of chlorine gas dissolved in water, usually in a special applicator designed to contain the gas fumes generated and also to assist in more level application of the chlorine to the fibre. Kroy produces the most widely used applicator machinery, in which the sliver web is held by two polypropylene belts and passed through a J-tube approximately one metre in depth where it is in intimate contact with the treatment liquor [34]. In such processes, water temperature is very important, and in most warm climates, the water used for chlorination is cooled by refrigeration.

Table 11.1 Typical set-up and running conditions for a continuous chlorine/Hercosett system

Bowl	Temp.(°C)	pH	Make-up	Feed ^b
(1) Chlorination	10–15	1.5	0.3 g l ⁻¹ available chlorine ^a 5.0 ml l ⁻¹ sulphuric acid 2.5 ml l ⁻¹ wetting agent	1.8–2.2% chlorine ^a 0.02% solids wetting agent
(2) Anti-chlor	40	9.0	5.0 g l ⁻¹ sodium bicarbonate 5.0 g l ⁻¹ sodium sulphite	0.8% sodium sulphite sodium carbonate to pH 9.0 ± 0.3
(3) Rinse	30–40	—	water	300% water at 30 °C
(4) Polymer	35	7.5	10 g l ⁻¹ sodium bicarbonate 5 g l ⁻¹ polymer solids	0.2% polymer solids
(5) Softener	40–45	7.0	5 g l ⁻¹ sodium bicarbonate 2.5 g l ⁻¹ softener solids 7.5 ml l ⁻¹ lubricant	0.15% softener solids 0.4% lubricant solids

a This is calculated by analysis of the available chlorine in the sodium hypochlorite (or other chlorine source) used, as this may vary. Dose rates are then expressed as a percentage of chlorine by weight on weight of wool treated.

Treatment levels for feed vary according to fineness of fibre as follows:

1.8% coarser than 25 mm

2.0% 20–25 mm

2.2% finer than 20 mm

b Feed rates are calculated according to production rate from the formula:

$$P = N \times S \times W \text{ g min}^{-1}$$

where P = production rate (g min⁻¹)

N = number of ends of top used

S = speed of processing (m min⁻¹)

W = sliver weight (g m⁻¹)

Chemical feed rate is then derived from this using the following formula:

$$\text{flow rate (l min}^{-1}\text{)} \text{ of stock solution} = (P \times T) / (100 \times C)$$

where T = required treatment level (% on weight of wool)

C = concentration of stock solution (g l⁻¹)

In this process, as described above, the top slivers are aligned into a web some 1.0–1.5 m in width in a creel prior to the entry into the first wet stage. As the individual bumps or balls of top are exhausted, they are replaced by fresh ones, which are knotted in by hand. After the web has passed through the chlorinator bowl or applicator, it is passed into a solution of sodium sulphite at a mildly alkaline pH to remove any remaining active chlorine and to raise the pH of the slivers.

The slivers are thoroughly rinsed in subsequent bowls to remove sulphite, and then enter a bowl containing the polymer. There are a number of these materials now available around the world, all based on the same basic chemistry. A water-soluble polyamide is first produced by reacting adipic acid with diethylenetriamine, and the resultant material is then reacted with epichlorohydrin to both crosslink the precursor polymer, but more importantly to create reactive sites on the polymer backbone. The exact nature of the polymer and the reactive groups so formed varies depending on the exact reaction conditions used, and has been the subject of some research. Polymers from differing sources thus have slightly different properties during storage before use as well as during and after application to the wool.

Because of the cationic nature of the polymer, it has a tendency to exhaust onto the wool fibres, which have been made receptive to adhesion and spreading of the polymer by the chorine pretreatment. The process is in part a padding operation and in part one of exhaustion during the brief period that the sliver spends immersed in the liquor (about 5–10 s). As polymer is removed from the bath, it must be replaced; therefore, there is a constant feed to the bowl of a polymer solution at such a rate and at such a concentration that it replaces the polymer removed by the wool passing though. Similar constant supplies of fresh liquor must of course be provided to the chlorine and sulphite liquor bowls.

The polymer is then cured on the wool as the wool is dried in the drum dryer. It is usual to arrange for the temperature in the dryer to increase from the start to the end of the process so that the sliver reaches 105 °C, and the polymer cures properly. This is an essential feature of this type of polymer. Unfortunately, the wool so produced is very dry and difficult to process mechanically. Therefore, moisture is added in some way, either by water spray, steam, or even by re-immersion in water and subsequent lower-temperature drying.

Various additions are usually made to the process. Fibre processing agents may be added to the wool in a further bowl immersion after the polymer treatment. These materials assist in subsequent gilling and spinning processes. Softeners may also be applied in this bowl. Softeners are used because the polymer used has a rather harsh handle and this detracts from the aesthetics of the final product. Most of these softeners are removed during subsequent wet processing and therefore new softeners have to be applied as a top-up treatment after dyeing, for example. Precision Processes Textiles have patented the use of silicone polymers, which can alter the handle of the wool by reacting with the uncured polymer, giving the fibre a permanent soft handle, but also assisting with later mechanical processing [35].

Other polymer types have been used on wool, some of which have been promoted as needing no special curing step, but none have achieved significance. One remaining drawback of this process is the affinity of dyes for the fibre, resulting in rapid dyeing and thus significant risk of unlevelness. The fibres are therefore predominantly dyed in top form or as yarn in hanks.

The search for new processes continues, and the main thrust of this is to avoid the use of chlorine, with the ensuing generation of AOX. A number of technologies have been developed and some have been commercialised, but to date none have yet achieved serious market share. The majority of these processes are based on either hydrogen peroxide with some type of activator, or permonosulphuric acid. Some type of polymer is also used to achieve suitable levels of shrink resistance. To date, the author is only aware of one process – the Dylan EXO-S process – that can achieve the full Total Easy-care Standard of washability [36]. This is based on a modified permonosulphuric acid/hydrogen peroxide oxidation system, together with a specially developed polymer.

Loose wool

Pre-scoured loose wool has for some time been treated in batch form in the machinery used for loose fibre dyeing. Standards of protection, however, are low due to the poor levelness obtained in such treatments. One loose wool continuous process has achieved some commercial utility. This is the Kroy system, based on the proven Kroy wool top processing technology, but modified for use with loose wool. Instead of using backwashers, the process uses standard loose wool scouring bowls with modifications. The chemical conditions are similar to those used on wool top, and a polymer of the Hercosett type may also be used.

11.8.2 Batch treatment

Since batch treatments have a lower productivity than continuous ones, it is to be expected that they comprise a smaller segment of the shrink-resist treatment market. They have the advantage that the equipment used is lower cost than that for continuous treatment and is generally also capable of being used for other processes such as dyeing. The main advantage of treatment in batch form is when the product can be dyed in the same process cycle and thus save energy and time compared with the alternative of treating the fibre in a separate step.

Garments

After wool top, the next largest volume of wool treated for shrink resistance is taken through the garment route, in one or other form of aqueous process. The wool, first scoured in a preparation step to remove contaminants, is oxidised either with chlorine, produced by the addition of acid to sodium dichloroisocyanurate (DCCA), or with potassium permonosulphate. One or more polymers are then added. Additional preliminary steps include anticockle for worsted garments, and milling for woollen spun garments.

The main process using chlorine in terms of volumes of wool treated over many years is the Dylan GRB process [37]. This is usually performed in a side paddle machine (Table 11.2) and has been used for treatment of both woollen and worsted garments. A substantial proportion of this production has been dyed in the same wet process. The DCCA is added in solution carefully to the side paddle in such a way as to diffuse as evenly as possible into the goods, which are being

agitated in a pre-acidified bath, the chlorine being liberated from the DCCA slowly by the careful control of bath pH and water temperature. Care must be taken to ensure that as little reaction between the wool and the unacidified DCCA occurs – otherwise the wool then becomes much yellower in appearance without significant shrinkage control being achieved.

Table 11.2 Typical conditions for batch treatment of garments with Dylan GRB

Step	Conditions
Preparation	<p>Woollen spun:</p> <p>(1) Scour Fill bath with water^a at 40 °C and add goods 3–6% of Mills scour XBN Run paddle for 5–10 min and drain</p> <p>(2) Mill Fill bath with water at 40 °C 1–3% of Mills scour XBN Run paddle until mill is achieved (by examination), usually 5–45 min Drain Rinse warm 3–5 min Rinse cold 3–5 min</p> <p>Worsted spun:</p> <p>(1) Anticockle Fill bath and bring to boil before garments added Add garments slowly so boil is maintained; leave to soak for 10 min, only operating paddle for 10–20 s periodically; cool to 40 °C over 5–10 min by adding cold water with the paddle running</p> <p>(2) Scour Fill bath with water at 40 °C 1–3% of Mills scour XBN Run paddle for 5–10 min and drain Rinse cold 3–5 min</p>
Chlorination	<p>Fill bath with cold water (20 °C) Set paddle speed at 12–14 rpm Add 0.5% Mills scour XBN and 3% formic acid Run bath for 3–5 min and check pH is 3.0–3.5 Increase paddle speed to 14–18 rpm Drip feed a solution of the required amount of Dylan Auxiliary^b dissolved in cold water over 20–30 min Reduce paddle speed to 12–14 rpm Continue until no chlorine is detected^c</p>
Neutralisation	<p>To the exhausted bath from chlorination, add 5% sodium sulphite anhydrous Adjust pH to 6.0–6.5 with sodium carbonate if needed Run for 20 min then drain bath Rinse cold for 3–5 min</p>

Continued

Table 11.2 *Continued*

Step	Conditions
Polymer addition	Fill bath with cold water and set paddle speed to 14–18 rpm, then add 1% acetic acid Check pH is 5.0–5.5 Add 2.0% Polymer GE, diluted 10 times with water, steadily over a period of 10 min Reduce paddle speed to 12–14 rpm Run for 5 min Warm bath to 40 °C and run for a further 15–20 min Add 1–3% cationic softener as desired Add 0.5–2.0 ml l ⁻¹ hydrogen peroxide Run for 10 min and drain

a In a side paddle, the liquor to goods ratio is kept to 30:1, by choice of size of paddle or control of batch size.

b Dylan Auxiliary is sodium dichloroisocyanurate. Dosage varies according to product type as follows:

Shetland	1.5–2.0%
Lambswool (woollen)	2.0–3.0%
Botany	3.5–4.0%
Lambswool (worsted)	4.0–4.5%

All percentages are calculated as percent weight/weight on the dry weight of wool being processed.

c Exhaustion can be detected by the reaction with starch/iodide paper, or with iodine and starch indicator.

Sodium sulphite or metabisulphite is then used to neutralise any residual chlorine, and the garments are rinsed. Polymer GE is then added to achieve full protection. Other polymers and softeners can also be used especially if the higher standards of wash and tumble-dry performance are to be achieved. If the garments are to be dyed, then part of the polymer is usually added before the dyeing stage and the balance after dyeing, together with any other additions such as softeners.

When worsted garments are treated, an anticockle stage is incorporated into the process as a first step. This essentially consists of plunging the garments into boiling water, sometimes containing sodium metabisulphite or other additives. In the case of woollen spun garments, the garments must be milled to produce the classical surface finish. This is usually carried out as part of the scouring process.

Processes based on potassium permonosulphate have been used for some time, but are more limited in terms of the performance they can achieve, and are used only on woollen spun garments for this reason. A number of silicone polymers have been used or offered as part of such processes, as has Basolan SW [38], produced by BASF, which produces a handle rather different from the very slick hand obtained from silicones.

The main advantage of this type of process is that the action of this oxidant on wool is slower than chlorine at room temperatures and therefore more even treatment can be obtained. The limitation is in the lower level of protection afforded. Potassium permonosulphate is usually applied at a pH of around 4, and takes approximately 40–50 min to exhaust onto the fibre. The effect of the oxidant in this case must be fully developed by treatment with sodium sulphite.

A new variant introduced now achieving wide utility is the Dylan SIMPL-X process [39]. This is a modified version of the standard potassium permonosulphate process, using proprietary polymers and know-how, but which can easily achieve full Total Easy-care performance with a variety of handle types according to the end-user requirements. In addition to the environmental benefit of not using chlorine, it has the advantages of using less water and being faster than chlorine processes, as well as being much easier to operate in hot climates. It can also be easily performed without modification in modern rotary machines, thus giving the most efficient processing route.

Garments can also be processed in solvent using conventional commercial dry-cleaning machinery. The dominant method used is the DC109 process, developed by Dow Corning, using a silicone resin and a silane catalyst, which is applied to the garments as a final finishing process [40]. This is the only example of a commercially successful 'spot welding' process for knitted garments. The main advantage lies in the avoidance of oxidative degradation of the wool, and the concomitant short processing times. Garments must be allowed to age for 3–4 days after processing before testing to allow the full polymer cure to develop. This process is becoming less popular as pressures against solvent-based cleaning systems increase.

Loose wool

Although loose wool treatment in batch has been used to impart shrink resistance, it is generally able to impart only limited protection, well below current standards of performance. The problem is derived from the tight packing of the fibre in loose stock dyeing machines, the only device usable for this process, and therefore the poor levelness of treatment afforded. The degree of protection is dictated by the least treated fibre, so, even extensive mixing by carding of the fibre subsequent to treatment will have no significant effect on the protection afforded. As a word of warning, it should not be assumed that later partial treatments can up-rate the performance. Any subsequent oxidative treatment will tend to attack the more heavily treated fibre in preference to the untreated material, and will only result in degradation of the treated fibres eventually by over-treatment. Application of polymers can to some degree mitigate the effects of the unlevel treatment, but very powerful systems are needed and no guarantee of success is likely.

Yarn

Treatment of yarn is not widely practised, because the machinery available does not lend itself to even treatment and therefore the degree of protection afforded is limited. Treatment can be performed on hanks, preferably in a machine with reversible liquor circulation and provision for rotation of the hanks during the process cycle. The same processes applied to garments can be used on hanks, though dyeing can only be performed in advance of shrinkage control treatment as the unlevel treatment would lead to grossly unlevel dye strike if dyeing were to be performed after treatment.

11.8.3 Fabric processes

Various finishes have been applied to wool fabric, and this treatment accounts for a small but significant sector of the treatment market. Fabric treated in this form has superior smooth drying characteristics when compared with fabric produced from pretreated yarn. Since most of these finishes probably operate through the 'spot welding' mechanism, this property might be expected.

Fabric is usually treated by padding and subsequent drying and curing. Padding is carried out using standard equipment, which is preferably located directly in front of the dryer to be used, so as to avoid premature dry patches forming and incorrect curing. Precautions have otherwise to be taken to prevent this premature drying from occurring. As a variant to this process, the fabric may be padded with Basolan DC, a form of DCCA, and then with Basolan SW in a two-step padding process. This is more akin to the batch treatment of garments or top in its chemistry, and suffers from the disadvantage of needing two padding operations, one of which needs careful fume venting as the Basolan DC operation generates a large amount of chlorine fumes. As an alternative, the process may be performed in dyeing machinery using exhaust techniques, as can a number of other processes used for the batch treatment of garments. The processes are very similar to those used in batch garment treatment without the special steps needed to address specific knitwear processing issues such as cockle. They must be used with care, however, to minimise relaxation shrinkage.

Before a polymer finish can be applied to fabric, it is essential that the material is free from contaminants such as size, spinning oil and so on, and it is usual therefore to scour the fabric to reduce the oil content to less than 1.0% as measured by extraction with solvent. Wet scouring –

Table 11.3 Typical requirements for fabric one-step padding processes

	Isocyanate	Silicone
Fabric pH	6–8	7–8
Dosage	1–2% on weight of wool of both Synthappret BAP and Impranil DLH 3–5 g l ⁻¹ sodium bicarbonate	9–16% on weight of wool (oww) of Ultratex ESB 130, plus Ultratex EW in the ratio of 1 part EW to 80 parts ESB 130
Pad liquor concentration	May be calculated as follows: $C = 1000 T/P$ where C = concentration in g l ⁻¹ T = treatment level desired in % oww P = pad liquor pick-up in % (assuming a density of 1 for the solution)	
Curing	150–160 °C fabric temperature at end of drying	120–140 °C plus batch in crease-free state for 7 days

either in rope form or in open-width – is the usual route taken, with some type of detergent, typically today a non-ionic type, in the scour bath. During this process, the fabric internal pH can be adjusted to the desired value for application of the polymer.

Resins used in the single-step padding process fall into two classes: the isocyanates [41], typified by Synthapprett BAP (Bayer), Braxan WF (Ciba) and Protolan 367 (Rotta), and the silicones, typified by Ultratex ESB (Ciba) (Table 11.3). The isocyanates are applied at a slightly alkaline pH and heat-cured by drying at high temperatures (150–160 °C). As this type of polymer imparts a harsh handle to the fabric, it is usual to add a polyurethane dispersion to the bath, which gives a better handle and acts synergistically with the isocyanate to give better shrinkage control. In contrast the silicone systems give very soft slick handle, and are applied at slightly acidic pH. The Ultratex system, however, takes some days to cure and the fabric must therefore be carefully stored to avoid development of permanent creases.

The main problem with this type of finish is that the fabric can appear to be well protected but will develop pronounced cuff edge felting at the creases and folds. The isocyanates are better able to control this problem and are therefore normally preferred, despite their poorer handle. Sufficient polymer must be used even in these cases such that cuff edge felting does not occur. As may be expected with a ‘spot welding’ mechanism, it is easier to stabilise tighter constructions of fabric such as gabardines and twills. It is also known that any process that results in a reduction in crimp, such as blowing or kier decatising, will enhance the tendency to felt. Polymer dosage levels are therefore determined by experience or by laboratory testing.

11.9 THE FUTURE

As process technology continues to develop, new processes will emerge. The pressure to produce wool with good shrink resistance and better aesthetic properties coupled with less environmental impact will provide the driving force for this [42]. Attention is heavily focussed on the value of plasma treatments for this purpose. It remains to be seen how effective they prove to be in commercial practice, but consideration of the fundamental principles outlined in this chapter would suggest that any treatment limited only to the outer surface of the fibre will not easily deliver all the desired attributes. Greater promise probably lies in the use of alternative chemical technologies, either in the polymer field, or through the use of biotechnology and enzymes to replace the current oxidants available to the market. Whatever emerges, careful consideration should always be given to all the principles outlined here in order to judge the viability of the technology.

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CHAPTER 12

Mechanical finishing of wool fabric

A G De Boos

12.1 INTRODUCTION

There are many operations and many combinations of processes that may be used to finish wool fabrics. The particular process or route chosen depends primarily on the quality and type of fabric and its intended use. However, the type of machinery available, the experience of the finisher and the economic factors related to the particular situation are also important in the final choices made.

Wool finishing may be loosely divided into mechanical and chemical processes. The first group includes the topics discussed in this chapter (milling, setting, raising, and so on) as well as others dealt with in other chapters (scouring, drying, and so on). Chemical processes include shrink-resist treatment, flameproofing and those designed to impart functional finishes to wool. However, this division is of limited use since many so-called ‘mechanical’ processes depend on the unique chemistry of the wool fibre and many require the use of ‘chemicals’ such as surfactants and reducing agents for their effectiveness.

A large number of books and review articles have been written on various aspects of wool finishing since the early 1980s [1–6]. Some of these, such as that by Rouette and Kittan [1], deal more extensively with mechanical finishing than can be done in this chapter. The reader is referred to these more extensive works for detail on the processes discussed below.

12.1.1 Aims of finishing

Mechanical and chemical finishing processes used on wool fabrics can be categorised according to their aims and objectives. These objectives include:

- (1) to clean the fabric;
- (2) to set or stabilise the fabric;
- (3) to dry or add moisture to the wool fibres;
- (4) to change the dimensions of the fabric;
- (5) to change the geometry of the fibre surface;
- (6) to confer the required handle to the fabric;
- (7) to colour the fabric;

- (8) to assist handling the fabric in subsequent operation;
- (9) to confer a particular functional property, such as oil-repellency or shrink resistance, to the fabric.

Naturally some finishing operations, such as bagging or hydroextraction, may be restricted to one of these aims while others, such as milling, may encompass several.

Although finishing processes used on wool have, in some instances, been developed over many centuries, work on the mechanistic understanding of these processes, particularly those that involve chemical processes within the wool fibre, only began during the twentieth century with the work of scientists such as J B Speakman at Leeds University. Improvement of both the understanding and technology of wool finishing is ongoing.

12.1.2 Assessment of the effectiveness of wool finishing operations

Although each finishing process is carried out to achieve or contribute to a specific change or group of changes on the fabric, many processes have side effects that may either improve or have a detrimental effect on overall fabric quality. Assessment of both the desired outcome and the side effects is an important part of the total evaluation of finishing processes. A good example of this combination of desired outcomes and side effects is piece dyeing. The operation is designed to colour fabric but, in addition, dyeing increases fabric extensibility, thickness and hygral expansion [7,8] and sometimes imparts unwanted distortions such as running or rope marks to the fabric. Evaluation of a dyeing procedure or machinery must include measurement of these side effects as well as the quality of the coloration.

Finishers have traditionally used a mixture of subjective and objective techniques to evaluate the effectiveness (or otherwise) of the many operations used in a wool finishing mill. However, test methods have been standardised only for the most recently-developed procedures for imparting functional finishes such as shrink or flame resistance. These methods are contained in the publications of regulatory bodies, standards organisations (for example, ISO, International Wool Textile Organisation) and wool marketing bodies (for example, The Woolmark Company.).

There are many objective test methods that can be used to evaluate the effectiveness of the more traditional wool finishing processes. These tests include the measurement of physical, mechanical and chemical properties of both the fabric and the fibre from which it is made. Those test methods that measure the most important mechanical, dimensional and physical properties of the fabric (in terms of their subsequent use in apparel) have now been compiled in sets of instruments such as the KES-F [9] and FAST [10] systems. In addition, standard methods for measuring chemical damage (for example, alkali solubility) and ultimate properties (abrasion resistance, tear and tensile strength) are widely available. However, there remains considerable scope for further use of these methods and a need for other test methods to evaluate the more subtle aspects of fabric finishing. Discussions of techniques suitable for measuring the effectiveness of various mechanical finishing operations on wool fabric will form an important part of this chapter.

12.2 SETTING

Setting operations are among the most critical processes in the conventional finishing of wool fabrics. Depending on the finish required, the fabric may be ‘set’ two or three times during a complete finishing routine. Setting is carried out in loom-state or early in a finishing routine to stabilise the fabric by removing residual stress in the fibres and yarns imparted in prior spinning, twisting and weaving operations. In this way, when the fabric is subsequently processed in rope form during wet finishing, the formation of distortions due to uncontrolled relaxation of the fibres can be minimised. After wet finishing, a wool fabric may be set to remove any unwanted distortions (such as rope marks) that have been introduced. In dry finishing, wool fabrics are set to ensure that they maintain their dimensions, flat appearance and surface geometry during any subsequent finishing operations or garment manufacture, or in use.

Although their primary purpose is to stabilise the fabric in a flat form, permanent setting processes have many side effects. These operations improve the suppleness and smoothness of wool fabrics, the modification of handle resulting from profound changes in the mechanical and physical properties of the fabric [11,12,13]. Setting operations also modify the dimensional properties of wool fabrics, and this can, depending on the nature of the fabric and its end-use, improve or impair its overall dimensional stability.

12.2.1 Principles of setting

Looseness in the use of the terms ‘set’, ‘stabilise’ and ‘setting’, and in the mechanisms by which wool may be set, have created specific difficulties for wool finishers that are not normally experienced by their counterparts in the cotton and synthetic industry.

Three types of set have been defined [14] in wool fibres:

- (1) ‘Cohesive set’ is defined as the set lost when the fabric is immersed in water at room temperature and is imparted in stenter drying and in continuous dry finishing operations such as pressing. Cohesive set is also the type of set associated with the formation of wrinkles in wool apparel during wear and steam pressing of garments.
- (2) ‘Permanent set’ was originally defined [15] as the deformation that is stable to release in boiling water for 60 min. This type of set is conferred by wet and/or high-temperature operations such as crabbing, piece dyeing and pressure decatising. More recently, permanent set has been re-defined [16] as the deformation remaining after the wool has been relaxed in water at 70 °C for 30 min. These conditions are considered to be more realistic and avoid the problems associated with supercontraction of the fibre.
- (3) ‘Temporary set’ is defined as the difference between the set released in water at room temperature and that released at the higher temperature used to assess permanent set. There is some confusion between cohesive and temporary set and, in many parts of the wool industry, the terms are used interchangeably.

A wool fibre is a chemically complex, crosslinked, amino acid copolymer, which has disordered (matrix) and ordered (crystalline) regions. In wool, the mechanical and chemical properties of

the fibres are further complicated by their complex morphology. Three major structural components (cortical cells, cuticle cells and intercellular material) have been identified [17,18]. Each of these components exhibits mechanical, chemical and physical heterogeneity. Much of the early work on wool setting tended to overlook the complex morphology of the fibre. However, separation of the roles of the ordered and disordered components is now an important part of modern theories of wool setting [19,20].

The disordered matrix component of wool fibres is normally associated [19] with setting phenomena. Movement of the macromolecules in this component is limited by a number of types of intra- and inter-molecular interactions, namely:

- (1) hydrogen bonds between amino, alcohol and amido groups;
- (2) polar interactions between ionised acid and basic groups;
- (3) disulphide and other covalent bonds.

There is also considerable evidence that, in wet wool fibres, there is interaction between the non-polar side-groups on the protein macromolecules, which contributes to the stability and mechanical properties of the fibre. These interactions have been called 'hydrophobic bonds'.

Early research placed greatest emphasis on permanent setting of wool fibres [21] and less work was done on cohesive or temporary setting in spite of their importance in finishing as well as in the wrinkling, smooth dry performance and pressing of wool garments. Cohesive set was originally described in terms of the re-arrangement of hydrogen bonds (or the hydrogen bond network) in wool fibres under the influence of heat and/or moisture [22,23]. This model was, at best, qualitative and did not allow prediction of fibre properties. More recently, an alternative approach [24–26] has been published that describes cohesive set in terms of the stress-relaxation behaviour of the fibre above and below its glass transition temperature (T_g) without reference to the type of intermolecular bonds restricting the mobility of the polymer chains. The rate at which all polymeric materials stress-relax increases dramatically above their glass transition temperatures because of the greater mobility of the macromolecules.

In spite of the physical and chemical complexity of wool fibres, a glass transition can be detected using differential scanning calorimetry [27,28] and other thermo-analytical techniques [29]. This transition is thought to be associated with the proteins in the matrix or disordered regions of the fibres rather than those in the fibrils or ordered regions.

As a result of the complexity of the fibre and the nature of the bonds stabilising the material, the glass transition is probably broad and, as with other materials, it is, to some extent, dependent on ageing effects within the fibres. Wool is plasticised by water so that the glass transition temperature also depends on the moisture content or regain [29] of the fibres (Figure 12.1). The T_g is around 170 °C when the fibre is dry and approximately –10 °C when wet. Under normal conditions (20 °C, 65% relative humidity), the fibre is below its T_g and the proteins in the matrix have mechanical properties similar to other glass-like polymers. The matrix can be transformed to a rubbery material by heating the fibre without loss of moisture or by increasing its regain (that is, wetting out).

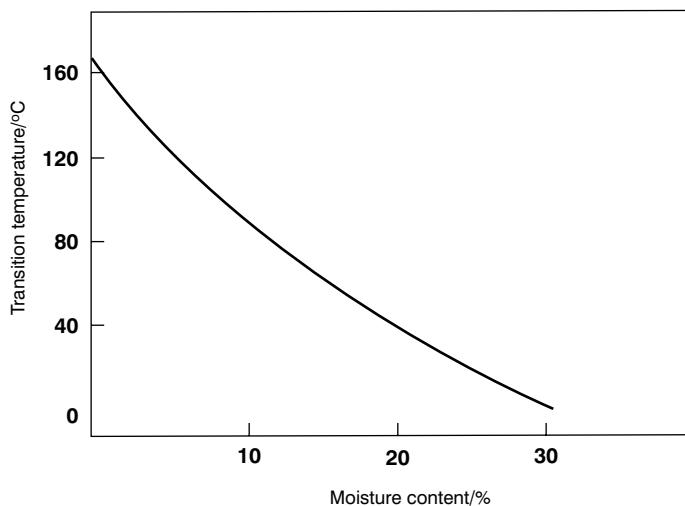


Figure 12.1 Effect of moisture content on the glass transition temperature of wool fibres (derived from [29])

Cohesive set is most effectively imparted by deforming the fibre above the glass transition temperature (where it stress-relaxes rapidly) and then removing the constraints on the fibre or fabric only when it has been cooled (or dried) to a point below the transition (where it recovers slowly). However, it is not necessary to cross the transition temperature to impart some cohesive set, provided the molecular mobility of the fibre is greater during deformation than when the constraints on the fabric are removed. Alternatively, some cohesive set can be imparted if the time of setting greatly exceeds the time, after removal of the constraints, when set is assessed. Cohesive set, imparted in early finishing operations or in use, is most effectively released by placing the unconstrained fabric in conditions in which the glass transition temperature of the fibres is exceeded, such as in steam or water.

In addition to the increased molecular mobility required for cohesive setting, permanent setting requires the rearrangement of covalent disulphide bonds in the fibre [30,31]. This is thought to occur by nucleophilic attack of free ionised thiol groups on strained disulphide bonds in the deformed wool [32–34], a process called thiol-disulphide interchange (Figure 12.2). However, alternative mechanisms have been proposed to describe the chemistry of disulphide bonds rearrangement, including a catalytic action by free hydrogen sulphide formed within the fibre and the formation of alternative intermolecular bonds (such as lanthionine and lysinoalanine). Extensive reviews of the chemistry and technology of permanent setting have been published [21,35,36,131]. A review of industrial practice for permanent setting of wool was published by Breuers [37] in 1987.

The rate at which permanent set is imparted to wool depends on the concentration of free ionised thiol groups in the fibre [32]. This can be increased by treating the wool with reductive chemicals (for example, thioglycollic acid or sodium bisulphite), as occurs in chemically-assisted

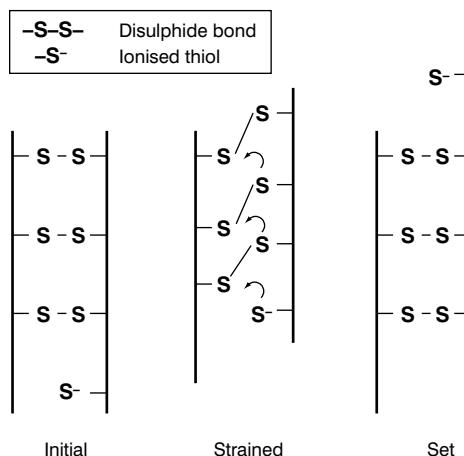


Figure 12.2 Thiol-disulphide interchange

setting processes [21,35] or by the use of high pH. Under alkaline conditions, thiol groups are ionised and more likely to react with strained disulphide links. The rate at which permanent set is imparted to wool is reduced at low pH or after treatment of the fibres with oxidising agents or other electrophiles that react with free thiol groups (and hydrogen sulphide).

The greater mobility of protein macromolecules provided by the plasticising action of water is extremely important in permanent setting operations. For this reason, hot water (crabbing) and/or high pressure steam (decatising) are normally used to permanently set wool fabrics.

A transition temperature around 60–70 °C, which is associated with the formation of permanent set in wet wool, has been reported [38–41]. This transition may also be observable at higher temperatures in wool at lower regains. It is not clear whether this is a mechanical transition analogous to the glass transition temperature or the result of an activated chemical process, although recent data suggests the latter. The difference between the temperature of this transition (60–70 °C in wet wool) and the T_g of wool in water (approximately –10 °C) clearly demonstrates that much higher temperatures are required to impart permanent set than to impart cohesive set. In wool at normal regain (approximately 10–15%) temperatures in excess of 100 °C are required to permanently set the fibre, whereas cohesive set will form if the temperature of the fibre exceeds only 50–60 °C. Naturally the amount and type of set imparted to the wool will depend on the time as well as the temperature of the setting operation.

The exact nature of temporary set is unclear. This form of set does not appear to have its origin in any transition behaviour within the fibre but may simply be a consequence of the effect of temperature on mobility of the protein macromolecules in wet wool. Temporary set appears to be merely a measure of the different rates at which set is released in water at 20 °C and at 70 °C.

Hydrophobic interactions within wet wool fibres appear to contribute to their setting characteristics in two ways: by restricting the mobility of the chain segments in wet wool, and by limiting the reactivity of disulphide bonds. Fibre relaxation rates are higher in water/solvent mixtures than in water alone [42]. The plasticising action of alcohol/water mixtures increases

with the chain length of the alcohol until the alcohol is no longer soluble in water. The mixture at which the combined plasticising actions of water and alcohol are maximised depends on the structure of the alcohol. Similar effects can also be achieved using surfactant/water mixtures [43]. Temporary set can be imparted to wool if the fibres are deformed in a solvent/water mixture (for example, alcohol/water) and the solvent washed (or dried) from the fibre before the constraints on the fabric are removed [44]. If disulphide interchange is avoided (by blocking free thiol groups), the set imparted is stable to release in water at room temperature but not stable to release in hot water or alcohol/water mixtures [44].

The rate at which permanent set is imparted to wool is also increased by inclusion of water-soluble organic compounds in the setting bath or steam [45] used to permanently set the fibres or fabric. The reactivity of disulphide bonds is greater in solvent/water mixtures than in water alone [46] and this, combined with the more effective plasticising action of solvent/water mixtures, contributes to the formation of permanent set [43]. In spite of the enhancement of the setting action, solvent/water mixtures are rarely used, presumably because of the safety, cost, health and environmental hazards associated with their use.

12.2.2 Wet setting operations

Wet setting operations are designed to permanently flat set wool fabrics. The greater mobility of the protein macromolecules in the wet fibre allows permanent set to be imparted more rapidly, or at lower temperatures, than to the fibre at normal regain. These operations do not impart cohesive set because, even at room temperature, the wet wool fibre is above its glass transition. Cohesive set is only imparted in subsequent drying operations.

Crabbing and wet decatising are the most common forms of wet setting. Traditional 'crabbing' is a process in which the wet fabric is wound (often interleaved with a blanket or wrapper cloth) onto a drum which is partially immersed in hot or boiling water. The fabric is held in the hot water for 10–20 min, then rewound from the other end of the piece and re-treated. The re-treatment is necessary to avoid differences between the two ends of the fabric. The traditional Yorkshire crab also has additional rollers for steaming the wet fabric. The hot fabric is normally quenched by unrolling it through a trough of cold water. Traditional crabbing imparts large amounts of permanent set (often in excess of 60% using crease angle tests) to wool fabric.

'Potting' is a labour-intensive and time-consuming variation on traditional crabbing, which is designed to impart large amounts of permanent set and is reserved for very special applications such as billiard cloth. The fabric is wrapped on a canvas-covered roller. The roll is itself wrapped in canvas and then placed vertically in a tank of hot water (approximately 60 °C) for up to three days. In some cases, the fabric is cooled on the roll.

A further variation on crabbing is 'beaming', in which the fabric is again rolled onto a beam but held in warm water (approximately 40 °C). The procedure is designed to remove crease marks formed in scouring or dyeing. Although beam dyeing is strictly a coloration process, it is also an effective crabbing operation. Under the conditions in the dyebath, large amounts of

permanent set are imparted to wool fabric. However, because a wrapper cloth is not used in this operation, there is a danger of moiré formation, so that beam dyeing is more often used to colour milled woollen rather than clear-finished, worsted cloths.

'Wet decatising' ('decating' in the USA) is also a type of setting operation in which wet fabric is rolled, sometimes interleaved with a cotton wrapper cloth, onto a perforated drum. However, in this instance saturated steam (rather than hot water) is passed through the roll to heat the wool (and wrapper) to temperatures around 100 °C. Again, it is often necessary to rewind and re-treat the fabric to avoid end-to-end differences. The fabric is normally cooled before it is unrolled by drawing air through the roll. This avoids the possibility of distorting the fabric while it is still in a condition where permanent set can be imparted.

Chemically-assisted wet decatising is widely used in parts of Europe, especially Italy, to improve the handle and dimensional stability of wool fabrics. However, the use of reducing agents and wet fabrics can damage wrapper cloths and decatising machinery. Sperotto Rimar now markets a conventional decatising machine (Chemiset SKB/900) specifically modified [47] to overcome the problems associated with the chemically-assisted wet operation. All components that come into contact with the fabric, wrapper and exhaust air are manufactured from special stainless steel and the wrapper is dried using two steam-heated rollers.

The traditional batch crabbing and wet decatising processes are labour-intensive, suffer from end-to-end and batch-to-batch variation and have low production rates. Continuous crabbing machinery was first introduced in the 1960s. In these machines (Figure 12.3), the fabric is wet out in a trough containing hot water, squeezed to give the fabric the correct water content and then sandwiched between a heated drum (up to 160 °C) and an impermeable belt. The wet fabric rapidly heats to temperatures at which permanent set can be imparted. After passage around the heated drum, the fabric is then quenched in a cold water trough. The residence time of the fabric in the heating zone is short (typically 1 min), so that unless the temperature of the wet fibres exceeds 100 °C, little permanent set is imparted. Early continuous crabbing machines did not seal the fabric well and were relatively ineffective [48]. In more modern machinery, improved belt technology allows higher belt tensions and a better seal, so that, when combined with the higher drum temperatures (up to 180 °C), higher temperatures can be achieved on the fabric and more permanent set can be imparted to the wool. A number of machinery manufacturers offer this type of continuous crab as part of their range – for example, Supercrab-2 (M-Tec), Multiset (Sperotto Rimar) [49], Vulcano (Biella Shrunk).

An alternative approach has been used in the MAT Conticrab (Figure 12.4), a machine in which hydrostatic pressure is used to produce water temperatures up to 110 °C [50,51]. In industrial trials, this machine has been shown to impart high levels of permanent set (approximately 50%) to pure wool fabric.

Naturally, the effectiveness of conventional continuous crabbing machinery can be greatly enhanced by the inclusion of chemical assistants (usually reducing agents) in the wetting trough [52]. Modern continuous crabs normally incorporate pad mangles to ensure the even application of such assistants. This is necessary to ensure uniform setting and, because setting operations can affect the uptake of dyes, uniform coloration in any subsequent dyeing process.

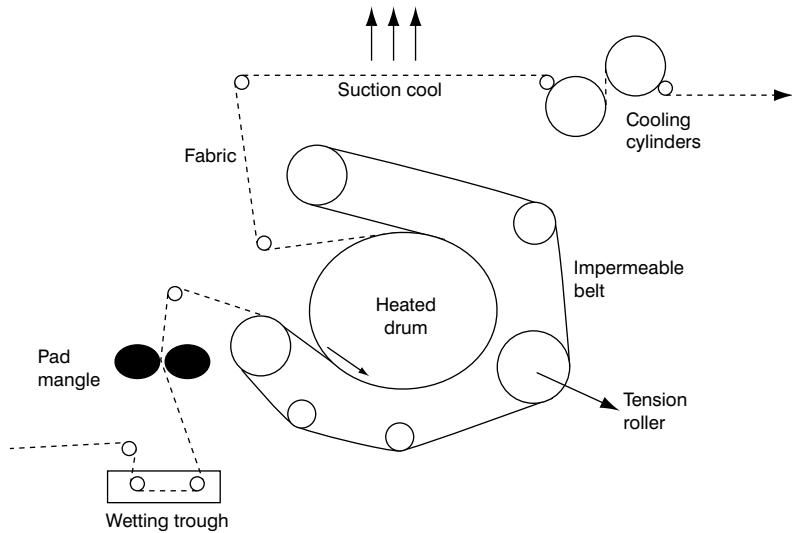


Figure 12.3 Schematic diagram of a continuous crab – the example is the Supercrab from M-Tec (formerly Menschner)

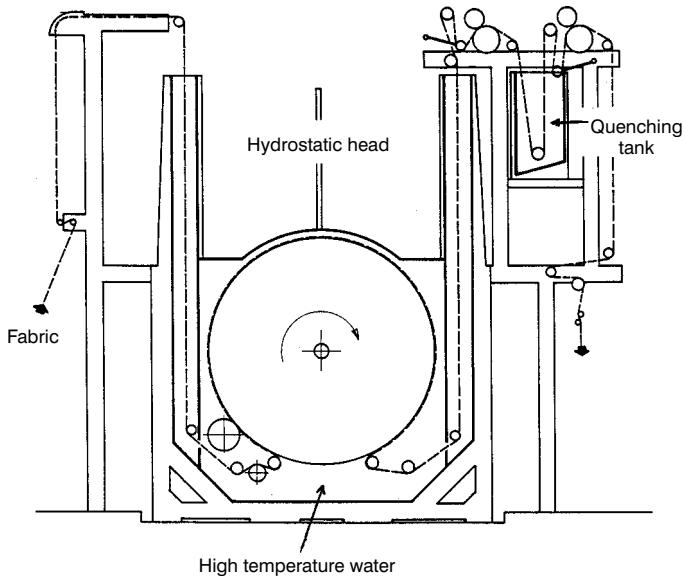


Figure 12.4 Schematic diagram of the MAT Conticrab

12.2.3 Dry setting operations

Dry setting is a term used to describe operations used to set wool fabrics at normal regain (that is, not wet). What constitutes 'normal' regain varies widely and, in practice, the regain of fabrics

in a mill environment can vary from around 5% after drying to 15% after conditioning. Depending on the conditions, dry setting operations can impart cohesive, temporary or permanent set or, more usually, all these forms to wool fabric.

Decatising

Decatising, as described above, is a type of setting operation in which fabric is rolled, interleaved with a cotton or cotton-blend wrapper cloth, onto a perforated drum. Saturated steam is then passed through the roll to heat both fabric and wrapper. The terminology used in this area of dry finishing can sometimes be confused. If the steam used to set the fabric is vented to the atmosphere so that the fabric temperature is limited to around 100 °C, the operation can also be called 'blowing'. 'Semi-decatising' describes the procedure where the fabric is rolled up with the wrapper and steamed only once. 'Full decatising' describes the procedure where the fabric is semi-decatised, unwound, reversed and then fed into the machine from the other end to be semi-decatised a second time. Two-drum decatising machines are designed to facilitate this rewinding and double steaming operation. The German industry also uses the terms 'lustre (pressglanz) decatising' and 'finish decatising' to describe semi-decatising operations carried out on machines with different sized drums, under specified conditions (time, temperature, wrapper tension) to impart different surface effects to the fabric [1,2].

If the drum onto which fabric and wrapper have been rolled is placed in an autoclave, the temperature of the steam (and fabric) can be increased to values as high as 135 °C. The operation is then called 'pressure (or autoclave) decatising' or occasionally 'KD-setting' (after the German, 'kessel dekatier'). In such machines, the time and temperature as well as wrapper type and tension can be varied to impart different effects to the wool. In addition, the steam can be passed from the outside to the inside of the roll, or from inside to outside, which is claimed to change the effect of the process on the thickness, surface properties and ultimate handle of the fabric. All decatising machines have the facility to cool the fabric by drawing air through the roll before it is unwound. This facility is used if a firmer, flatter handle is required.

The amount of permanent set imparted to wool in decatising and the effect on the properties of the fabric have been extensively studied [16,53,54] and reviewed [58]. The amount of permanent set is determined by the regain, pH and temperature of the wool and the time of the treatment [55,56]. For the reasons described earlier in this section, the regain and pH of the fibre are critical in pressure decatising. The amount of permanent set imparted is reduced dramatically if the pH of the fibres is low ($\text{pH} < 3$) or their moisture content is below 10% [16]. The critical moisture content depends on the temperature of the operation and the extent to which the moisture content of the fibre increases due to the condensation of steam during heating of the fabric.

Laboratory studies have shown that the type (cotton, cotton blend, and so on) and moisture content of the wrapper cloth [59,60] also affect the setting process. These effects reflect modification by the wrapper of the heat and moisture transfer process between the steam and wool [59]. Furthermore, the properties of decatised fabric depend on the construction of the

wrapper and the tension used in winding. The wrapper may be hard (satin) to impart a smooth, lustrous finish, or soft and compressible to impart a fuller finish.

The presence of oxygen in the autoclave can cause rapid yellowing of wool at the high temperatures used, so that many modern autoclave decatising machines are fitted with vacuum pumps to assist purging of the air before high-temperature steam setting.

Laboratory studies have refuted conventional beliefs that increased dwell time of the fabric in the roll after decatising improves the handle of fabrics [57]. However, the amount of cohesive set imparted is determined by the temperature at which the fabric is unrolled and the rate at which it is cooled [61]. If the fabric is cooled (by passing air through the roll) before it is unrolled, cohesive set contributes to the flat smooth appearance of the fabric. If the fabric is unrolled hot (above the glass transition point), the fibres can relax during cooling and less cohesive set is imparted to the fabric. This is reflected in the resultant properties (for example, thickness, handle, lustre) of the fabric.

These principles can be seen in Table 12.1. A wool fabric was semi-decatised for various times and its thickness measured after decatising and release in water. The initial thickness depended on the amount of cohesive and permanent set imparted whereas the thickness after release in water depended only on the permanent set imparted. Permanent set was imparted only slowly and required steaming times in excess of 10 min to reach high levels. Provided the fabric was cooled before unrolling, cohesive set was imparted quickly, requiring less than 0.5 min steaming. If the fabric was unrolled hot (not cooled) much of the cohesive set was lost and the initial thickness was much higher.

Table 12.1 Cohesive and permanent setting in decatising [61]

Decatising Time (min)	Unrolling	Fabric thickness (mm)	
		Initial	Relaxed
0.5	Cold	0.64	0.80
2.0	Cold	0.64	0.77
5.0	Cold	0.66	0.74
10.0	Cold	0.62	0.68
15.0	Cold	0.63	0.68
2.0	Hot	0.73	0.76

Relaxed in water for 30 min at 20 °C and reconditioned

Continuous decatising machines were developed in an attempt to overcome the perceived low production rate and the end-to-end variation sometimes encountered with traditional batch machinery. Advances in batch pressure decatising machines, which now use up to 1500 mm drums to process up to 600–800 m in a single batch, have done much to overcome these problems. In the continuous machines, the fabric is steamed and/or cooled while passing over a perforated drum with a continuous, permeable wrapper cloth (Figure 12.5). The wrapper is tensioned and so the fabric is compressed between it and the drum in a manner analogous to

continuous crabbing. While under this constraint, steam (to heat) and then air (to cool) is passed through the wrapper and fabric.

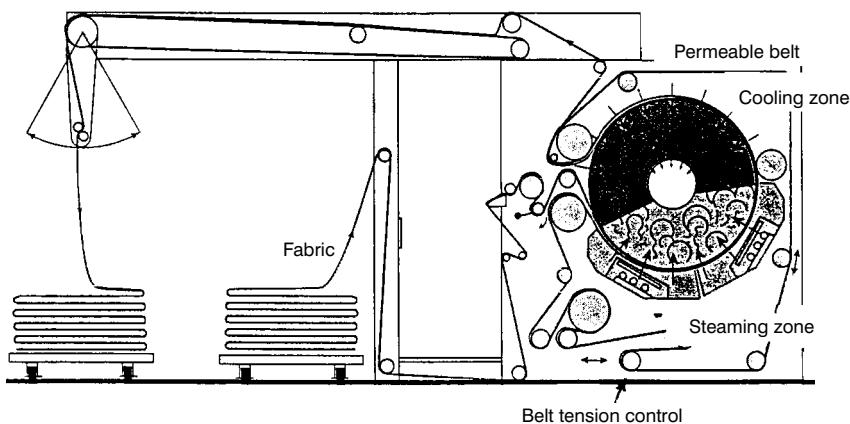


Figure 12.5 Schematic diagram of a single cylinder continuous decatiser (example is M-Tec model DEK)

There are three distinct mechanical arrangements used for continuous decatisers [62]. The first arrangement is to steam and cool the fabric (and wrapper) as it passes around a large perforated cylinder – for example, Thermo Duplex 90 (Biella Shrunk). The second (Figure 12.6) is to steam and cool the fabric on separate cylinders – for example, Contidec 614 (M-Tec). Tension control between the steaming and cooling rollers in these machines is critical since the hot fabric (above T_g) may be easily deformed and the deformation cohesively set during subsequent cooling. Finally, a newer concept has been developed [63], in which water is sprayed onto the fabric (or an interleaved wrapper) and steam is generated by bringing the water droplets on the fabric into contact with a heated cylinder – for example, Superfinish (M-Tec), Figure 12.7. The M-Tec machines incorporate the patented 'Hygromat' system, which regulates the amount of water applied to the fabric by measuring the liberated steam using a special sensor [64]. This arrangement is claimed to save on steam usage and electricity [63].

The treatment times in continuous machines are short so that the effects achieved are, in most cases, not equivalent to those obtained using traditional batch machines. It has been found that none of the conventional continuous decatisers imparts any permanent set to wool fibres.

Many attempts have been made to develop a continuous machine that will impart permanent set to wool and produce a pressure-decatised finish. The Mather and Platt Ekofast, developed in the 1970s [4,65], uses patented pressure seals and Nomex belts to transport the fabric through a pressure vessel containing saturated steam at temperatures up to 140 °C. Under these conditions, considerable permanent set is imparted even in the relatively short time required by the fabric to pass through the vessel. Other manufacturers are working on continuous machines claimed to give an effect similar to pressure decatising – for example, Vapopress (Bisio) [66],

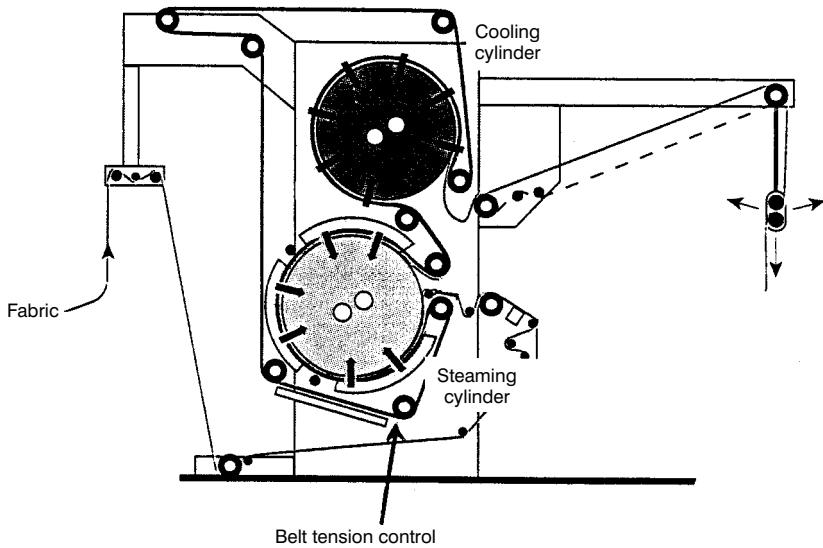


Figure 12.6 Schematic diagram of a twin cylinder continuous decatizer (example is M-Tec Contidec 614).

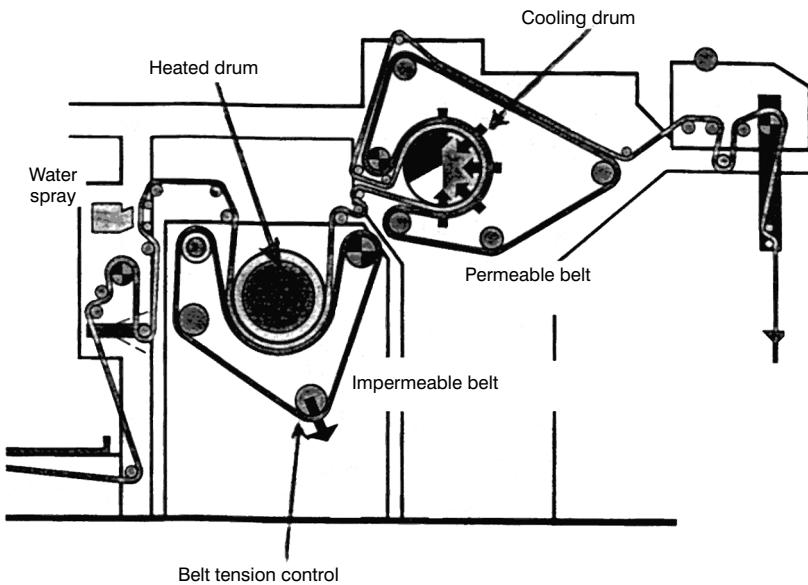


Figure 12.7 Schematic diagram of the M-Tec Superfinish

Permafix (M-Tec). At ITMA '99, Sperotto Rimar released their Decofast continuous decatising machine, which is claimed to use high pressure steam to heat the fabric to temperatures in excess of 120 °C and thereby impart a more permanent finish than conventional continuous decatisers. The machine is also designed to cool the fabric while it is still constrained so that

cohesive set adds to the effect of any permanent set stabilising the fabric. Information on the performance of the machine was presented at the tenth quinquennial wool conference in Aachen [132].

Chemical assistants have also been used to enhance the permanent set imparted by blowing or continuous decatising machinery [79]. In the MR Process, developed jointly by M-Tec and Rotta GmBh, the fabric is impregnated with an organic reducing agent, which is 'activated' in later pressing (Contipress from M-Tec) and decatising processes to process a more permanent flat set [67]. Although reducing agents can be highly effective in wet setting processes [52], the increase in permanent set imparted to wool in processes that operate at normal regain, is usually small.

Workers at the German Wool Research Institute using a solution of a reducing agent (sodium bisulphite) dissolved in a mixture of water and an organic solvent (benzyl alcohol) were able to enhance the permanent setting action of both batch and continuous decatising machines [68,69]. The solvent acts as a plasticiser to increase the mobility of the macromolecules within the fibre, and thus, increases stress-relaxation rates [42]. However, studies [69] on the steam setting of wool at regain around 20% showed that the solvent had only a small effect on permanent set without the chemical assistant (Table 12.2). This suggests that an important part of its action was to increase the reactivity or accessibility of the disulphide bonds in the fibre to the reducing agent.

In the same study, it was shown that the suction cooling cycle during decatising reduced the mobility of the macromolecules not only by cooling the fabric but also by reducing the number of free thiol groups remaining in the fibre.

Table 12.2 Use of solvent to enhance setting [69]

Pretreatment	Initial thickness	Relaxed thickness
Water	0.76 (1.04)	0.96 (1.26)
Benzyl alcohol	0.76	0.97
Bisulphite	0.74	0.90
Bisulph/benz	0.72 (1.01)	0.88 (1.04)
Press. dec.	0.72	0.89

Thickness of untreated fabric: 1.14 mm [72]

'Pressglanz' decatised for 5 min steam, 3 min suction

Relaxed in steam (5 × open steam and suction-off)

Benzyl alcohol: 2 g l⁻¹

Bisulphite: 2 g l⁻¹

Bisulph/benz: bisulphite 2 g l⁻¹ and benzyl alcohol 2 g l⁻¹

Press. dec.: pressure decatised 5 min at 2.5 gf cm⁻²

Number in parenthesis: Raxhon continuous decatiser

12.2.4 Evaluation of setting operations

Several techniques can be used to measure, directly and indirectly, the amount of set imparted in any setting operation. The simplest is the 'crease angle test'. This method [16] involves release of

yarn snippets taken from a crease that has been set in the fabric. The angle formed by the snippets after release under appropriate conditions is a good measure of the set imparted in the process.

$$\text{set (\%)} = \frac{180 - \text{angle}}{180} \times 100 \quad (12.1)$$

To measure permanent set, snippets are normally released in water at 70 °C for 30 min. The advantages of this method are its simplicity, flexibility and its ability to measure both cohesive and permanent set directly. However, the method is relatively insensitive at low levels of permanent set. Nevertheless, where relatively low levels of permanent set are imparted, milder release conditions (water at 20 °C) can be used to obtain comparative measurements. Naturally, a crease must be sewn into the cloth prior to the setting operation. Alternatively, a piece of test fabric, sewn to form a fold, can be attached to a batch of cloth. For fabrics or processes where this preparation is not possible, other methods of assessment can be used.

Relaxation shrinkage may also give information on the effectiveness of permanent setting operations used in *dry* finishing. Wet fabrics have, by definition, no relaxation shrinkage and so wet setting processes cannot affect this fabric property. Relaxation shrinkage is imparted only when the wet set fabric is subsequently dried. There are several methods used to measure relaxation shrinkage in wool fabric [70], which include the WIRA steaming cylinder (BS 4323: 1979), the FAST-4 dimensional stability test as well as The Woolmark Company and DIN test procedures. This test can only be used to assess permanent set if the fabric has high relaxation shrinkage before the setting operation [71]. Moreover, the results are often not reliable. A reduction in measured relaxation shrinkage may indicate that permanent set has been imparted but equally may indicate only that fabric has shrunk during the operation. Shrinkage during setting processes can be easily checked by measuring marks placed on the selvage of the cloth.

Fabric thickness measurements have also been extensively used to provide a direct measure of the effectiveness of decatising operations [72]. A method has recently been proposed to the IWTO [73] in which fabric thickness, before and after release in steam, is used to evaluate the stability of the finish on wool-containing fabric. A modification of this method can be used to obtain a measure of the permanence of the deformation imparted in decatising operations. The permanence of the finish imparted can be calculated from measurements of the thickness and relaxed thickness of the fabric prior to and after the setting operation.

$$\text{set (\%)} = \frac{\text{RT}_{(\text{before setting})} - \text{RT}_{(\text{after setting})}}{\text{RT}_{(\text{before setting})} - \text{T}_{(\text{after setting})}} \times 100 \quad (12.2)$$

where T = set thickness of the fabric

RT = relaxed thickness of the fabric

Alternatively, where changes in length or width are sought, the dimensions and relaxed dimensions of the fabric may be used.

In practice, a variety of release conditions are used to evaluate the set imparted in decatising from fabric thickness. Finishers and garment makers usually use release conditions that approximate those expected in later processes or in use. However, stricter control of release conditions is required when objective measures of permanent set are made. Release of the fabric in boiling water can be used to give some information on the effectiveness of decatising when used to stabilise fabrics for piece dyeing.

More recently, a new approach has been described, in which the 'finish' and the stability of that 'finish' are characterised in terms of two properties: 'effective flat set' and 'stable flat set'. Both properties are determined from the surface thickness (ST) and the relaxed surface thickness (RST) of the fabric measured before and after any pressing or decatising operation [133].

$$EFS = \frac{RST_{(\text{before setting})} - ST_{(\text{after setting})}}{RST_{(\text{before setting})}} \times 100 \quad (12.3)$$

$$RSFS = \frac{RST_{(\text{before setting})} - RST_{(\text{after setting})}}{RST_{(\text{before setting})}} \times 100 \quad (12.4)$$

The technique is particularly useful in evaluating the finish imparted by final pressing and decatising operations. The data is normally graphically represented; the position of the fabric on the graph gives information on the type and stability of the surface finish on the fabric. The technique can also be used to optimise the operation of pressing and decatising machines. Typical 'zones', characterising the type of properties imparted by different classes of finishing machine can be described.

Measurement of fabric thickness is a direct measure of set but can only be used to measure set in operations that reduce the thickness of a fabric, such as pressing and decatising. Changes in fabric thickness are easily measured using FAST-1 (Figure 12.8) or other thickness meters and give good determinations of set. For operations such as piece dyeing, in which the fabric is not constrained, thickness changes cannot be used.

Permanent setting also affects several low-stress mechanical properties of wool fabrics including extensibility and behaviour in bending and shear [74,75]. The shear rigidity, bending rigidity or bias extensibility of wool fabrics can be used to assess the amount of permanent set imparted in setting operations; the greater the set, the greater the reduction in shear rigidity, shear hysteresis (Figure 12.9) and bending hysteresis [77] and the greater the increase in bias extensibility. Several instruments are commercially available to measure the shear (for example, KES-F1B, TNO shear tester), bending properties (KES-F2B) and bias extensibility (for example, FAST-3 or a tensile test instrument) of fabric.

Unlike the crease angle and thickness measurements, these tests are only an indirect measure of set and depend on the properties of the fabric before the setting operation. The



Figure 12.8 FAST-1 thickness meter

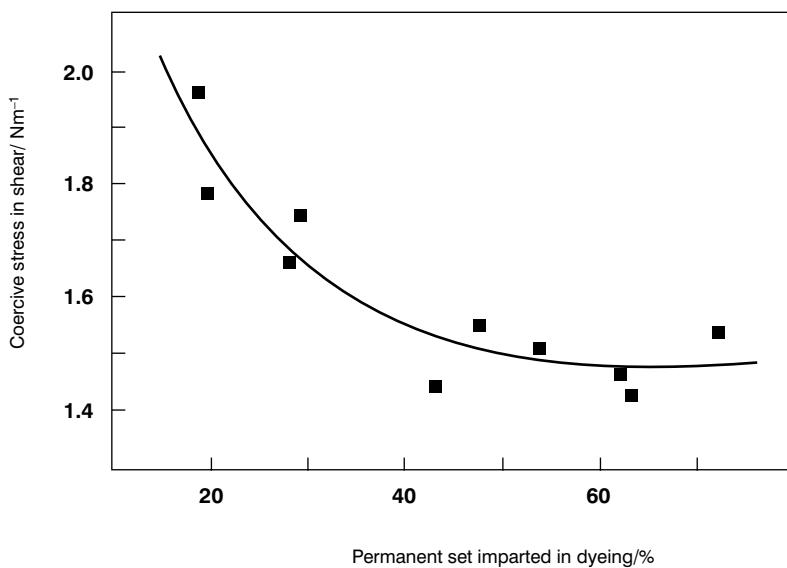


Figure 12.9 Effect of set on fabric shear properties

sensitivity of the shear measurement depends upon the tightness of fabric construction, its finishing history and the amount of set imparted. Fabrics with high cover factors show the greatest changes [74,76] in shear properties. Shear rigidity and hysteresis measured on the KES-F1B instrument change rapidly when low levels of permanent set are imparted and more slowly when the set is higher. The shear and bending properties of a fabric that has already been permanently set in earlier finishing can be unaffected by a second setting operation. In the case of a piece-dyed fabric (where the shear rigidity has normally already been reduced to a low value), pressure decatising will not further reduce shear rigidity or hysteresis, even if the operation imparts high levels of permanent set.

Shear properties can also be affected by any change in thickness conferred on the fabric by the setting operation [75]. Mild decatising operations reduce fabric thickness and, as a result, increase yarn interaction and can increase the rigidity of piece-dyed fabrics. Unset fabric with a high cover factor, in which the rigidity and hysteresis in shear and bending are initially high, are most appropriately used to measure the effectiveness of setting operations. Measurements of shear properties are particularly useful in optimising the performance of continuous crabbing machines. Few of these machines impart more than 50% set (crease angle measurement) to loom-state fabric.

In addition to the desired beneficial effects of the permanent and cohesive setting operations, there are unwanted side effects that may also be objectively measured. Damage to the wool fibres is one of the most important side effects of permanent setting operations including piece dyeing [78]. Damage can be assessed using chemical tests (cystine content, alkali or urea-bisulphite solubility), or from reductions in the abrasion resistance, wet burst or tear strength of fabric [79]. Damage in setting often results in yellowing of the wool fibres, which can be measured most effectively on undyed fabric using a suitable spectrophotometer.

Inadvertent stretching of fabric in the warp direction is a common feature of both batch and continuous setting machines. The consequences of stretching depend upon the type and amount of set imparted during the operation. When the operation imparts only cohesive set (for example, semi-decatising), then the stretch results in increased relaxation shrinkage that can be removed by subsequent relaxation of the fabric (sponging). When an operation imparts permanent set (for example, pressure decatising), the new (stretched) dimensions of the fabric are stabilised and this results in a permanent reduction in the warp extensibility of the fabric. This can lead to sewing problems in light-weight colour-woven fabrics. Extension of the fabric during setting is easily determined by measuring the distance between suitable selvage marks before and after the operation. Alternatively, the extensibility or relaxation shrinkage of the fabric can be measured directly.

Another side effect of batch setting operations is the end-to-end difference in fabric properties. These result from changes in lateral pressure between inside and outside of the roll of wrapper and fabric on the decatising cylinder [80]. The change in wrapper tension modifies fabric thickness so that 'ending' can be most easily assessed by measuring the change in thickness, shear rigidity, air permeability [80] and/or colour of fabrics from end to end (Figure 12.10). Modern pressure decatising machines include control of wrapper tension, which is designed to reduce these end-to-end effects.

All permanent setting operations tend to increase the hygral expansion of colour-woven wool fabrics. The appearance of garments manufactured from fabrics with excessive hygral expansion is prone to deteriorate in humid environments. Hygral expansion can be measured directly [81].

12.3 MILLING, FULLING AND FABRIC DEVELOPMENT

'Milling' (called 'fulling' in the USA) is one of the more important processes for finishing wool-containing fabrics. It is designed to induce controlled felting of the wool fibres that make up the

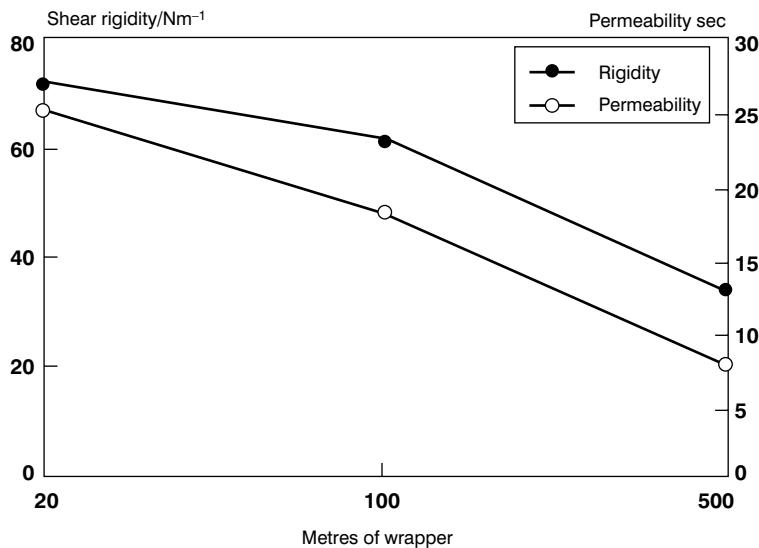


Figure 12.10 The shear and air permeability of fabric samples taken from various positions in a decatriser roll (derived from [80])

fabric and has been used since early Roman times to improve the serviceability of cloths. Milling is used extensively on woollen fabrics as well as on certain worsted cloths such as flannels.

Although milling is a conceptually simple operation, it is used to achieve a wide range of diverse effects. One important aim of milling is to increase the thickness of the fabric and reduce its air permeability. This results in an increase in the subjective ‘fullness’ and thermal resistance of fabrics used in overcoats and related outerwear. Another aim is to shrink and consolidate the fabric and thus increase its strength. With some types of fabric, it is the practice to weave cloth with a cover factor lower than that required to achieve a serviceable product. The fabric is then milled and only when sufficient shrinkage has occurred does the fabric develop the strength or ‘body’ for use in apparel or interior textiles. The increased strength is a result of interlocking of fibres both within and between yarns.

Milling raises fibre to the surface of fabric so that it is used to obscure the weave for aesthetic or functional reasons. The extent to which the weave is obscured can be varied from slight (in worsted flannels) to extensive (in melton cloths) according to the requirements of the end-user. Completely matt finishes used in certain overcoats and in billiard cloths are usually obtained with a combination of milling, raising and cropping operations. The increases in surface fibre and fabric strength produced by milling are often important prerequisites for later raising operations.

Many worsted fabrics are harsh, crisp or too firm even after setting and scouring operations. Such fabrics are often lightly milled or treated in related processes to soften the handle. Terms like ‘cracking’, ‘bursting’ and ‘developing’ are applied to such processes. More detail on the nature of these processes is given later in this chapter.

12.3.1 The principles of milling

The propensity of wool to entangle progressively when masses of the fibre in loose form or fabric are subjected to mechanical action from ‘undirected external forces’ has been recognised and used for centuries. This phenomenon, known as ‘felting’, results primarily from the unique structure of the surface of animal hairs.

In most processes involving wool, felting is more of a nuisance than a help. It contributes to problems as widely separated (in the wool-processing pipeline) as fibre entanglement in the scouring of loose wool to the shrinkage of wool garments in laundering. In only two areas, milling and felt-making, is this property of wool used to advantage.

The felting properties of wool have been studied since at least the late nineteenth century and were extensively reviewed in the late 1970s by Makinson [82]. In the ‘ratchet’ theory of felting, when a mass of wool fibres is repeatedly compressed and released, the fibres tend to migrate preferentially in their root direction. The overlapping scales (cuticle cells) on the surface of the fibre inhibit the return of the fibre so that entanglement increases. The rate at which the fibres entangle or felt has been related to the difference in the frictional coefficients in the with-scale and against-scale directions – the so-called directional frictional effect (DFE), which is usually measured on fibres immersed in water. Wool must be wet (or at least at a high moisture content) to felt at a significant rate.

The physical properties, mechanical properties, stress-relaxation behaviour, length, fineness, bilateral structure of the fibre as well as the form of the fibre mass (loose wool, top, yarn or fabric) are all important in felting. Different wools felt at different rates and to different extents even in structures of similar form. The relationship between the surface and bulk properties of the fibre and its felting behaviour is highly complex.

There are three essential elements required to induce felting of wool fibres: moisture, heat and mechanical action. In pre-industrial times, wool fabrics were fulled ‘manually’ by treading or beating the warm, wet fabric, usually in a vessel containing soap or some other aid to the milling process. The development of milling stocks that incorporate mechanically-driven hammers to pound the fabric was an obvious first step in the introduction of machines. Although used into the twentieth century, stocks were eventually replaced by the rotary milling machine, except for some knitted fabrics.

Wool fabrics also felt in other situations such as laundering and piece dyeing if the mechanical action in the machine is too severe. Rotary combined scouring–milling machines (for example, Dytex) are widely used in the UK and parts of the Far East to mill garments or preformed garment pieces. These machines induce felting by subjecting the wool to random mechanical action. Knitwear can also be milled in conventional dry-cleaning machinery using solvent (usually perchlorethylene) that contains, in an emulsified form [127], a relatively small amount of water (typically 15–20% on weight of wool). Dry-cleaning machines are not used for fabric processing except in unusual circumstances [126].

12.3.2 Milling machinery

The rotary milling machine, which was invented in the early nineteenth century, felts the fabric in rope form. Although modern machinery incorporates many improvements to control and facilitate the milling action, the principle used has not changed (Figure 12.11). The essential parts of a rotary milling machine are the rollers, the throat and the milling box (or trap).

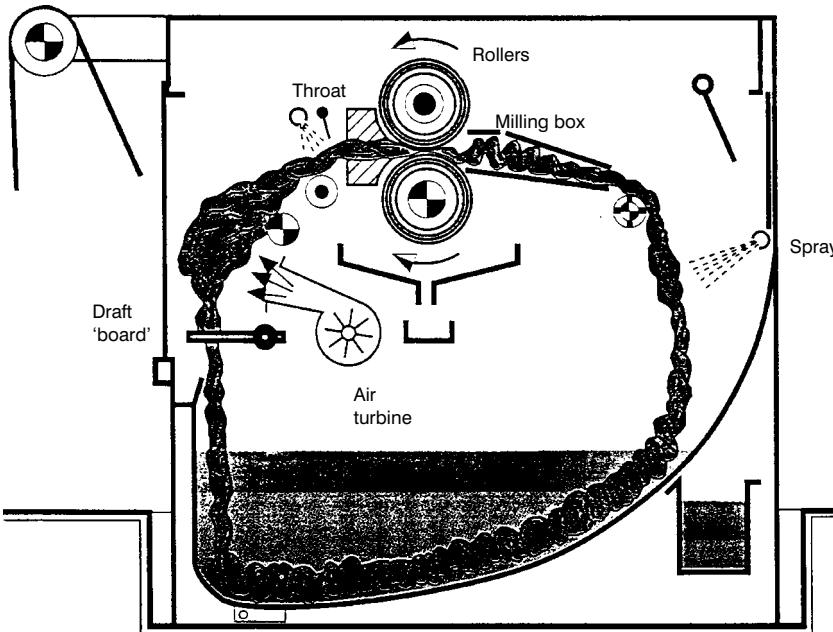


Figure 12.11 Schematic diagram of a rotary milling machine (example is M-Tec CMS 200)

The rollers are traditionally made from wood and grip the fabric to pull it from the floor of the vessel, through the throat, then force it into the milling box at speeds up to 200 m min^{-1} . While effective over a wide range of fabric types, wooden rollers are expensive and require considerable maintenance. In recent years, several alternative roller designs have been developed. Synthetic rollers have replaced wooden rollers in some applications but are not as suitable for light-weight worsted fabrics because they are more prone to cause slipping and to tear holes. In the Folatrice BP4 (Biancalani) milling machine, the rollers are fabricated from steel but have wooden inserts to obtain the required grip. In the Serracant Feltra and CIMI Folatex [84] milling machines, slotted synthetic rollers are used to obtain better grip on light-weight fabrics. At ITMA '95, the Famit Futura was shown with a three-roller set to allow the fabric to be driven more rapidly without slipping.

The throat, which is normally made from wood, steel or ceramic material, is adjustable to squeeze the fabric rope. This action combined with the squeezing action of the roller imparts the shrinkage in the weft direction.

The milling box or trap originally consisted of a wooden trough onto which was placed a lid that inhibited the movement of the fabric and imparted the lengthwise compression required for warp-ways shrinkage. Several variations of the traditional milling box have been developed to give additional control over the milling process. One simple variation is the lining of the box with surfaces that more closely control movement of the cloth. Another is the incorporation of a drive roller at the exit of the box to control the fabric movement and thus modify the rate of milling (Figure 12.12). This is found in the M-Tec Folatex and the Serracant Feltra. The use of rollers and belts [85] rather than the classic wooden trough (Figure 12.13) to control the movement of the fabric has also been incorporated by some machinery makers.

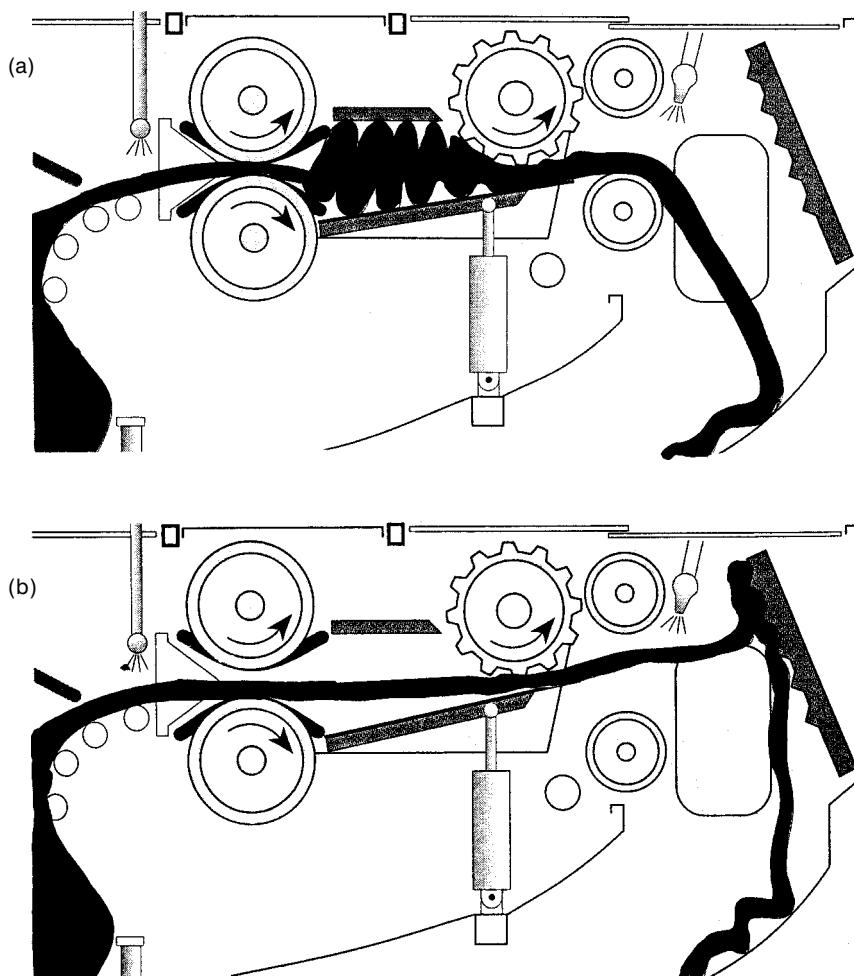


Figure 12.12 Rollers used to control action of the milling box (CIMI Folatex), (a) conventional milling action (b) high-speed scouring action

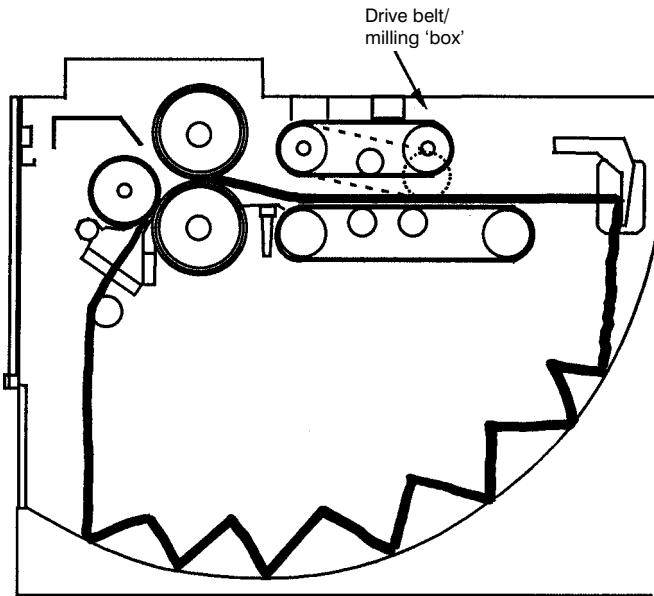


Figure 12.13 Rollers and belt drives used to replace milling box (derived from [85])

Regulation of the milling process to give the appropriate balance of warp and weft shrinkage is achieved by correct adjustment of roller pressures, throat, milling box loading and fabric speed. Width milling shrinkage is increased by closing the throat and increasing the weight on the rollers; warp milling shrinkage is increased by increasing the load on the lid of the milling box.

Wool fabrics are traditionally milled containing around 100% moisture at temperatures around 40–45 °C [83]. Normally this heat is generated by friction between the cloth and the components of the milling machine but auxiliary heating can be used. Milling aids, usually surface active agents, are used to lubricate the fibres and facilitate the felting action.

One of the major problems in milling is the formation of crack or rig marks in the fabric. Folds form in the rope and the additional mechanical action on the edge of the fold increases the rate of felting in this small area. The folds, observed as lines running down or at a slight angle to the warp when the fabric is opened out, are fixed by the felting action and are difficult or impossible to remove in later processes. The use of air or air/water turbines to open out the rope and encourage the fabric to re-fold in a different manner is an important development in modern machines (Figure 12.11). These turbines are normally positioned to open the fabric prior to it entering the throat – as in, for example, the Turbomat (MAT) and the Serie CMS 2000 (M-Tec) – or after the milling box – for example, in the Feltra (Serracant) and Kombinova (M-Tec).

At ITMA '99, two new concepts in fabric transport were shown to overcome the formation of rope marks. The ROTOrMAT from MAT, rather than using air to transport the fabric, sucks the fabric onto a high-speed roller, which then propels the fabric at speeds up to 1000 m min^{-1} onto a plate. In the new Blow Mill from Holmes-Heaton, combined air/water jets are used to transport the fabric with a stuffer bar to force the fabric through the trap.

In many finishing rooms it is normal to mill after scouring and rinse after milling. Normally it

is not cost-effective to do these operations in separate machines and, for this reason, few machines are produced simply to mill the fabric. The simplest combined machines are the scouring–milling machines in which, by changing the throat setting and lowering or raising the lid on the milling box, the machine is converted from scouring to milling and back. Flexibility is an increasingly important part of machine design and recently-developed scouring–milling machines – such as Indra (Biancalani), Twin 400 (Zonco) and Flexifola (CIMI) – offer independent programming of the individual heads that make up the machine [86]. Like the Airo, Multifinish, Combisoft and related machines, the manufacturers of the ROTOrMAT claim it can be used for scouring, softening and bulking, fibrillation of lyocells, treatments with enzymes or caustic and for relaxed drying, using an attached heat exchanger for the air, to modify fabric handle.

12.3.3 Woollen milling

A range of additives/lubricants is used to assist the milling of woollen fabrics. These are usually surface-active agents that reduce fibre–fibre friction in wet wool. Wool felts least rapidly around neutral pH so that woollen fabrics are usually milled under alkaline (pH 9–10) or acid (pH 2–3) conditions. It was common practice for woollen fabrics milled in the greige, to merely add alkali (sodium carbonate) to the liquor. The basic conditions cause saponification of the spinning oils (oleine) remaining on the fibres to provide the required lubricant. A mixture of soap and soda or, alternatively, a mixture of a synthetic detergent with soda or ammonia to control the pH, is used for scoured goods.

Acid milling is sometimes used for cloths that are difficult to mill (crossbred wools) or that require extensive milling (heavy overcoats). The lack of stability of soap in acid solution has been overcome by the development of acid-stable milling lubricants. The other advantages of acid milling are that it is less expensive, there is thought to be less damage to the fibres and the wet stability of dyestuffs need not be as high as for cloths milled under alkaline conditions, making it suitable for high-contrast, yarn-dyed fabrics. The handle of cloth milled in acid is claimed to be harsher but this opinion is not universally held and there is little objective information to confirm this effect or determine its origins.

12.3.4 Worsted milling

With the exception of flannel cloths, few worsted fabrics are extensively milled. However, many are lightly milled to soften the handle, consolidate the fabric and remove reed marks. This process is often called development and is used to improve the handle of blend as well as pure-wool worsted fabrics. In addition to the use of a milling machine, this effect can be achieved in conventional scouring machines, although at a much slower rate because of the absence of the throat and milling box and because their speed is limited to about 200 m min^{-1} .

As stated earlier, conventional milling machines cannot always be used to develop light-weight worsted fabrics, such as those with weights suitable for ‘Cool Wool’ labelling. On such fabric, rollers can slip and damage, or form distortions in, the cloth. This has led to the

development of high-speed scouring machines that impart a finish similar to that of light milling. Examples include the Velotex [125] (CIMI), Flexirapid 600 (Zonco), Lavarapid (Hemmer), Supervelox (MAT) [87] and Combisoft (MAT) machines. In these machines, the fabric is ‘thrown’ by drive belts (rather than conventional rollers), pneumatically or by large drums onto a corrugated baffle plate (Figure 12.14). The inertia of the fabric (moving at up to 800 m min⁻¹) provides the mechanical action required to ‘burst the yarns’ and soften the handle. Control is achieved by varying the speed of the belts driving the fabric. Although high-speed scouring induces little shrinkage, fabric stiffness is reduced (softer handle) and some surface fibre is produced (normally removed in later processes). The extent to which felting and mechanically-assisted relaxation processes contribute to the change in handle during fabric development in high-speed scouring is unresolved since similar effects are observed even on wool-poor polyester blend fabrics where felting rates are normally low. Like the milling machines, some of these high-speed scouring machines incorporated turbines to open the fabric and inhibit the formation of running marks. The incorporation of heat exchangers in the turbines used to disturb fabric folds also allows the user to dry the fabric in the machine to maximise the softening effect and produce a wide range of finishes.

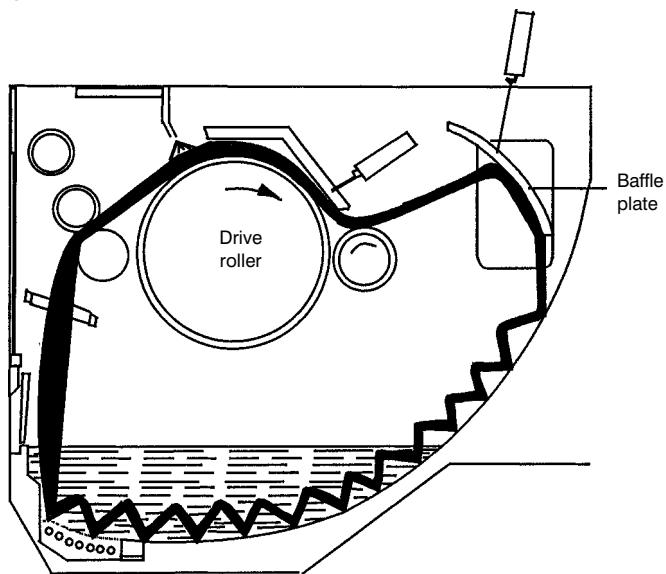


Figure 12.14 Schematic diagram of a high-speed scour (CIMI Velotex)

In keeping with the need for flexibility in the wool finishing industry, machines are available that will perform simple and high-speed scouring as well as light and heavy milling by simple changes of roller, belt and milling box configurations – for example, Turbomat 4 seasons (MAT) [88].

As discussed earlier, all wet operations in which the fabric is processed in rope form are prone to impart running marks. Although open-width processing avoids this problem, the lack of fabric

development in open-width scouring of wool fabrics is a source of major concern to machinery makers. One open-width machine – Vibrocompact (MAT) – uses special vanes formed in racks to hydraulically and mechanically agitate the fabric. This machine is claimed to impart an effect similar to high-speed rope scouring [89]. The same company also exhibited a prototype machine at ITMA '91 (Jolly Joker) for high-speed scouring of fabric in rope or open-width. This machine uses a combination of mechanical and pneumatic techniques to propel the fabric and also incorporates heat exchangers to allow simultaneous drying and softening of the fabric. However, to date there is little objective information on the effectiveness of this machine in an industrial environment.

12.3.5 Evaluating the effects of milling

At present, most finishers use only the changes in fabric dimensions and subjective handle to monitor the milling process. In woollen fabrics, large dimensional changes are required, whereas in worsted fabric the changes in dimensions are often small and provide a relatively insensitive indicator of the required changes in handle.

In order to objectively evaluate or optimise the milling process, the finisher needs to know which measurable properties best reflect the desired outcome and which are related to the unwanted side effects. The changes in handle produced in milling can be assessed from the changes in the low-stress mechanical and physical properties [90,91,77] of the fabric (Figure 12.15). The 'development' or softening action can be monitored using properties of the fabric such as thickness or specific volume.

Low-stress mechanical properties such as shear rigidity or shear hysteresis can also be used to monitor the stiffening of the fabric caused by milling. Likewise, development of surface fibre

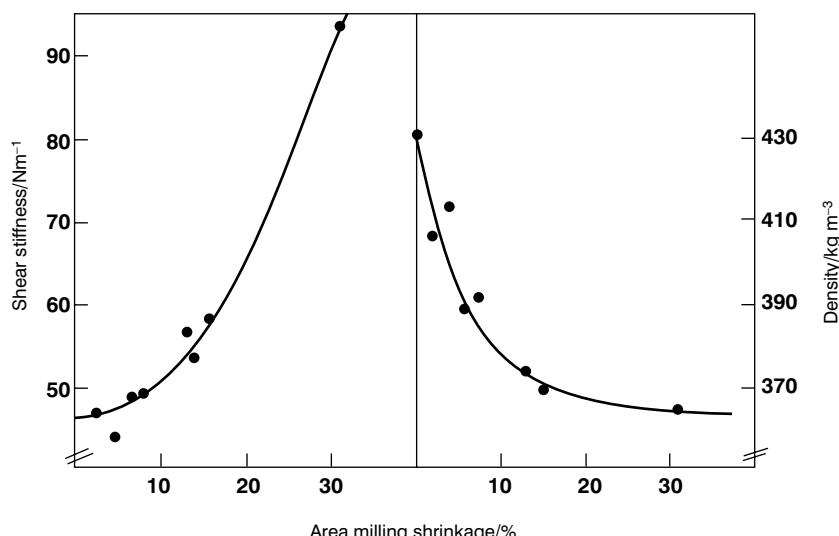


Figure 12.15 Effect of milling on fabric properties (derived from [90])

and subjective fullness can most easily be followed by measuring fabric thickness or, less satisfactorily, the geometry of the fabric surface (using the KES-F4B). Air permeability and light transmission are also useful techniques for monitoring the changes in surface and structure of the fabric caused by milling. The strength (tensile or tear) of the fabric may be measured directly using suitable dynamometers, which are widely available.

12.4 CROPPING/SHEARING

Cropping or shearing is another of the wool finishing operations, in which the basic principle of the machine, developed in the eighteenth century, has not changed in spite of the many design improvements that have been, and continue to be made (Figure 12.16). Cropping machines are designed to cut and remove fibres projecting further than a specific distance from the surface of the fabric. Cropping forms an even and flat nap on pile fabrics, such as velours, whereas, on clear-finished worsted fabrics, cropping removes the surface fibres to leave a clean finish in which the weave is not obscured. A clean surface is also required to inhibit the formation of pills during use, especially on some wool/polyester blend fabrics.

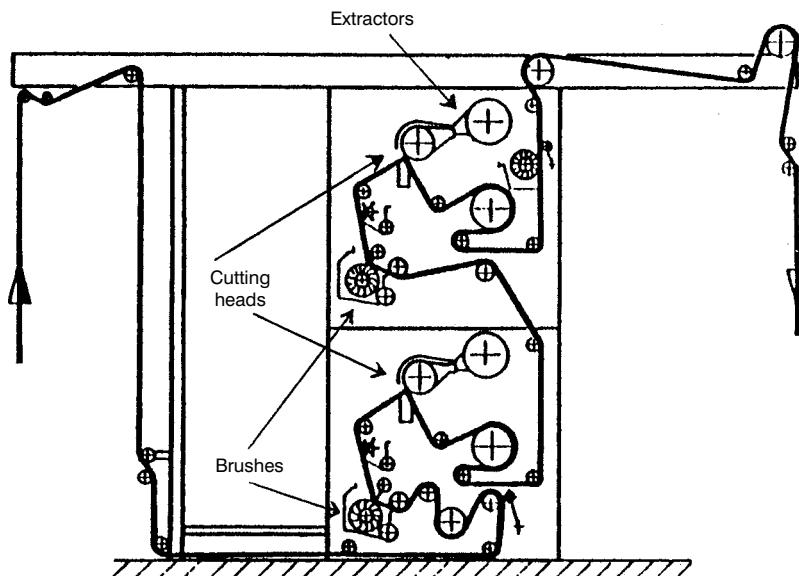


Figure 12.16 Schematic diagram of cropping machine (example is a Lafer CMS series cropper)

Cutting in a cropping machine occurs between a fixed blade, called the ledger blade, and a series of blades that are helically wound onto the surface of a rotating cylinder. The angle formed by the helix and the axis of the cylinder is called the shearing angle. The cutting action is not dissimilar to that of simple hand shears, but occurs at a rate (cuts cm^{-1}) that depends on the number of blades on the cylinder, the speed of the cylinder and the speed of the fabric. The

cylinder blades on modern machinery can be varied to meet the particular requirements of the user. Naturally the effectiveness of cropping machines depends greatly on the rate of cutting and on the sharpness of the cutting blades. A number of auxiliary machines have been developed for grinding and sharpening of blades.

The cutting bed is the third important component of a cropping machine. The bed supports the fabric at the point of cutting so that the fibres are presented properly to the blades. Several types of bed have been developed: solid, hollow, spiral spring, plate, roller, rubber tube and cushion, although the first two (Figure 12.17) are the most commonly used.

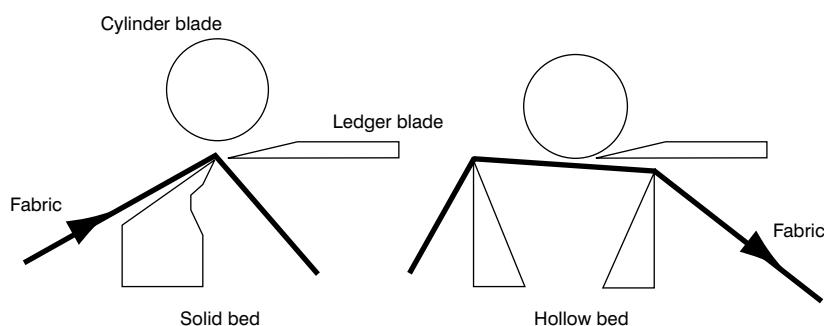


Figure 12.17 Geometry of cropping beds

The geometry of solid bed machines can vary. The cutting bed can present the fabric so that the fibres stand up and are cut. Such beds are used for close shearing and consequently any knots on the back of the cloth must be removed before the fabric is cropped. The 'shearing height' is the distance set between the bed and ledger blade. Hollow beds support the fabric at two points and the cutting point is between these points. Obviously knots present little problem in this type of bed although the cropping action is affected by the tension on the fabric. Again the geometry of hollow beds and, in particular, the distance between the support points can be varied.

Selvages, because they vary in thickness and flatness, can cause problems in cropping, especially when clear-finished (mohair, wool/polyester blend) fabrics are being processed. Formerly, to avoid damaging the selvage on clear-finished fabric, considerable skill was required and compromises had to be made on the closeness of the cropping action. In order to overcome this problem, most modern machines incorporate piano key beds (Figure 12.18), formed from small (4 mm) segments that can be lowered independently. By incorporating edge detectors on the machine, the sections of the bed under the selvage can be lowered thereby avoiding damage or any contact between the blades and any high or variable edges on the fabric. At ITMA '95 a machine was exhibited that claimed to achieve pattern cutting by use of independent movement of individual keys under microprocessor control.

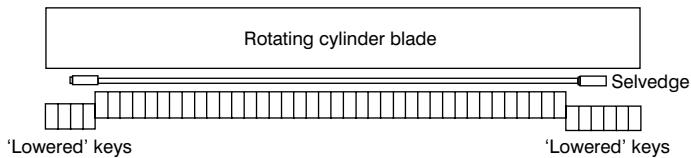


Figure 12.18 Action of piano key bed

The brushes and beaters are also important components of modern cropping machines. They have a number of roles: to clean loose material (fibres, threads and so on) from the surface of the fabric and to lift the fibres and pile so that they are properly presented to the cutting head. The brushes and beaters operate at the back and front of the fabric at each cutting head before and/or after the cut is made. Instead of the usual bristle brush normally used on cropping machines, special raising brushes can be used to lift the pile on velour and similar fabrics.

Suction cleaners are used to remove cut fibres and reduce dust levels in the mill. In addition to their use at the cutting head, suction cleaners are also used with the brushes to remove any loose material taken off the fabric.

Most modern cropping machines are built in modular form, allowing a range of cropping configurations (for example, 2 × face and 1 × back) to be adopted [92]. Machines are normally customised from these modules specifically for the particular requirements of individual customers. In the Lafer machine [92], each module comprises a cropping point, a brush, a beating cylinder and a drag cylinder. The drag cylinder, placed immediately after the shearing head, allows control over cloth tension in the cutting zone.

Modern cropping machines now include a range of mechanical and electronic devices to increase their productivity. Seam detection (mechanical and optical) and automated setting and adjustment of shearing height are important requirements of continuous operation and have become essential components of modern machinery. The Justomat system (Sucker and Muller) automatically monitors fabric thickness and corrects shearing height to allow for seams and new qualities and to ensure reproducible operation [93,94]. After the shear height has been set, a feeler head scans the fabric and continuously adjusts the shear height in steps of 0.1 mm. Two feeler heads, working in conjunction, ensure that the bed is pivoted out of the way to allow any seam to pass without stopping the machine. The use of two detectors also eliminates problems associated with seam skewness. After the seam has been detected, the feeler head scans the new cloth and, if the thickness deviates from that of the former piece (for example, processing a different cloth type), the shearing gap is re-adjusted to the new position while the bed is out of position allowing the seam to pass. The makers claim that differences up to 6 mm can be accommodated.

Metal detectors to avoid damage to the cutting edges and length meters complete the requirements for automated operation.

12.5 FABRIC CONDITIONING

Fabric conditioning is an extremely important process in wool finishing but one that was neglected until recent years. This neglect occurred in spite of the widely-held belief that the effectiveness of finishing operations and the quality of the finished product is greatly improved if the fabric is allowed to 'condition' for one or two days between operations [1,102]. This practice is no longer viable and, in modern mills, it is not uncommon for the fabric to be wet finished, dry finished, inspected and despatched on consecutive days. The need to condition wool has, in many cases, been overlooked in the need for rapid production.

12.5.1 Principles of conditioning

Finishers normally over-dry fabrics to ensure there are no wet patches on the fabric resulting from uneven hydroextraction. Consequently, after stenter drying, the moisture content of fabrics may often be as low as 5% [96] and, in some cases, even lower. For optimum dry finishing of wool fabrics, moisture contents in excess of 10% [11,96] and preferably nearer 15% are required. Although wool will slowly re-absorb moisture from the surrounding air, the moisture content of cutted stacks of stenter-dried wool fabric can remain low for days and, in some instances, such as at the centre of rolls, re-equilibration can require weeks.

Conditioning generally refers to processes that add moisture to dry wool fabrics, thereby increasing the regain or moisture content of the fibres. This can be done in two ways:

- (1) by promoting absorption by the wool fibres of water from the environment;
- (2) by adding water directly to the fabric.

The role of the moisture content of the fibre on pressing and setting was described in the earlier section and will again be described in the section on relaxation and sponging. However, in addition to its effect on setting and relaxation processes in the wool, moisture reduces static in fabrics making them easier to handle during dry finishing.

In less time-sensitive eras, it was common practice to increase the moisture content of wool by 'conditioning' the fabric in cool, humid rooms between drying and dry finishing operations. The fabric absorbed water slowly from the air to reach a moisture content that was more suitable for subsequent processing. When fabrics were conditioned in this way, the relaxation and ageing [26] processes that occurred in the fibre may also have contributed to the improved performance of the fabric.

12.5.2 Conditioning machinery

There are several machines used by the finishing industry to increase the moisture content of wool fabrics. These fall into three broad categories: dewing, damping and steaming. The terminology used by industry to describe these machines is not always consistent. Some writers apply the term 'dewing' to all forms of fabric moisturising and conditioning [102].

Dewing machines

Dewing machines increase the moisture content of wool fibres by passing cold and/or humidified air over and through the fabric. Cold air lowers the temperature of the fibres, which then absorb moisture from the ambient atmosphere as they warm to room temperature. Humidified air establishes a new equilibrium between water in the wool and that in the air, which favours an increase in the moisture content of the wool fibres.

The 'Fridg' system of Sellers passed cloth through a chamber, the air in which was cooled by refrigeration. Hemmer also developed a refrigerated cooling and conditioning unit that cooled the fabric to 12–15 °C and was claimed to produce a 2–4% increase in moisture content [97,101]. The Unipolar machine of Kettling and Braun [98] and the Juki machine use a liquid nitrogen spray to cool the fabric [99,100]. In these machines the fabric is cooled to temperatures as low as –45 °C so that water from the surrounding atmosphere can condense on the fabric. In the Sjostrom machine [128], the dry wool fabric is passed several times through a humid environment created by wet felt screens. However, this approach was not very effective unless the residence time of the fabric was high. In 1970, Bissit described [95] a prototype machine under development by WIRA in which the cloth was 'passed around a perforated drum and air at an elevated temperature and a high humidity was forced through the fabric, thereby increasing its regain quite rapidly'. At ITMA '99, three machines based on this general principle were exhibited – Clima (Sperotto Rimar), CU/2 (TMT Manenti) and CZ Plus (Biella Shrunk). All of the machines use a water spray to saturate air, which is forced through the fabric and recirculated. The airflow in the Clima can be controlled over a range of temperatures and humidities, offering flexibility in the conditioning process. The relative merits of the machines have yet to be ascertained, but the positive effect of their use in wool finishing has been clearly documented [134]. Holmes-Heaton (UK) also manufactured a machine that conditions the fabric using partially recirculated air that is both cooled and humidified. The unit was used by a British worsted finisher in tandem with a rotary press to replace moisture lost in the pressing process. In an alternative design (Monforts), a mist of water is sprayed into air, which is then sucked through the fabric [102]. The mist is designed to cool and humidify the air but, it seems more likely that this machine would, in practice, combine the actions of both dewing and damping (see below).

Dewing machines are ideal for use after machines such as rotary presses, which dry the fabric, but which impart a surface finish to the fabric that is only held by cohesive set. The dewing operation is designed to replace, fully or in part, the water removed from the fabric by high-temperature processes, such as pressing, but under conditions where the temperature of the fibres does not exceed the glass transition. In this way the loss of cohesively-set finish is slowed (but not avoided).

The rate of heat and mass transfer from the humid air to the dry fabric is the rate-determining step in this form of conditioning. For machines that act by passing humidified air through the fabric, adsorption of water vapour by the dry fibres depends on the temperature of the air and the fabric as well as the humidity and velocity of the air passing through the fabric.

For machines that cool the fabric using refrigerated air or liquid nitrogen, the rate of adsorption of the moisture depends on the conditions in which the cooled fabric is exposed to moisture-containing air. Without suitable design, this latter type of machine can be relatively inefficient.

Damping machines

Damping machines increase the moisture content of wool by spraying fine droplets of water onto the surface of the fabric [102]. This can be done using a spray and deflector plate or a rotating brush that dips into an open trough containing water. This simple technology (Figure 12.19), which has been used since the middle of the nineteenth century, allows metering of water onto the fabric (by controlling spray pressure, brush and fabric speed) and can be used to add large amounts of moisture rapidly to the fabric. Unfortunately, the technique has a number of disadvantages. First, wool fabrics are normally difficult to wet out and some time is required to allow droplets to penetrate the fibres and for the moisture to redistribute itself evenly within the fabric. Also, in the initial stages of absorption, localised wetting of the surface fibres can remove any temporary finish imparted in earlier operations. Finally, the heat generated by the absorption process will cause a rise in the temperature of the fabric reducing the effectiveness of the conditioning operation. However, the amount of water added in damping machines can be considerably more than that applied by dewing. At ITMA '95, Biella Shrunk exhibited a machine (Igrofast) using a high-speed brush to 'flick' water onto a passing fabric, which is claimed to overcome the problem associated with the rate of wetting of the fibres. The machine is claimed to add up to 30 l min^{-1} water.

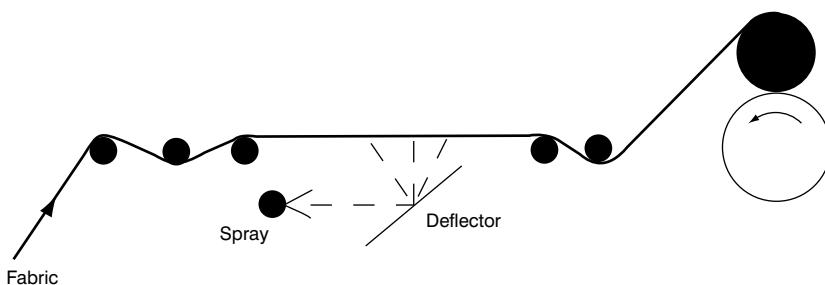


Figure 12.19 Schematic diagram of traditional damping machine

Spray units such as those manufactured by Weko (spinning disk) and Mutschink (Muwa Spray) developed to allow accurate metering of liquids onto fabric, have also been adopted for fabric conditioning as well as low liquor applications [103]. The Contipress and Superfinish decatising machine (M-Tec) both incorporate Weko spray units immediately prior to the pressing zones [63]. The added water has two roles: to increase the moisture content of the fibres and to provide the source of the steam required for the decatising process.

The Hygrocot (M-Tec) exhibited at ITMA '91 used a different principle to increase the moisture content of the fabric. In this machine the fabric is steamed, then dipped briefly into heated water and then dried by drawing air through the fabric. A permeable blanket is used to

hold the fabric onto a perforated drum during these steps. M-Tec claimed that moisture contents in the range 18–35% could be achieved compared to less than 12% added by conventional humidifying methods.

Other approaches to fabric conditioning might include the use of minimum application techniques that are used to apply finishes to fabrics at very low add-on [4]. Sprays (Figure 12.20), kiss transfer and engraved rollers as well as foam and printing systems can be modified to apply water in very low amounts required for conditioning.

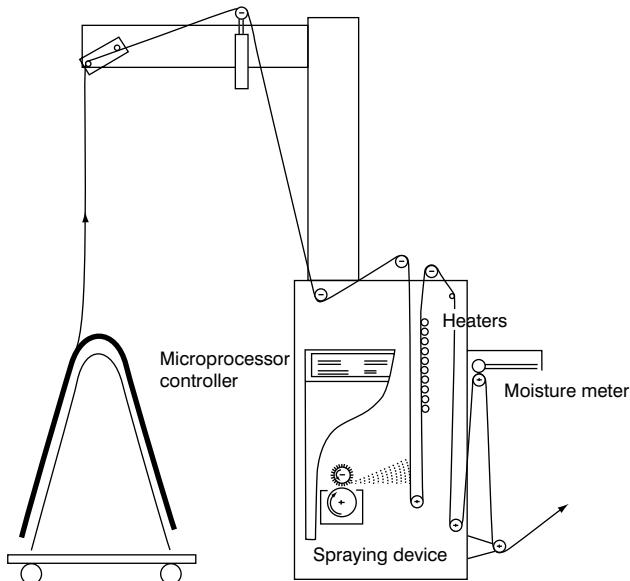


Figure 12.20 Schematic diagram of Igrofast (Biella Shrunk) conditioning machine

Steaming machines

Continuous steaming machines that are used to relax fabric (Section 12.8) also add moisture to dry fibres, although they are rather less efficient than the other types of machine. Typically a steam conditioning machine will increase the regain of a fabric by 4–5% but it is less effective if the fabric is already warm [96]. The rate of moisture uptake is initially rapid as the steam condenses on the cooler fabric but is slow once the fabric has reached the temperature of the steam. Some of the added moisture is lost during the cooling process. The increase in moisture depends on the initial temperature of the fabric as well as well as the temperature and humidity of the steam. A steaming zone on the front of the M-Tec Contipress is claimed to both preheat the fabric as well as increase the moisture content, which, in turn, improves the pressing action. If the fabric is cooled using refrigerated air or liquid nitrogen, the moisture adsorbed in steam can be increased. Sequential steaming and cooling of fabric will also increase the moisture content of wool more than a single steaming operation but this principle is not used by industry.

The major problem with this approach is that, because steam raises the fibre above its glass

transition point, it removes any temporary finish (for example, from pressing) from the fabric. However, when used as part of a sponging line, which is designed to relax the fabric, steam can add moisture so that any subsequent decatising operation is more effective.

12.5.3 The effectiveness of fabric conditioning

Lack of equipment suitable for on-line measurement of the moisture content of wool fabric has been a considerable problem in wool finishing. Many meters were not considered very useful for checking fabric moisture content because the reading depended on fibre type as well as fabric construction and they were not accurate below 10% moisture. However, in recent years, more reliable meters have been developed and, although used mainly to monitor the drying process, have application in fabric conditioning. Meters are of two types:

- (1) contact types measure some aspect of the electrical properties of fabric to determine moisture content – for example, Pleva [104], Streat;
- (2) non-contact types use capacitance or infrared reflectance for the same purpose – for example, Mahlo.

Many conditioning machines currently used by industry are quite old and not fitted with moisture meters. The relatively modern machines, such as Igrofast (Biella Shrunk), use meters (for example, Pleva) to monitor the moisture content of the fabric. As originally designed, the M-Tec Hydrocor did not measure moisture content directly but used feedback from the 'Hydromat' incorporated on the pressing or decatising machines used subsequently. The widespread availability of modern meters means that if the regain of a wool fabric is too low for effective processing, it should be easily detected and corrected.

12.6 RAISING/TEASELLING

Raising and teaselling (sometimes called gigging and napping) are widely used to modify the surface of wool and blend fabrics. The general aim of these processes is to develop a fibrous or pile surface (sometimes called a nap) on the fabric by drawing fibres from the yarns to the surface of the cloth. This surface can be required to obtain the visual and tactile (full and soft) characteristics of meltons and velours, to conceal the weave or to impart a smooth, planar surface to those fabric where it is required in later use (for example, billiard cloth).

12.6.1 Principles of raising

Over the past 20 years, raising has received comparatively little scientific attention compared to the research effort that has been spent on other areas of finishing such as setting. Although prior to this time some important studies were undertaken, some aspects of this operation are still not well understood [105].

Raising is achieved by causing a sharp needle-like object to penetrate a small way into the fabric and then to be withdrawn, pulling any fibres with which it has entangled to the surface.

The needle can be the spike on card wire or on a teasel, which is the dried head of a special thistle grown in Mediterranean climates. The angle of entry and exit of the wire from the fabric is designed so that the point can entangle with fibres in the yarns and draw them to the fabric surface as the point is withdrawn.

Although now not common, teasel gigs were prized for their gentle action. Fibre damage and breakage are common side effects of the raising operation and are normally least severe when teasel gigs are used to raise wet fabric. Natural teasels are fitted on special bars and the bars inserted onto a rotating drum. The fabric is pulled over the drum in a path that allows one or more contacts between the teasels and the fabric (Figure 12.21). As the fabric contacts the teasel, the tip penetrates the fabric and as the cylinder moves on, the tip is withdrawn from the fabric occasionally drawing wool fibres to the surface. Teasel gigging is normally a slow, batch operation in which the fabric passes through the machine several times.

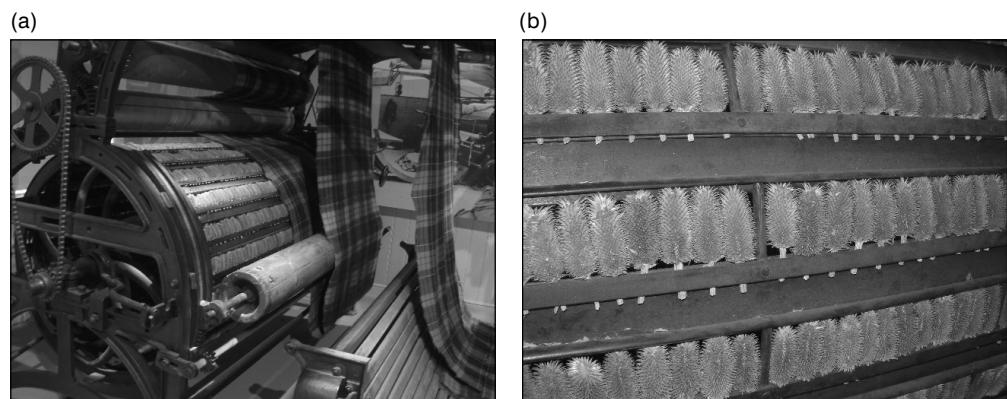


Figure 12.21 Photographs of (a) teasel raising machine and (b) mounted teasels. Machine exhibited in Geelong Wool Museum

Synthetic and metallic teasels have been developed to overcome the problems associated with the brittleness and supply problems of the natural teasels. Modern teaselling gigs (for example, the MS series of Comet) can be fitted with either metal or natural teasels. The usual practice is to teasel with a gentle action in the initial stages of raising to avoid fibre breakage and then to increase the action with successive passes. Teasel raising is suitable for the production of long, dense piles on the surface of a fabric.

The ‘planetary-action’ raising machine was invented in the mid 1800s and the principles have remained essentially unchanged. In this machine, rollers covered in card wire are mounted on a cylinder and the fabric is drawn over the machine in a manner shown in Figure 12.22. The rollers and drum rotate in opposite directions so that the surface speed of the rollers is much less than that of the drum. The fabric normally moves in the same direction as the rotating drum although in modern machines fabric movement can be in the same or opposite direction to that of the roller drum [106].

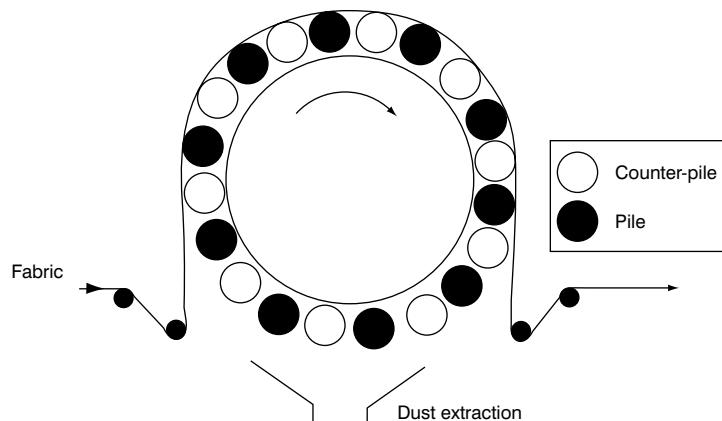


Figure 12.22 Schematic of double-action raising machine

The card wires are bent so that at the point of contact they form an angle of 45° with the surface of the fabric. Those rollers in which the card wires point in the direction of the movement of the fabric are called 'pile rollers' [107]. Conversely, those rollers in which the card wires point against the direction of the movement of the fabric are called 'counter-pile rollers' (Figure 12.23).

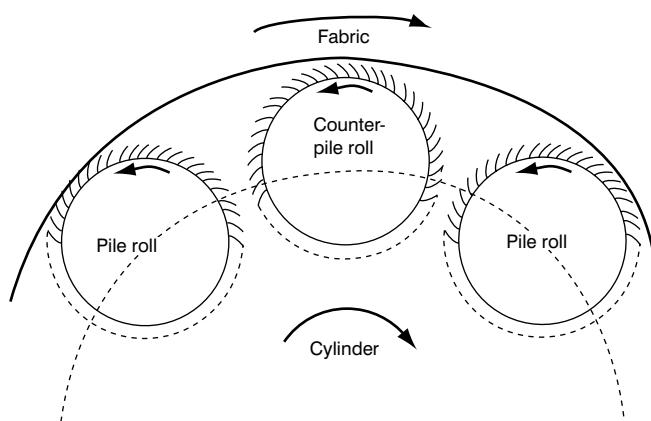


Figure 12.23 Pile and counter-pile rollers

As the cloth runs through the machine, the card wires on the pile rollers are pushed into the cloth by the forward motion of the cylinder to a degree determined by the relative speeds of the drum, rollers and fabric. The slower the surface speed of the rollers, the greater the speed differential between card wires and fabric and thus the more severe the raising action. The wire points on counter-pile rollers face the oncoming fabric and their action is increased by increasing

the surface speed of the rollers. The condition of zero raising occurs when the relative speeds of the cloth, drum and rollers are such that the rollers merely turn on the cloth and the points of the wire do not act on the running cloth [108].

In both cases the wires have two functions: to open the yarns or felted fabrics, and to lift clear fibre ends without breaking other fibres. This may be a multistage process with the first wires penetrating and opening the yarns on the fabric surface and later wires lifting the fibres, possibly progressively. There are many more penetrations of the fabric by the wires than fibres drawn to the surface.

Several papers have been published on the physics and mechanics of raising [109–112]. Heinrich analysed the raising action in terms of the relative velocity of the fabric and the tips of the wire clothing on the working rollers. In this work the effect of roller, drum and fabric were analysed. Where the drum and fabric move in the same direction:

$$V_r = d_T \pi n_T - d_R \pi n_R - V_w \quad (12.5)$$

where V_r = relative surface speed of fabric and wire tips

d_T = diameter of the drum

d_R = diameter of the rollers

n_T = rotational rate of drum

n_R = rotational rate of rollers

V_w = surface speed of the fabric

The effect of small changes in the diameter of the worker rollers caused by grinding of the wire was used to illustrate the sensitivity of the raising action to small changes in processing conditions.

Fabric structure and moisture content are important in raising. Generally, wet wool is more easily raised than dry wool, presumably because the stiffness of the fibre (in bending and extension) is reduced. Wet raising produces a silky laid pile. Wool fabrics are raised more easily when acid or alkaline rather than neutral, when dyed with acid rather than chrome dyes and when lubricants are used [113]. The lubricants, originally anionic surfactants, facilitate the movement required when the fibre is drawn to the surface of the fabric. In recent years newer products have been developed to facilitate the raising process, improve machine productivity and reduce fabric damage. Silicones have been shown to be highly effective assistants in the raising process [4]. On the other hand, silica dispersions, which inhibit relative fibre movement, retard raising [114].

Raising is often not achieved in a single process and rarely in a single pass through a machine. If the pile is produced too quickly it can be uneven and there can be excessive strength losses in the fabric. There is considerable skill associated with raising a fabric at the optimum rate and fabrics can be raised more than once during the entire finishing route.

12.6.2 Raising machinery and practice

Single-action raising machines utilise only pile rollers whereas double-action machines normally

have both pile and counter-pile rollers mounted alternately. By manipulating the speeds of the two types of rollers, the raising action can be closely controlled and very different surface effects created by the use of single- and double-action machines. Single-action machines produce a drawn pile that is layed and fleecy whereas, on a double-action machine, the majority of the raising is normally achieved by the counter-pile rollers and the pile is denser and tends to stand erect. Teasel gigs, on the other hand, impart a brushing and polishing action.

From the original concepts, a number of major developments in the design of raising machines have been made. These include stepless independent control of the drum and roller speeds, the use of more robust wire teasels and card clothing and the manufacture of multi-drum machines that combine teasel and wire raising (such as the Lafer GRC-90 Combi). The Comet Gedeone Mini-T combines raising cylinders and metallic teasels on the same drum. The Multisystem 6728 (Gemtex) has three rollers in a star configuration allowing the fabric to be worked with one or two pile or counter-pile rollers at each of 12 working points.

Modern machines have greater flexibility and productivity and produce fabrics with greater uniformity. Most incorporate automated zero raising point determination [115], sophisticated fabric tension controls, fabric turning and reversing mechanisms and continuous wire cleaning. Some machines also have a facility for re-grinding of the wire without removing the rollers. All machines use menu-driven microprocessor control systems allowing simple control of raising and teaselling parameters. Both Comet and Gessner offer machines that can be connected to a central computer; the Gessner can be connected, via modem, for on-line diagnosis of operational problems by technicians half a world away.

Single or multi-roller machines can be used alone or in tandem with other machines, or with other finishing processes such as cropping or setting. There is also a wide range of wire types including needle point, mushroom and hammerhead types, each designed to produce a specific effect.

However, even with modern machinery, raising and teaselling are the least well understood finishing operations and have received least academic study. Techniques for drawing out piles, for 'running in' roller clothing, and for predicting or optimising the action of different types of roller clothing remain more of an art than a science. Much of the information used by finishers to optimise raising and to achieve specific effects remains empirical or anecdotal.

12.6.3 Evaluation of raising/teaselling

Changes in thickness, light transmission, surface geometry and air permeability can be used to assess the raising action [113,116]. Whewell and coworkers gently lifted the pile by means of a small comb before measuring fabric thickness [129,130]. Heinrich [110] rejects the use of fabric thickness, claiming that the technique cannot distinguish between long sparse piles and short thick piles. While this may be true of thickness measurements made at a single applied load, more detailed information can be obtained at several loads or from continuous measurement of thickness over a wider range of loads [129]. Thickness measurements have been used by machine makers [117] for on-line measurement of raising effects. Heinrich examined two

techniques for evaluating raised piles. The first was based on measuring the force required to run a comb through the pile, the second was based on air permeability [111].

The British Rayon Research Association has developed the 'Raisemeter' [118], which measures the pneumatic pressure required to force a constant amount of air through the pile of a raised fabric. It is claimed that this instrument should be suitable for on-line measurement of raising.

The shorn weight of the pile, measured directly or by difference, can be used to assess the effectiveness of raising. A technique in which the pile was progressively shaved from the fabric so that the length and density of the raised pile could be analysed has been described [113]. This sophisticated technique, while highly suitable for laboratory studies, is too complex for mill use and is inappropriate for on-line testing. A technique based on the use of laser technology [104] has also been developed to measure the length of pile on raised fabrics.

The side effects of raising include stretching of the fabric in the warp direction, which can be measured directly or assessed from the relaxation shrinkage or extensibility of the fabric. Weight and strength losses that result from raising can also be measured directly [113].

12.7 PRESSING

Pressing operations are designed to flatten wool and wool-blend fabrics and modify their surface geometry by squeezing them between two smooth surfaces under high pressure and using elevated temperatures. Pressing reduces the thickness of wool fabrics and imparts the smooth handle and lustre required in a range of fabric types. The conditions used (time and temperature) in pressing are only sufficient to impart cohesive and temporary set to wool, so that the reduced thickness and modified surface of the fabric are not stable to release in warm-to-hot water or steam. A subsequent permanent setting operation is required to 'stabilise' or render permanent the effects imparted by pressing.

12.7.1 Pressing equipment

In the paper press, the fabric is layered between cardboard sheets in a formed stack and pressed using a hydraulic ram. In most paper presses, the 'papers' are electrically heated, reaching temperatures of the order of 60–80 °C. The pressing time is usually several hours, during which the stack is first heated and then allowed to cool. Paper pressing imparts a relatively stable (at least to short steaming) and highly-prized finish to the fabric but is time-consuming, labour-intensive and expensive. Semi-continuous machines, developed by Hattersley-Pickard and by Nikki, can be used to press fabrics using an intermittent motion through a set of electrically-heated plates [4].

In the rotary press, the fabric is pressed between a heated cylinder and a polished plate. Rotary pressing is continuous and inexpensive but stretches the fabric, reducing warp extensibility and introducing dimensional instability [119,120]. Moreover, the operation dries the fabric, making it difficult to set in later decatising operations unless it is reconditioned.

Machines in which the fabric is pressed between an impermeable belt and a heated cylinder represent a more recent innovation in pressing technology. Belt presses such as the M-Tec Contipress (Figure 12.24) are claimed to be more effective than rotary presses, operating at pressures up to 6 kg cm^{-2} and drum temperatures of 160°C , and are also claimed to avoid excessive tension and stretch in the fabric [67]. These presses normally incorporate a spray or steaming zone, which adds moisture to the fabric prior to pressing to facilitate the (cohesive) setting action.

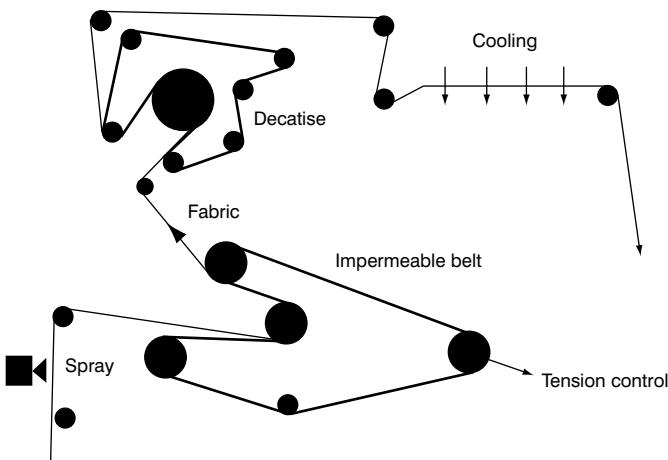


Figure 12.24 Schematic diagram of a belt press

At ITMA '95 several manufacturers of continuous crabbing machines developed modifications of their machinery so that they could be used as a belt pressing machines. In this application the fabric was re-routed so that it passed through a conditioning spray rather than the wetting trough and avoided the cooling bath after pressing.

The effectiveness of pressing can be determined by measuring the change in the thickness or surface geometry [119] of the fabric after the operation and/or subsequent decatising. Lustre can also be measured directly but the instrumentation required is complex and expensive.

The data in Table 12.3 demonstrate the effectiveness of electric paper pressing over conventional rotary pressing in producing a smooth finish on the fabric. It is also interesting to note that subsequent pressure decatising reduced both the measurable and subjective [119] differences between the variously-pressed fabrics.

The most important side effect of pressing is that the fabric may be stretched in the warp direction and temporarily set in the extended form. As in other processes, extension of the fabric during pressing can be determined directly by measuring the distance between suitable selavage marks before and after pressing or can be continuously monitored using pick counters. Alternatively, changes in warp extensibility or relaxation shrinkage can be measured directly. The lower extensibility and higher relaxation shrinkage in the warp direction of the rotary-pressed fabric (Table 12.3) are consistent with the stretching action of this machine.

Table 12.3 Effectiveness of paper pressing over rotary pressing

Property	Rotary press		Calender		Paper press	
	Semi-decatised finish	Pressure decatised finish	Semi-decatised finish	Pressure decatised finish	Semi-decatised finish	Pressure decatised finish
Extensibility in warp (%) ^a	4.1	7.1	6.0	7.6	7.7	7.6
Extensibility in weft (%) ^a	6.5	10.8	7.1	10.6	8.2	11.3
Contour ^b	14.6	13.4	12.8	12.2	9.0	12.0
Thickness (mm) ^c	0.59	0.57	0.60	0.58	0.50	0.54
Relaxation shrinkage (%) ^d	2.9	1.4	0.9	1.2	0.8	1.2

^a KES-F1^b Surface contour measured in KES-F4^c KES-F3 at 0.5 gf cm⁻²^d [121,70]

12.8 RELAXING/SPONGING/SHRINKING

Relaxation processes remain an important part of the finishing of wool fabrics in many countries and were especially important when techniques for producing fabrics with the required dimensional stability were not so well advanced. Sponging, relaxation and shrinking describe processes used to reduce or eliminate residual shrinkage in fabrics and thereby improve their dimensional stability. Knitted and some woven fabrics are easily stretched or distorted in finishing and handling operations. The dimensions of garment panels cut from fabrics with high residual shrinkage can change dramatically in garment-making operations, particularly during fusing, steaming and pressing, causing considerable problems for the garment maker. Shrinkage or panel distortion during wear or laundering is also of considerable concern to the consumer.

Sponging processes are designed to improve stability by relaxing the fabric and allowing or promoting the dimensional changes that occur. Wool fabrics normally contain some residual shrinkage, which results from tensions applied in finishing and handling, and, as a result, usually shrink during sponging. Sponging processes are also called 'shrinking' for this reason. In some industry sectors, sponging is performed by specialist companies who act on behalf of the garment maker to both inspect and 'stabilise' the fabrics prior to cutting.

12.8.1 The principles of relaxing

Wool fabrics have two major dimensional properties [121].

- (1) Relaxation shrinkage is the irreversible shrinkage that occurs when a fabric is relaxed in water (or steam) and allowed to dry/cool and recondition without constraint. This form of shrinkage is a direct consequence of the residual strains imposed on the fabric during dry finishing and handling, which are held by cohesive set.

- (2) Hygral expansion, on the other hand, is the reversible change in the dimensions of wool fabrics that occurs in response to changes in the moisture content of the fibres in different environments or during wetting and drying.

Pressing shrinkage, a measurement often used by garment makers to assess dimensional stability of fabrics, is a complex mixture of both relaxation shrinkage and hygral expansion [122]. Relaxing operations do not normally impart any permanent set to wool and, consequently, hygral expansion is not affected – only relaxation shrinkage is reduced.

As described in Section 12.2, relaxation occurs (cohesive set is lost) most rapidly when wool fibres are taken above their glass transition. The rate at which a fabric relaxes depends on the conditions used and the extent to which the fibre exceeds its glass transition temperature. In practice, relaxation is normally achieved by wetting the fabric or by heating it using steam (Figure 12.25). The temperature/regain profiles of wool fibres are quite different in the two procedures. When wool is heated in steam, both the temperature and the moisture content of the fibres increase to a point above the glass transition. In water, the moisture content of the fibres increases (to about 34%) but again the glass transition is exceeded.

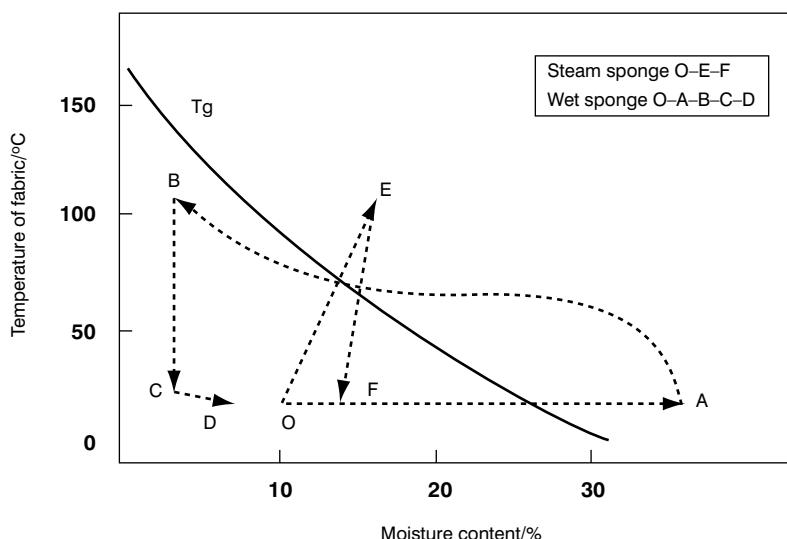


Figure 12.25 Regain-temperature profiles for two methods of relaxing wool fabrics

Relaxation occurs quickly in water and is virtually complete after 30 min [121]. Relaxation in steam (at 100 °C) depends on the moisture content of the fabric but generally is less extensive than in water. Steam relaxation often induces only half the shrinkage obtainable in water [70], although several cycles of steam and cooling can reduce residual shrinkage further.

12.8.1 Sponging machinery

Traditionally, shrinkage was induced by storing fabrics for long times in cool, damp rooms or in rolls with damp cloth. Such labour-intensive and time-consuming procedures are neither necessary nor possible in a modern mill. Modern steam sponging machines use firstly steam and then dry heat to raise the temperature of the unconstrained fabric. The fabric is then cooled, still in a tension-free condition, using an air draught or ‘shock’ cooled with refrigerated air (Figure 12.26). In steam relaxation machines, cooling the fabric without tension or distortion is the most critical part of relaxation process. In steam, wool is above its T_g and easy to deform. Any tension on, or other deformation of, the fabric (for example, creases) while the fabric is cooling will be cohesively set and contribute to subsequent dimensional instability. Avoidance of both warp tension and creases requires appropriate machine design. If the wool fibres can be cooled rapidly using, for example, refrigerated air, the time required to reduce the mobility of the protein molecules is considerably reduced and with it the probability of deformation while the fibres are still in a rubber-like condition.

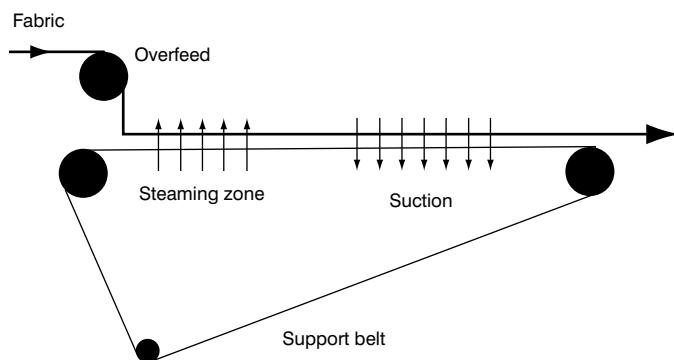


Figure 12.26 Schematic diagram of steam relaxing machine

In the original ‘London shrunk’ process, the fabric was steamed as it passed over a roller and then allowed to cool relaxed on a sloping table. Festoon transportation modes have also been used to move the fabric in a tension-free condition while it is cooling [1].

Modern relaxing machines usually use a mesh conveyor belt and/or rollers to transport the tensionless fabric through steaming and cooling zones – for example, Vapofree (Bisio) and VAP-90 (Biella Shrunk). Some machines incorporate beaters that mechanically agitate the fabric, speeding the relaxation process by overcoming fibre–fibre and yarn–yarn frictional effects within the fabric – for example, Vibroshrink (M-Tec) and Stabila (Sperotto Rimar).

Fabrics with adequate moisture relax more rapidly than those that are too dry and a conditioning process prior to relaxation is thought to improve the effectiveness of the operation. This is achieved in the Bruckner permanent shrinking machine using a water spray immediately prior to the steaming cylinder. In steam, water droplets rapidly wet, and are

adsorbed by, the wool fibres. Alternative approaches include cooling the fabric prior to steaming using refrigerated air (Holmes-Heaton) or liquid nitrogen (Juki – Figure 12.27) so that the fabric will condense, then adsorb, more water when it enters the steaming zone.

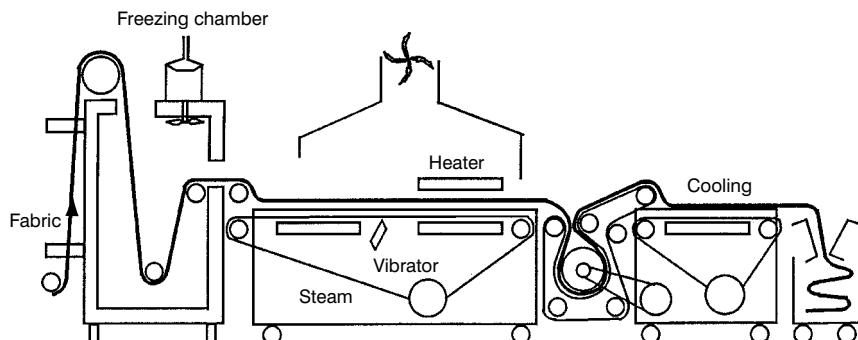


Figure 12.27 Schematic diagram of Juki sponging machine (derived from [100])

Excessive steam usage is a problem in this form of relaxing process. The Stabila machine (Sperotto Rimar) is designed to trap the steam in the chamber through which the fabric passes [123]. This feature is claimed to dramatically reduce steam usage by up to 70% with no loss of efficiency. The Shrinkomat SP (M-Tec) is also designed for low steam usage.

Wet sponging is an alternative approach to fabric relaxation in which the fabric is wet out and re-dried. Although water is the more effective medium for relaxing fabric, the problems associated with this form of relaxation occur in drying. Drying is a cohesive setting operation. A typical drying curve is shown superimposed on a glass transition curve in Figure 12.25. A wool fabric will adopt its relaxed dimensions only if it is not constrained in drying. This can be achieved using brattice or festoon dryers, provided the length of the festoon is not so great that the fabric distorts under its own weight.

If a conventional stenter is used, determination of the stenter settings required to ensure the fabric is dried to its relaxed dimensions is complex. The shrinkage that occurs when a fabric is dried is determined by its hygral expansion [124]. Moreover, it is normal mill practice to over-dry fabric, typically to moisture contents as low as 5%. The stenter-dried fabric will expand as it reconditions to the factory environment, so that the final dimensions are normally very difficult to predict. Unless the stenter is set to allow for the shrinkage that occurs as it dries, the fabric will not cohesively set at its relaxed dimensions. Unfortunately, it is normal mill practice to dry fabric at a dimension greater than the wet width to prevent the fabric from lifting off the pins in response to the air currents generated within the drying zones. This practice imparts weft relaxation shrinkage to the fabric.

Finally, it is common practice to decatise fabrics after both wet and dry sponging to re-impart any finish that was lost. Unless tensions are carefully controlled, the relaxed fabric can be stretched and relaxation shrinkage re-imposed in decatising. In practice, it is not uncommon to

find sponged fabrics with negative relaxation shrinkage in the weft direction. A common cause of this fault is relaxation followed by decatising under tension. The warp tension in decatising reduces the weft dimension to a value below that it achieved in sponging (relaxed), and decatising cohesively sets the fabric in this form. Consequently, when the fabric is subsequently relaxed in garment manufacture or in a dimensional stability test, the weft dimension increases (negative relaxation shrinkage) and this can cause some problems in the garment manufacture.

12.8.2 Evaluating the effectiveness of sponging/relaxing operations

The effectiveness of sponging can be evaluated by measuring the relaxation shrinkage after the operation [70]. Naturally, this procedure is only valid if the fabric had high relaxation shrinkage before sponging. Loss of press or 'finish', which is often a side effect of sponging, can be evaluated by measuring fabric thickness, surface thickness or lustre before and after the sponging process.

12.9 CONCLUSIONS

Although derived from essentially empirical beginnings and a craft-based industry, the mechanical finishing of wool fabrics is rapidly becoming the realm of the scientist and engineer. Modern wool finishing machines, although often based on traditional principles, are very different from their predecessors. Automated control, designed for high-speed continuous or semi-continuous processing, with minimal operator intervention is an essential part of any new machinery. However, a lack of specific information on the effects being sought in finishing, especially in the area of fabric aesthetics, is inhibiting this growth in understanding and technology. While finishers can only describe their requirements in vague, qualitative terms, machinery makers are restricted in what they can develop.

The wool industry is still a long way from being able to engineer – in quantitative terms – even the most simple of fabric properties (extensibility, bending rigidity and so on). Determination of the properties of the finished product from those of the loom-state fabric, other than by empirical methods, is still in the future. Modern machinery has given the finisher the ability to process fabrics more reliably, quicker and with less operator intervention – the challenge of using this machinery to engineer the fabric remains.

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CHAPTER 13

Coating, laminating, bonding, flocking and prepregging

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13.1 INTRODUCTION

Although the coating, laminating, bonding, flocking and prepregging processes represent but a small part of the total textile processing industry, they are nonetheless an extremely important, rapidly growing, and very high added-value sector, which has arguably the greatest growth potential of any textile technology.

Although the origins of all of these processes go back 100 years or more, the extent and importance of any of those processes prior to 1940 was relatively insignificant. Today, however, there are literally hundreds of applications for these technologies with many new applications being developed each year, some of them of a very considerable volume and value. For example, it is estimated that:

- (1) in 1992, 64 million linear metres of upholstery fabric was back-coated in the UK to make it fire-retardant in compliance to UK standards at an overall cost of approximately £48 million; this volume has grown steadily over the subsequent years, and in 1998 over 100 million linear metres was so coated at a total income for the coaters of around £75 million.
- (2) Europe alone would need more than 12 million air-bags per year if all cars were fitted with just two air-bags and many in fact incorporate many more than this. An air-bag is available at Euros 730 per bag, making a total value of the market Euros 9.5 billion or £6 billion, at current exchange rates.

Clearly, any relatively new market that can grow at such a rate has to be of considerable significance, and needs to have a greater level of attention paid to it than is currently the case.

13.1.1 Definitions

- (1) *Coating* can be described as the application of a continuous or discontinuous layer of an appropriate chemical system, generally to form a layer of the coating compound on or in the substrate, creating a non-homogeneous composite structure. This differentiates coating from most finishing processes, where the general aim is to produce a homogeneous distribution of the finish throughout the substrate;

- (2) *Lamination* is essentially the same process as coating, with a second fabric caused to be joined to the first by the coating applied;
- (3) *Bonding* utilises the coating to effect interstitial bonding of the substrate within itself (that is, the fibres within a non-woven fabric can be caused to adhere to each other to form a stable structure by the use of powders or water-based resin systems in what are known as powder-bonding or spray-bonding processes);
- (4) *Flocking* refers to the process by which a substrate is coated (as in (1) above) with a layer of 'flocking adhesive' into which a large number of precision-cut or ground fibres are partially embedded, to create a product with an artificial velvet appearance;
- (5) *Prepregging* involves the impregnation or coating of appropriate resins into or onto fabrics or fibres, in the form of tow or uni-directional tapes, generally based upon carbon, Aramid, ceramic or glass fibres, followed by drying and partially curing the resins. The composite structures are subsequently fully cured after laying them up into the finished product form in appropriate moulds, to produce a finished moulded product such as aircraft wing flaps, formula one racing car bodies, tennis rackets, golf clubs, crash helmets, rowing oars, and even mould formers themselves (for example, jet engine cowling moulds).

13.2 MARKET CONSIDERATIONS

13.2.1 Recent developments that have led to current industry status

Until some 50 years ago, only a minute percentage of textile fabrics were anything other than single component or homogeneous materials made by spinning yarns and weaving or knitting the yarns together to produce a fabric structure, which could then be dyed, printed and finished as appropriate. A very small quantity of fabrics were treated with natural rubber, wax, or certain other fairly rudimentary chemicals to create waterproof fabrics – and these two-component materials were the fore-runners of today's two- or multi-component coated, laminated or flocked fabrics, which make up a vast wealth of heterogeneous fabric structures generically classified as 'composites'.

This growth has been made possible by a number of factors that, acting complementarily together, have resulted in a major and rapid expansion in the total market sector to make it arguably the fastest growing and one of the most value-added sectors in the textile industry today. These developments are described below.

Fibre types

Instead of fabric construction being limited to natural fibres such as wool, cotton, linen and silk, many synthetic fibres have become available that have easier and more consistent processing requirements, higher physical performance standards, and which, when used alone or in blends with other fibres, allow fabrics with entirely new properties to be produced. These new synthetic fibres are manufactured by a good many companies around the world, and each company's

product has its own particular characteristics, but generically they can be grouped into the following:

- (1) viscose;
- (2) polyamide (nylon);
- (3) polyester;
- (4) acrylic;
- (5) polypropylene;
- (6) polyethylene;
- (7) glass;
- (8) carbon;
- (9) Aramid (Kevlar from Du Pont and so on);
- (10) ceramic;
- (11) metallic (including core spun metallic yarns).

Fibre decitex (formerly known as denier)

While there is some variation in the denier of naturally occurring fibres according to the animal type or geographic location where the fibres are produced, there is no significant control that can be exercised by manufacturers over the fibre denier or fibre length. For synthetic fibres, however, by the appropriate control of the manufacturing conditions, an infinite range of fibre diameters can be produced to meet the specific performance properties required in the end-product applications. Variations in cross-section and variations in additives are also used to achieve different levels of strength, performance and lustre. Most recently we have seen the development of 'microfibres' (those fibres having a denier of less than 1.0).

Fabric construction

Not only have the methods of weaving, knitting and non-woven fabric formation improved and diversified so that fabrics of an increased width and range of constructional characteristics can be produced, but a number of different methods of producing non-woven fabrics have evolved. Thus, there is now a vast range of different fabric constructions, decitex, and fibre types, which can be selected to achieve the required characteristics in the substrates that are to be coated or laminated.

Polymer types of coating compounds and laminating/flocking adhesives

Instead of being restricted to a small number of natural compounds that could be applied to the substrates, we have today an enormous range of different polymer systems available, each having its own particular characteristics in respect of end-product performance. As with the fibres, these can be grouped into a number of generic compounds, the more important of which are:

- (1) rubbers (natural and synthetic);
- (2) polyvinyl chloride (PVC);

- (3) acrylics;
- (4) polyurethanes (PUs);
- (5) silicones;
- (6) epoxies.

The physical forms in which the polymer is available

Increasingly, the polymers detailed above can be obtained in a number of different physical forms, so that the most appropriate can be selected according to the characteristics of the substrate, the machinery to be employed, the end-product to be produced, and the environmental regulations under which the processing has to be carried out. Compounds are available in the following forms:

- (1) solvent-based solutions utilising either flammable or non-flammable solvents (both of which have their advantages and disadvantages); however, increasingly tight legislation on the use of solvents and other materials that give rise to discharges to atmosphere are resulting in a rapid reduction in the use of solvent-based systems – where there is no alternative, it is now almost always obligatory to have efficient solvent recovery or incineration systems operational to reduce the emissions to almost zero;
- (2) water-based solutions, dispersions and emulsions;
- (3) 100% solids materials, which may take a number of different forms: film, powder, hot melt, UV-cured, heat-cured, radiation-cured, moisture-cured, and so on.

Methods of application

In the nineteenth and early twentieth century, the application of the polymers was both crude and inaccurate. Today, there are dozens of methods (as will be discussed later in this chapter). The technique that is selected for any given product will be dependent upon a number of factors, including the required coat-weight, the nature of the compound to be applied in terms of its viscosity and other physical characteristics, the degree of penetration required into the substrate, and the cost that can be accepted in the end-product.

Summary

By virtue of the enormous diversification in raw materials and application techniques, it has been possible to develop a range of new end-products having performance characteristics not previously available. This in turn creates entirely new markets, which grow in size very rapidly as the technical and commercial advantages of each product are perceived in the market place.

13.2.2 Current markets for products produced by coating and laminating

A detailed list of some of the more important applications for coated, laminated and flocked fabrics appears below (Section 13.3). However, to demonstrate the importance of these markets

in the context of the textile industry and the economy as a whole, the following statistics make interesting reading. Different industry sources give different figures for the same product, and therefore the figures quoted below are either an average of several industry statistics, or are those believed by virtue of their source or independent confirmation to be the most likely.

Automotive industry

The following tables show the enormous volumes of cars now being manufactured in just some of the more important producing countries. There are in fact many other countries where what was originally just the assembly of components manufactured elsewhere has been scaled up to become genuine manufacture and the overall total production around the world is at least 30% higher than the figures indicated by the following tables.

Table 13.1 Sales of Cars and Light Trucks in the United States of America

Cars and light trucks	May 2002		Jan–May 2002		Market share		
	Units	02/01 (%)	Units	02/01 (%)	2002	2001	01/00 (%)
Chrysler Corporation	216 563	4.4	959 183	-3.3	13.9	14.0	-9.9
Ford	324 906	-11.5	1 446 088	-10.5	21.0	22.9	-5.6
General Motors	398 870	-11.9	1 935 714	-2.7	28.1	28.2	-1.2
'Big Three' Total	940 339	-8.5	4 340 985	-5.6	63.1	65.1	-4.7
Korean brands	53 638	0.4	269 278	12.5	3.9	3.4	30.6
Japanese brands	386 997	-1.6	1 896 711	1.4	27.6	26.5	3.2
Asian brands total	481 174	-1.4	2 165 989	2.7	31.5	29.9	5.8
BMW	23 624	16.8	10 201	17.2	1.5	1.2	12.5
Mercedes ^a	18 127	-6.0	87 038	5.0	1.3	1.2	0.3
Porsche	2 242	-6.7	9 293	-16.6	0.1	0.2	2.8
Audi Division	7 710	-0.1	34 896	2.7	0.5	0.5	3.6
VW Division	32 109	-6.7	137 36	-0.9	2.0	2.0	0.0
VW total	39 819	-5.5	172 256	-0.2	2.5	2.4	0.7
Domestic prod.							
German brands	27 671	-11.8	119 766	-9.0	1.7	1.9	-3.4
Import German brands	56 141	6.6	250 831	13.0	3.6	3.1	7.6
German brands total	83 812	-0.3	370 597	4.8	5.4	5.0	3.3
Light vehicles total	1 505 325	-5.9	6 877 571	-2.6	100.0	100.0	-1.3
Total of domestic production ^b	1 218 703	-7.8	5 539 034	-5.2	80.5	82.8	3.0
Total of imports	286 622	3.2	1 338 537	10.1	19.5	17.2	7.4

a Including production of Freightliner Light Duty Vehicles

b Domestic production = production in NAFTA countries, USA, Canada and Mexico

Source: Ward's Communications

Table 13.2 Car production in Turkey

Production	Apr 2002		Jan–Apr 2002		Market share		
	Units	02/01 (%)	Units	02/01 (%)	2002	2001	01/00 (%)
Cars ^a	17 301	-14.9	61 622	0.1	65.1	66.6	-40.3
Light trucks	8 861	56.1	26 958	13.8	28.5	25.6	11.4
Light vehicles total	26 162	0.6	8 858	3.9	93.5	92.2	-30.4
Medium trucks ^b	403 000	48.7	1 195	57.9	1.3	0.8	-77.4
Heavy trucks ^c	563 000	36.3	1 626	-11.3	1.7	2.0	-75.4
Medium/heavy trucks total	966 000	41.2	2 821	8.9	3.0	2.8	-76.2
Buses	1 156	70.5	3 292	-29.5	3.5	5.0	-67.0
Total production ^a	28 284	3.4	94 693	2.4	100.0	100.0	-36.6

a excluding assembly by Opel in Turkey

b gross vehicle weight rating from 3.5 t to 12 t

c gross vehicle weight rating above 12 t

Source: OSD

Table 13.3 New car registrations in Western Europe by country

New registrations by country	May 2002		Jan–May 2002		Market share		
	Units	02/01 (%)	Units	02/01 (%)	2002	2001	01/00 (%)
Belgium	41 074	-11.3	254 964	3.8	3.9	3.6	-5.1
Denmark	11 433	13.3	46 861	12.0	0.7	0.6	-14.7
Germany	284 000	-14.0	1 386 847	-5.0	21.4	21.7	-1.1
Finland	12 731	11.5	53 939	4.4	0.8	0.8	-18.7
France	186 265	-8.6	957 611	-2.7	14.8	14.6	5.7
Greece	23 403	-18.7	124 54	-5.2	1.9	1.9	-3.4
United Kingdom	208 669	5.1	1 140 363	8.2	17.6	15.6	10.7
Ireland	18 457	-0.3	108 074	-5.8	1.7	1.7	-28.6
Italy	209 100	-11.0	1 051 400	-12.7	16.2	17.9	0.1
Luxembourg	4 068	-2.8	22 703	5.6	0.4	0.3	2.2
Netherlands	44 728	-10.5	245 485	-6.4	3.8	3.9	-11.3
Austria	26 369	-13.5	130 044	-9.6	2.0	2.1	-5.1
Portugal ^a	25 969	-6.6	107 128	-7.5	1.7	1.7	-12.0
Sweden	24 617	-1.9	107 005	0.8	1.7	1.6	-15.1
Spain	128 911	-6.2	574 51	-7.2	8.9	9.2	4.0
European Union	1 249 794	-8.0	6 311 474	-3.7	97.4	97.3	0.5
Norway	7 912	-8.8	38 223	-1.1	0.6	0.6	-5.6
Switzerland	29 544	-10.8	129 222	-8.7	2.0	2.1	0.0
Western Europe total	1 287 250	-8.0	6 478 919	-3.8	100.0	100.0	0.5
WE without Germany	1 003 250	-6.2	5 092 072	-3.5	78.6	78.3	0.9

a sales

Source: ACEA VDA

Table 13.4 New car registrations in Western Europe by manufacturer

New registrations by manufacturer	May 2002		Jan–May		Market share		
	Units	02/01 (%)	Units	02/01 (%)	2002	2001	01/00 (%)
BMW	57 784	10.9	283 483	18.5	4.4	3.6	9.3
Smart	9 600	-2.7	45 809	19.0	0.7	0.6	2.5
Mercedes	69 900	-4.7	324 932	-0.2	5.0	4.8	4.2
Chrysler	10 479	4.1	47 687	9.1	0.7	0.6	1.6
DaimlerChrysler total	89 979	-3.5	418 428	2.6	6.5	6.1	3.7
Audi	48 753	-8.4	245 725	3.3	3.8	3.5	11.4
Seat	34 872	-13.7	163 515	-12.9	2.5	2.8	-5.7
Skoda	21 308	-9.2	103 626	-7.3	1.6	1.7	13.6
Volkswagen	140 651	-9.0	661 427	-11.0	10.2	11.0	-0.7
Volkswagen total	245 584	-9.6	1 174 293	-8.2	18.1	19.0	1.8
Ford Group	144 014	-7.9	750 785	-2.1	11.6	11.4	3.7
Opel/Vauxhall	121 760	-18.4	601 49	-15.2	9.3	10.5	0.6
GM Group	129 882	-17.3	638 901	-14.3	9.9	11.1	0.2
Fiat Group	106 557	-22.6	567 894	-19.1	8.8	10.4	-3.6
PSA	183 534	-3.3	964 81	4.1	14.9	13.8	10.9
Renault	138 984	-1.1	709 417	2.6	10.9	10.3	1.0
Rover	11 970	-12.3	63 587	-7.7	1.0	1.0	-19.0
Japanese make	147 012	-3.6	722 919	1.7	11.0	10.6	-8.1
Korean make	32 621	-21.7	172 849	-4.2	2.7	2.7	-19.3
Western Europe total	1 287 250	-8.0	6 478 919	-3.8	100.0	100.0	0.5

Source: VDA/ACEA

Table 13.5 New registrations of imported cars in Japan by marques

New registrations by brand	Apr 2002		Jan–Apr 2002		Market share		
	Units	02/01 (%)	Units	02/01 (%)	2002	2001	01/00 (%)
American brands	1 183	-1.8	5.3	-8.7	6.0	6.5	-22.5
French brands	1 346	-1.9	5 515	11.6	6.2	5.5	15.0
British brands	519 000	-18.1	2 593	10.4	2.9	2.6	-16.6
Italian brands	873 000	31.9	3 593	14.2	4.1	3.5	26.6
Korean brands	355 000	294.4	772	75.1	0.9	0.5	98.5
Other brands	1 677	13.8	7 399	19.5	8.4	6.9	13.5
Honda	732 000	27.5	3 438	47.2	3.9	2.6	-14.2
Isuzu	137 000	30.5	1 084	-18.7	1.2	1.5	-38.5
Mitsubishi	1 000	-96.0	1	-99.7	0.0	0.4	-6.9
Nissan	0 000	—	4	-66.7	0.0	0.0	37.1
Toyota	43 000	-71.3	315	-65.1	0.4	1.0	-60.0
Japanese brands (imports)	913 000	5.9	4 842	-1.5	5.5	5.5	-29.8

Table 13.5 continued on next page

Table 13.5 *Continued*

New registrations by brand	Apr 2002		Jan–Apr 2002		Market share		
	Units	02/01 (%)	Units	02/01 (%)	2002	2001	01/00 (%)
Opel	767 000	-29.4	3 579	-27.5	4.0	5.5	-17.6
Porsche	188 000	-20.3	759	-13.8	0.9	1.0	22.6
Ford	157 000	-31.4	1 063	-32.5	1.2	1.8	-24.1
Audi ^a	655 000	89.3	3 696	100.7	4.2	2.1	16.7
Mercedes ^a	3 180	-21.6	15 133	-20.8	17.1	21.3	9.8
VW ^a	4 158	13.2	21 539	-2.6	24.4	24.7	4.5
BMW ^a	3 045	40.4	12 664	11.5	14.3	12.7	1.2
German Brands Total	12 150	3.0	58 433	-5.5	66.1	69.0	3.3
Imported Brands Total	19 016	5.1	88 447	-1.3	100.0	100.0	0.3
New Registrations Total	311 108	5.6	1 569 688	1.3			0.7

a including marques of the corporate group

Source: Jama

Table 13.6 Production and sales of motor vehicles in China

Production and sales of motor vehicles in China	Year 2002		Jan–Feb 2002		Market share	
	Units	01/00 (%)	Units	02/01 (%)	2002	2001
Production:						
Passenger cars	703 521	16.3	100 425	8.9	27.2	28.9
Commercial vehicles	1 630 919	11.4	269 317	18.4	72.8	71.1
Trucks	802 353	5.0	134 611	19.1	36.4	35.4
Buses	828 566	18.3	134 706	17.7	36.4	35.8
Total	2 334 440	12.8	369 742	15.7	100.0	100.0
Sales:						
Passenger cars	721 463	17.7	10 633	13.5	30.7	30.1
Commercial vehicles	1 642 202	11.4	23 983	10.2	69.3	69.9
Trucks	818 433	5.6	112 006	8.9	32.4	33.0
Buses	823 769	17.5	127 824	11.4	36.9	36.9
Total	2 363 665	13.2	34 616	11.2	100.0	100.0

Source: CATARC

Table 13.7 Use of coated and laminated fabrics in cars produced in 2000

Application ^a	European production ^b (million m ²)	World production ^c (million m ²)
Seating fabrics (three-ply laminates)	120	250
Headliners (mostly two-ply laminates)	30	60
Door panel laminates (mostly two-ply)	12	25
Moulded car carpet (coated and frequently also laminated)	100	250

a In addition to the above, there are also significant quantities of coated and/or laminated products used in the boot floor and side linings, seals, gaskets, sun visors, rear parcel shelves, and acoustic and thermal insulation products in the engine compartment and between it and the passenger compartment. Each car uses approximately 12 kg of fibre

b Total number of cars made in 1990 in Europe: 18.37 million

c Total number of cars made in 1990 in the world: 38.15 million

In the industrialised world (Western Europe, North America, Japan, and so on) the automotive industry is the second most important industrial activity, and represents a major outlet for very many industrial products, including coated and laminated fabrics (Table 13.7).

The figures in the Table 13.1 relate only to passenger cars. There is a very significant additional market for all of the products in the van, truck, bus, tractor, caravan, boat, train, and aircraft industries. Here the individual volumes may be smaller, but in many cases the technical demands are higher and the added-value is considerably greater.

Air-bags

There can be no doubting the life-saving and trauma-reducing advantages of having air-bags fitted in cars, particularly if they are used in conjunction with seat belts. Air-bags are designed to inflate in a fraction of a second under the influence of the rapid deceleration occurring in an impact collision, and then deflate almost immediately, to cushion the vehicle occupant against injury. The development of such a beneficial device has resulted in the extremely rapid creation of an entirely new market for coated fabrics, which form the essential main ingredient of the air-bag system.

Table 13.8 indicates the very large growth rate that has occurred in this particular market. The figures show the number of vehicles fitted with air-bags (generally driver-side only, but occasionally driver- and passenger-side).

An even more incredible fact is that, taking the selling price of the air-bag assembly from the car manufacturer and averaging out across the range of car models available with air-bags, the total 1993 European market was estimated to be worth £7000 million; current market value may be estimated at several times this level.

Table 13.8 Numbers of cars fitted with air-bags

Year	Number of cars fitted with air-bags	Quantity of coated fabric used (m ²)	Value of the coated fabric component alone (£ million)
1988	480 000	700 000	100
1990	2 500 000	3 600 000	540
2000 (estimated)	22 000 000	60 500 000	9000

Air-bags themselves are produced by coating a specific construction of synthetic woven fabric with a specific coating compound. In the USA, this compound is usually a solvent-based synthetic rubber, and although the raw material costs are somewhat lower than the prices that apply in Europe, the physical size of the American air-bag is larger than that employed in Europe.

In Europe, almost all the production has been based upon a solventless silicone elastomer being applied to a very special woven synthetic fabric at about 80 g m⁻² in order to achieve the required product performance.

In accordance with the positive policy towards air-bag equipment by Japanese car manufacturers, developments and operations in this sector in Japan will escalate through close collaborative activities involving fibres, fabrics, sewing techniques, assembling and car manufacture. The current position of product development and the outlook for the air-bag business are reviewed below. (This report is based on an interview with Mr Takao Aoki, General Manager of the industrial materials department at Toray Industries Inc.)

Composition of the air-bag system: Air-bag components include:

- (1) a sensor to detect an accident
- (2) an inflator to generate nitrogen gas
- (3) the air-bag itself
- (4) a control circuit
- (5) a storage box.

A key function of this module is that nitrogen gas must be exploded within 0.11–0.12 s after the crash and inflate the air-bag with a capacity of about 50–60 l in order to protect the driver or passenger against a strong impact. Moreover, the quality and function of the equipment must be maintained without deterioration in the compacted box for at least ten years. The required major functional qualities are durability, impact resistance, high-pressure resistance, non-flammability, light weight and compact storage. The required fabric characteristics are high tenacity, optimum elongation, no degradation at high temperature and humidity, non-air-permeability, heat-resistance and softness.

Fabric design:

- (1) *Raw materials* – Polyamide (PA) 6.6 is predominately utilised for air-bags owing to its well-balanced physical properties in respect of softness, heat-resistance, tensile strength and optimum elongation. Polyester (PET) was at one time presented as a challenge by PET

fibre producers for economical reasons, but has since been dropped owing to its hardness (low yarn modulus). PA 6 was not well accepted either because it offered lower heat resistant properties than PA 6.6. PA 4.6 ('Stanyl' by DSM, NL), reportedly providing superiority in terms of heat resistance with a melting point of 295 °C, has not yet been launched in the market owing to its relatively high cost. In consequence, leading fibre producers Du Pont, Akzo and Toray have promoted PA 6.6 for air-bag raw materials.

- (2) *Yarn and fabric specification* – In accordance with a continuous requirement for thin, light-weight fabric, the yarn denier (initially of 840 denier) has been modified to finer deniers (420 and 315 denier) to keep in balance with tenacity. High weaving density offsets the lower inherent strength of the fabrics. More or less 46 × 46 per inch of plain weave in 220 to 240 g m⁻² is an average basic specification of the fabric.
- (3) *Finishing* – Coating with chloroprene in the early days has subsequently been replaced by silicone rubber coating due mainly to the cost advantages. Moreover, a challenge in the form of non-coated, high-density fabrics with high shrinkable PA 6.6 yarn has been making headway in recent years. The market still takes half non-coated and half coated, based on the question of the advantage of air-tightness. Total quality and cost control from the fabric design and construction to the coating finish does not always conclude simply that the cost advantage lies with non-coated fabrics (Table 13.9).

Table 13.9 Properties and characteristics of coated and non-coated fabrics in air-bags

Items		Chloroprene-coated	Silicone-coated	No coating
Grey fabrics	Materials	PA 6.6	PA 6.6	PA 6.6
	Denier (D)	840	420	420
	Density (in)	25 × 25	46 × 46	48 × 48
Finished fabrics	Weight (g m ⁻²)	290–300	215–235	225–245
	Thickness (mm)	0.39	0.30	–
Bag	Capacity (l)	60 (driver) 130 (passenger)		
Physical properties	Tensile strength (kg cm ⁻¹)	>64	>56	>56
	Elongation (%)	>20	>25	>25
	Tear strength (kg)	>25	>20	>35

Production of the air-bag: Approximately 5000 tons of PA 6.6 yarns are produced in Japan exclusively for air-bags. Toray takes the major share with 75%, making them the leading manufacturers, followed by Teijin and Toyobo with a small share. Textile manufacturers from weaving to finishing, and assemblers of the air-bag module, operate in close collaboration with fibre producers and car manufacturers in respect of all aspects of product design, quality and production control so as to maintain the reliability of the products to ensure their high acceptance in the market.

Takata Corporation, a leading vertical operation from weaving to assembling, is in close cooperation with Toray to supply the best equipment to most of the car manufacturers.

In other markets similar situations exist, although with certain local preferences in terms of the fabric weight, construction and coating system employed.

Outlook: The positive policy of full standardisation of air-bags by Japanese car manufacturers for their new 1998 models will ensure a bright future for air-bags in Japan. Moreover, the current trend towards employing air-bags at passenger seats (which are twice the size of those at the driver's seat and need 640 g of fabric) and the development of air-bags for the back seats, as well as side air-bag application, are likely generate an enormous textile consumption for air-bags. The fibre consumption for air-bags in Japan can thus be estimated as shown in Table 13.10.

Table 13.20 Estimated fibre consumption for air bags in Japan

Year	1996	1997	1998	2000
Fibre consumption (tons per year)	4000	5000	7500	9000

Similar expansion of other geographic markets is expected and although all alternative techniques for producing the required product are under constant evaluation, there do appear to be certain technical and commercial advantages to be gained from the use of lighter weight fabrics with very light-weight 100% solids silicone elastomer coatings.

Tyre cord: Industry sources indicate that the volume of tyre cord production in the UK alone for 1990 was more than 13 million m², with a value of around £14 million.

No world-wide figures are available, but by extrapolation, it is estimated that the total production would have been around 400 million m², with a value of around £400 million.

Prepregs

Industry sources estimate that the 1993 production of prepgs (down slightly on 1990) were somewhere around 3 million kg. However, in line with the general recovery in most world economies and in the orders for aircraft, the decline in prepreg volume associated with the peace dividend from the collapse of the USSR has seen a steady growth in the total market for civilian aircraft and across the board for non-aerospace applications, resulting in a total market volume in 1998 estimated to exceed 7 million kg.

The cost of prepreg varies enormously from as little as £5 to as much as £500 per m² in the UK. Using the best available figures, one could estimate a total annual value of prepreg production at around £2000 million.

The outlets for prepgs are detailed below (Section 13.10.1), but include a significant utilisation in the aerospace industry, which has undoubtedly been responsible for generating the development of prepgs to their current status. A typical current generation wide-bodied

passenger plane will use around 11 000 kg. In the A340 Airbus, 13% of the weight of the airframe is of composite prepreg structure. The Boeing 757 has the whole of the tailplane constructed from composite materials being built at the Boeing facility in Melbourne, Australia, and the Boeing 777 has an increased percentage of prepreg material in its construction. The next generation of ultrasonic passenger aircraft planned by Boeing, and originally intended to be in operation by the year 2010, is understood to utilise around 50% prepreg material using solventless resin systems developed specifically for the very high temperatures to which the airframe will be subjected. Military aircraft use a significantly higher percentage, with up to 68% of one of the latest generation fighter aircraft being prepreg, and the entire body shell of the MacDonald Douglas MX18 being made of prepreg material.

Upholstery

Following a series of tragic fires in the mid-to-late 1980s, the UK Government introduced legislation requiring that all domestic upholstery fabrics used in the United Kingdom complied with certain very stringent fire retardancy standards.

Furthermore, while the polyurethane foam required to be used beneath the upholstery fabric in all new furniture has to be of a 'combustion-modified grade', the test procedures to confirm satisfactory performance of the upholstery fabric itself have to be carried out with a regular grade of flammable polyurethane foam placed behind and in contact with the upholstery fabric in the same manner as would be applicable in a chair or settee. (The regular grade of PU foam has to be used in the test because of the very large numbers of chairs and settees that will be re-upholstered and which will still have the standard flammable grade of foam.)

For retail upholstery applications, the sample described above can be tested by either:

- (1) the cigarette test, in which a lighted cigarette is placed in the right-angle joint between the swab and the back of the seat;
- (2) the match test, in which a standard gas flame is played onto the fabric vertical surface for a given period of time.

In either case, ignition – which will most probably occur – must be automatically extinguished within a pre-defined time. For contract applications, the severity of the test is considerably increased by the use of wooden pyramid structures (crib 3, crib 5 and crib 7, which indicate the number of layers of wood in the pyre), which when burned give off considerably greater quantities of heat and flame, and which therefore require higher levels of fire retardancy to be present in the fabric under test.

This is the most rigorous fire retardancy standard applicable anywhere in the world, but the indications are that the same or a very similar standard will be adopted throughout the European Community, and in many other countries where similar regulations are under consideration.

Until the late 1980s and the introduction of this legislation, the proportion of upholstery fabric that was coated was small, except in the USA. In the USA, the majority of upholstery fabric has

in fact been coated for many years, because it was realised at an early stage that by back-coating the fabric with a filled Styrene-Butadiene latex, the weight of fibre could be significantly decreased with the coating giving the required dimensional stability and physical properties at a lower cost than the fibre alone.

With the introduction of the regulations in the UK, a market of some 80 million linear metres was originally created, which has now increased to in excess of 100 million linear metres, all of which must achieve the fire retardancy standards. A small percentage of this is achieved utilising non-flammable fibres (Hoechst Trevira CS, and Lenzing FR Viscose). Another sector of the market, which originally used an impregnation technique with Ciba Geigy's Pyrovatex CP New or Albright and Wilson's Proban CC, has progressively moved to the use of back-coating as the most cost-effective method of achieving the required results. However, now the majority of the market (currently estimated at around 95%) utilises back-coating of the fabric, both to achieve stabilisation of a reduced-weight fabric construction, and to confer the fire retardancy standards required.

While there is a certain quantity of styrene butadiene rubber (SBR) employed in the United Kingdom on upholstery fabrics, the majority utilises a much lower coat-weight of an acrylic binder system incorporating the fire retardant chemicals, and achieves the same degree of stabilisation and fire retardancy without the same stiffening effect that the heavy coating weight of SBR gives.

SBR is used on temperature-sensitive fabrics (polypropylene and bulked acrylics) where the acrylic resin cannot be crosslinked satisfactorily because of the low temperature resistance of the fibre.

Current estimates would suggest that the UK market is worth around £55 million per year for the coating process only, without taking into consideration the value of the textile fabric.

Window fabrics

In the UK, as well as in most Northern European countries and the USA, many houses, offices and hotels use enormous quantities of curtain fabrics and blinds.

In the mid-1960s, the US hotel industry became a significant consumer of 'black-out' curtain liner to keep the interior of a room dark after sunrise. This industry has slowly grown around the world as technological improvements are made, and as commercial developments occur offering technical and financial advantages to the employment of this area of coating technology.

Today, on a world-wide basis, there are several hundred thousand square metres of curtain fabrics and curtain linings coated with a partially crushed mechanically foamed acrylic resin, which then has a low weight of viscose flock partially embedded in it, to give a textile feel to the coated surface.

An even greater quantity of vertical and roller blinds are also produced, coated with acrylic or other resin systems, and increasingly – particularly in hotter countries with stronger sunlight – these blinds are coated as 'black-out' and may also be flocked on the internal surface to create a textural effect and textile handle.

The total world market for these coated window products is undoubtedly enormous. Estimated volumes vary so widely, however, that it is extremely difficult to make any certain estimation of the market size, other than to indicate a probable minimum value of £1000 million, with a maximum of around double this value.

13.2.3 Future prospects

New applications

If one looks at the existing market, one can obviously identify certain product groups (air-bags, upholstery fabrics, and so on) where the use of coating or laminating technology is at a relatively early stage, and where a further expansion in the market will undoubtedly occur.

It is not possible to identify what new markets will arise in the future, but from a historical point of view there can be no doubt that such new markets will be developed, and the probability is that composite structures based upon the coating or laminating of fabric systems with appropriate resins will be the most likely source for such expansion.

New compounds

We can be sure that new chemical compounds will continue to be developed, so that new polymer systems will become available having different chemical and physical characteristics. These will become available in different physical forms, allowing the particular capabilities of the coating and laminating industry to be utilised, while at the same time meeting increasingly stringent environmental regulations.

These new compounds will probably be predominantly solvent-free, water-free, 100% solids materials, which will crosslink under appropriate conditions of temperature, moisture or radiation, resulting in fully crosslinked products having equal or improved performance properties over those previously available.

The PURs are a new generation of polyurethane adhesives, with incredibly high adhesion characteristics, which are applied as hot melt compounds at a temperature of around 120 °C but at coat-weights that generally vary from 2 to 10 g m⁻². At the lower level, the bond is not permanent, but does hold the materials together until they have been sewn, which is the purpose. At the higher level, products such as lingerie, automotive fabrics, water-vapour-permeable films and fabric-to-fabric laminates will withstand all of the conditions to which they will be subjected in subsequent use, without deterioration, including multiple washing.

PURs are reactive hot melt adhesives, which react with moisture in the substrate or in the air to produce a crosslinked polymer network. Typically, only 0.3% of water is needed to fully cure these materials. The speed of curing or crosslinking can be increased by the use of special catalysts, which do not affect the thermal stability of the molten adhesive, but which can considerably increase the reaction with moisture and hence the time to full cure. A wide range of properties can be built into the adhesives, such as open time, viscosity, adhesion, elastic modulus, wash-resistance, antistatic, flame retardancy, and so on.

Other polymer systems, currently still only at the development stage, offer further interesting characteristics that can be varied according to the processing conditions to which they are subjected, offering the possibilities of different end-product performance characteristics produced from a single compound system on common machinery.

New substrates for coating

Equally, new fibres and new constructional systems for fabrics will continue to be devised, giving rise to further opportunities in product development.

13.2.4 Product and market development: performance-, price- and legislation-driven

There are many factors that influence the development of new products and the change in existing products. Change costs money, and will therefore not be undertaken unless there is a commercial or technical pressure for it to happen.

Performance

The aerospace, military and many other high-tech industries are looking for higher and higher technical performance, generally with lower weights and so on, and the pressure upon these industries and their suppliers is therefore to constantly seek to develop newer and better technical products, achieving higher and higher performance specifications. Cost here is not the primary criterion.

Price

The automotive, and many other consumer product markets, by contrast, are constantly striving to achieve lower costs. The manufacturers supplying these industries, while being asked to achieve better technical performance, are primarily under price pressure to reduce the overall cost of the product they supply.

Such cost improvements can be achieved through technical developments such as decreasing the weight of the highest-cost components in a system, and replacing them – without loss of technical performance – with other lower-cost materials. Thus, a high percentage of carbon fibre can be replaced with glass fibre, without loss of physical performance, provided the fabric construction is correctly designed.

The weight and cost of an upholstery fabric can be decreased, while at the same time achieving an increased physical performance and fire retardancy, by back-coating the decreased weight fabric with a fire retardant acrylic resin system.

Legislation

The introduction of the Environmental Protection Act 1990 forced manufacturers to move away from techniques that give off environmentally harmful by-products in favour of other systems not having these disadvantages.

At first sight, these moves appear to be to the disadvantage of the industry, but very frequently they result not only in eliminating pollution but also in decreasing the overall production costs.

For example, solvent-based coatings are increasingly being replaced by the use of solventless coating systems applied at 100% solids materials cured by reaction with moisture or ultraviolet radiation or heat, in equipment that costs less, occupies less space and utilises less energy than the original solvent-based processing equipment.

13.3 APPLICATIONS FOR COATED FABRICS

Section 13.2 demonstrated that the market for coated fabrics is extensive and financially important. In this section, we look at some of the specific applications into which these products are supplied, the methods of application, and the reasons for utilising a coated fabric rather than any alternative system. The list below will of course vary from country to country in terms of significance, importance, volume and so on, depending on the climatic conditions, labour costs, the size of the defence industry, general lifestyle and influence upon the markets for specific purposes.

13.3.1 Garments

Domestic garments

Coated fabrics are used in domestic garments for either functional or decorative reasons.

Baby pants: A similar weight of woven nylon coated with a silicone elastomer, or a silicone elastomer/acrylic compound in two passes – the first blade-over-air, the second blade-over-roll (Figures 13.1 and 13.2) – achieves a washable, waterproof, sterilisable product with the softness and other performance characteristics required as overpants for infants and incontinent adults.

Footwear: Almost all shoes, boots, slippers, and so on, today incorporate a considerable quantity of coated and laminated fabrics. For example, the outer ‘leather’ is most commonly a polyurethane or PVC artificial leather coated onto a woven or non-woven fabric. The lining and insole will almost certainly be a coated non-woven fabric. The toe puff, heel counter and other elements will be coated or impregnated woven or non-woven fabrics, often ‘split’ to give a superficial appearance of a leather split, and then further coated with a thermoplastic adhesive in order to achieve the ‘hot lasting’ which is increasingly used in the assembly of the shoe instead of using solvent-based adhesives.

Fusible interlinings: Until about 1960, all garments were stiffened by sewing woven interlinings into the garment during the making-up stage. These interlinings, according to the position and nature of the garment, were either fine-woven cotton fabrics, or heavier-weight materials made of cotton or horse hair and so on, or blends of such materials, which added weight, body and shape to the garment.

Today, that market has almost totally been replaced by the use of 'fusible interlinings', which are the same sorts of fabrics coated with a thermoplastic adhesive, allowing the interlining to be adhered to the face fabric in a 'fusing press' generally employing a combination of pressure and heat (sometimes with the addition of steam) to bond the interlining to the face fabric.

In the earliest days, the thermoplastic adhesive was scattered onto the fabric, but this could give too much stiffness for certain applications. The development of the 'powder point' technique allowed a controlled weight of the thermoplastic adhesive in powder form to be applied in a regular pattern on the fabric, and this improved the drapeability and bending characteristics of the laminate, and hence opened up further markets for fusible interlinings. Today, the most important applications for the powder-point-produced system are in the manufacture of shirt collars and cuffs and similar products, where high density polyethylene powder is printed onto the interlining in a regular pattern. This achieves the stiffening of the collar without giving rise to any problems of appearance, and also allows the garment to be washed at high temperature without delamination occurring.

In recent years, non-woven fabrics have become increasingly important, and these are most satisfactorily coated with 'paste dots', which are an aqueous dispersion of fine particle size thermoplastic powders dispersed in appropriate binders, and applied to the non-woven, knitted or woven fabric through a rotary screen in much the same way as colour printing is carried out through a rotary screen.

The United Kingdom market for fusible interlinings in 1991 was estimated at 50 million m², at a time when garment manufacture within the UK had drastically reduced from its highpoint. This reduction occurred because the majority of garments are now manufactured in the lower-wage economies of the North African, Middle and Far Eastern countries where the production of fusible interlinings themselves has expanded dramatically since 1970.

The total world market for fusible interlinings is variously estimated at between 500 million and 1000 million m² per year, and constantly growing. The majority of the growth in fact is taking place in the non-woven sector, with woven and knitted fabrics staying fairly static. As a result, the main growth market in machinery/application techniques is for the paste dot system via the rotary screen.

Hats: Although the conventional hat market has been steadily shrinking for the past 50 years, those hats that are still produced mostly utilise coated or laminated materials. Conventional hats of any type will incorporate coated stiffening fabrics very similar to fusible interlinings.

The modern and popular 'baseball' cap in fact represents the single largest market for laminated materials in the USA, and its growing popularity throughout the rest of the world means a significant growth market sector for lamination. Traditionally this has been based upon a flame laminated fabric to a polyurethane foam with a knitted light-weight nylon lining, but more recently some manufacturers are eliminating the PU foam and laminating two textile materials together, utilising other (such as powder) laminating techniques.

Label stock: Until the 1970s, the majority of labels were produced by weaving into a woven fabric the appropriate words, and sewing the label so-produced into the garment. By the 1990s that product had almost completely disappeared, and labels are today produced primarily by

printing onto a woven fabric the relevant information, which can then be either sewn or stuck into the garment. In either case, coating plays an important part.

- (1) The 'label stock' is typically made from fairly light-weight woven fabric that needs to be stabilised and prevented from fraying by coating with a filled resin incorporating titanium dioxide in order to create a good smooth white base onto which the print can be applied.
- (2) Those labels that are not sewn into the garment will be stuck into it, or onto the back of carpets and other materials, using a thermoplastic adhesive generally applied either as a powder or as a hot melt after the printing process.

Pressure-sensitive adhesive tapes: These were traditionally based upon solvent-based natural and synthetic rubbers, but increasingly today are produced from water-based acrylic adhesives. They are extensively used in many industries, and as surgical dressings. Woven and non-woven fabrics and films are the primary products, with the adhesive generally being applied to a release paper, which is laminated to the primary substrate after drying.

Thermoplastic adhesive coated tapes: Essentially these are the same as pressure-sensitive adhesive tapes, except that the adhesive coating is heat-reactivated. The product can be produced either using thermoplastic powders or hot melt coatings.

Thermoset adhesive coated tapes: These are the same as the thermoplastic product, but when the tape is subjected to a higher temperature than required to reactivate the adhesive, polymerisation of the adhesive occurs, making further heat-reactivation impossible and thereby achieving an improved level of durability to the inter-product bond against washing, dry-cleaning, and so on.

Belts: A large volume of artificial leather is used for the production of belts.

Tee-shirt transfers: Tee-shirt transfers, which may be flocked or decorated with glitter, are essentially coated products, transferred onto the garment on a fusing press in much the same way as fusible interlinings are adhered.

Sport and leisure

Anoraks: The purpose of an anorak is to keep the wearer dry, warm and comfortable without restricting his or her movement. While anoraks used to be made from rubber-coated fabrics applied as multiple coats from solvent solution, the majority today are produced using water-based polyurethanes or acrylic resin systems applied as one or two coats, and in the more technically sophisticated products, 'breathability' of the coating can be achieved by the selection of the correct compounds.

Coat-weights of as little as 8–10 g m⁻² are adequate to achieve the performance standard required of the majority of domestic anoraks, and this therefore represents a relatively low-cost, high-volume market based generally upon 60 g m⁻² (2 oz per sq yd) woven nylon fabrics.

Motorcycle clothing: Artificial leathers are produced based on polyurethane materials coated onto woven or needlefelt fabrics and can closely simulate the performance of real leather.

Rainwear: Tradition rainwear can be made water-repellent by the application of silicone or fluorochemical water-repellents, but can have the level of waterproofness enhanced by coating the inner surface with urethane or acrylic resin systems. This gives a waterproof film on the fabric that can be 'breathable', permitting the passage of water vapour.

Sports clothes: By the use of 'breathable' acrylic or polyurethane coatings, garments can be produced that are light-weight, waterproof (but water-vapour-transmitting), and free from 'noise'. Garments can be created that are suitable for all kinds of sporting applications, including climbing, cycling, skiing, sailing, golf and angling.

Swim-wear: Even some swim-wear is coated on the inner surface in order to produce a dry surface in contact with the skin and thereby reduce the possible adverse effect on the skin of having a permanently damp fabric in contact with it.

Work-wear

Fire-retardant and waterproof garments: In designing a garment for use by Police, Fire Brigades and others working in high-temperature, hazardous environments, it is necessary to utilise materials that will not burn or melt, and which will not evolve any toxic fume when subjected to high temperatures or any other adverse environmental conditions.

To achieve these properties, non-burning, non-melting fabrics are coated with suitably fire-retardant coating compounds, which often also have high-visibility pigments incorporated. The resultant suits need to be flexible, comfortable, and to protect the wearer against all of the adverse conditions that may be experienced, and this is achieved by creating a multi-layer composite structure embodying not only fire retardancy and water-repellency but also thermal insulation, permitting the wearer to be exposed to high temperatures for extended periods without injury to the wearer.

Foul weather protective clothing: Foul weather protective clothing is primarily based upon solvent-based or water-based polyurethanes, acrylics, silicones or mixtures of these materials, and these systems have largely replaced PVC-based materials in the same applications, because of the lighter weight, greater flexibility and the fact that 'breathability' can be created by suitably formulating and constructing coatings based upon these chemical systems.

Garments produced from these systems (including high visibility garments) are widely used in the following fields: postal and courier industries, telecommunications industry; electricity, gas, water and sewerage utilities; building industry; coal mining industry; fishing industry; armed forces; airport and airline personnel; traffic-crossing personnel; traffic wardens; police, fire brigade and ambulance staff.

Protective clothing against mechanical damage: By the correct selection of coating compounds imbuing high abrasion and scuff resistance, garments can be produced with very high resistance to mechanical damage. Such garments are frequently employed by persons working in the following fields: police, prison service, military (garments, equipment and camouflage).

Nuclear, chemical and biological protection suits: Again, by the correct selection of the coating compounds, the wearer can be protected against the ingress of chemicals, biological agents and nuclear radiation.

Military: The military field utilises large quantities of coated fabrics in one form or another for tenting, gun covers, rucksacks, ammunition pouches, ponchos, camouflage for personnel and equipment, nuclear, chemical and biological protection suits, and so on.

13.3.2 Domestic applications

Artificial leather

Wholly synthetic artificial leather is produced by:

- (1) *direct coating PVC or polyurethane (PU) compounds onto fabrics*, followed by printing and post-embossing to give a leather pattern and grain effect. However, in direct coating, relatively expensive fabrics have to be employed and the resultant product tends to be rather stiff. These materials are therefore normally only used in those applications where such properties are required and can be afforded (heavy-duty belts and certain shoe applications, for example).
- (2) *nitrile rubber coatings* – nitrile rubber, which has until recently only been available in solvent solution, is now available in aqueous latex form, and can be coated onto fabrics at open-width, or in finished article form (gloves, boots, and so on). After appropriate processing, it will give rise to exceptionally hard-wearing yet soft and flexible products affording considerable protection for persons operating in environmentally hazardous conditions.
- (3) *transfer coating PU and PVC compounds* onto relatively light-weight and dimensionally unstable knitted, non-woven and woven fabrics. Transfer coating (Section 13.5.12) produces much softer products that more closely correspond to the characteristics of real leather. Dependent upon the weight of coating and the number of coats applied, the products can be used for upholstery, shoes, belts, and all of the various luggage products detailed below. After coating, the product will normally be printed and embossed, or may be produced from embossed release paper to give a surface texture by that method.
- (4) *coating onto pre-impregnated fabric* – for the best quality artificial leather, the coating will be applied not to a standard fabric, but to a fabric that has itself has been impregnated with a polyurethane or other type of resin system. The resin is coagulated by passing the material from a coating head into a water bath where a solvent exchange occurs, stripping the dimethylformamide from the coating compound, and creating the formation of a micro-porous structure within the textile, which simulates physically (if not chemically) the structure within leather. This ‘coagulated base’ can then be coated in the direct or transfer coating techniques described.
- (5) *leather split enhancement* – natural leather is split into two layers: the outer forms the natural leather as we know it, while the inner layer (sometimes called the ‘split’) is a much less valuable material. This may however be ‘enhanced’ by coating a film of polyurethane onto it

to produce a product that is genuinely leather-based, but which has a synthetic polyurethane surface. This product is very widely used for the production of shoes and garments, which can be genuinely described as real leather, because the artificial component is only a surface finish, and represents a relatively small percentage of the total weight of the product.

Baby pram covers and hoods

Pram covers are frequently made from either PVC-coated fabrics or fabrics laminated with pre-cast PVC film to achieve a wind- and waterproof protection that is easily wiped clean.

Bath mats

Bath mats are produced by coating a mechanically-foamed crosslinked rubber compound onto the back of a fabric. This is normally then embossed to create the maximum 'non-slip' characteristics in the finished product.

Blinds

Window blinds may be of several types:

- (1) roller blinds with warp-knitted, woven or non-woven fabrics;
- (2) pleated blinds, with warp-knitted fabrics;
- (3) vertical blinds, with warp-knitted, woven, or non-woven fabrics.

By selecting appropriate grades of resin systems, fabrics can be coated for all of the above blind types. In addition, by applying a carbon-black-filled resin system, 'black-out' blinds can be produced, which prevent the penetration of light into a room. Blinds may also be flocked on the inner side, to give an aesthetically attractive appearance.

Camping

By coating relatively light-weight woven synthetic fibres with solvent- or water-based acrylic or polyurethane, fabrics can be made waterproof for applications such as tents, groundsheets and sleeping bags.

Carpet backing

As with bath mats, tufted carpets are generally coated, both to anchor the tuft into the backing fabric, and to create a foam cushion on the under-side of the carpet. Secondary backing also utilises coating with non-foamed rubber systems. Needlefelt carpets are coated or impregnated with rubber or resin systems to achieve stability and abrasion resistance.

Curtaining

It is estimated that, in 1990, more than 100 million m² of fabric were coated with mechanically

foamed acrylic coating compounds for the UK market alone. The acrylic resin with appropriate fillers is mechanically foamed and coated onto the woven, knitted or non-woven fabric and a low weight of viscose or cotton flock is applied to the surface to give a textile feel to the material.

Curtain face fabrics, curtain linings and black-out fabrics are produced in this manner. The black-out fabric will have two or three layers of coating applied with one of these incorporating carbon black to prevent light penetration.

Curtains can be made fire-retardant by incorporating appropriate fire-retardant chemicals into the coating compound.

Shower curtains are frequently coated with acrylic or silicone acrylic mixtures in order to create a waterproof structure.

Electrical insulating tapes

The total market world-wide for electrical insulating tapes is enormous, and all of these are produced by coating solvent-based pressure-sensitive adhesives onto fabrics or films. Water-based systems cannot currently be used because the aqueous adhesives incorporate certain wetting agents that result in a residual moisture content, which adversely affects the insulation characteristics of the product.

Filter fabrics

The operation of domestic vacuum cleaners results in a flow of air through the vacuum cleaner that is discharged back into the room but contains considerable quantities of fine-particle-size dust. This can give rise to allergy problems for an increasing number of people. The problem can be significantly reduced by incorporating a suitable filter into the discharge air-stream. These filters are made by coating a woven or non-woven fabric with a mechanically foamed acrylic resin, which is caused to collapse in the drying oven. Dependent upon the compound formulation and the processing conditions in the mechanical foamer and the drying oven, the pore sizes left in the collapsed foam can be pre-determined and filter fabrics can be produced able to hold back all particles above a specified size.

At the other end of the scale, coal-fired power stations require to remove the particulate matter from their discharges. This is efficiently achieved by utilising filter rooms the size of a football pitch containing coated fabric filters supported on skeletal frames. The air is drawn into the filter sock with the particulate matter being held on the outside surface, which is the coated surface. By stopping the air flow and applying either a slight reverse air flow or vibration, virtually all of the collected dust can be caused to fall from the coated surface, regenerating the filter to its original efficiency level.

On such installations, cleaning procedures are automatically carried out under the control of differential pressure switches that determine the operating efficiency of the unit and effect the cleaning process at the appropriate intervals.

Floor coverings (soft)

With the exception of the best quality woven carpets, virtually all floor coverings are coated in one way or another. Tufted carpets will be coated for tuft stabilisation. Foam-backed carpets are coated with heavy-weights of heavily filled latex, which is mechanically foamed and gelled during the coating process, and may be embossed. Secondary-backed carpeting has a woven hessian or other backing material laminated to the primary tufted carpet. Needlefelts are coated with acrylic resins to stabilise and improve the performance characteristics. An important market also exists for flocked carpeting where the coarse denier nylon flock is adhered to the substrate in a coating and flocking process, with a mechanically or chemically foamed polyurethane or PVC 'cushion' layer being subsequently applied to the under side of the flocked substrate to create the finished product.

Floor coverings (hard)

A very significant market has built up over the last couple of decades, primarily based upon PVC plastisols applied to woven or non-woven scrims, generally made from glass, which give extremely good durability and dimensional stability, and which are printed, embossed and colourised according to the design requirements of the market.

Intumescent coatings

Certain coatings can be designed to create high-temperature, insulating, cellular structures when subjected to high temperatures, which cause the liberation of certain gaseous materials and in the process create thermally insulating barriers. If such materials are incorporated onto or into garments offering protection against high temperatures and flames, very considerable enhancement of the performance of the product can be achieved.

Kitchen items

There are many kitchen and domestic fabrics coated with a clear, high-gloss PVC on top of a printed fabric, achieving a cheerful, colourful and easily-cleaned finished product ideal for tablecloths, aprons, shopping bags, tea cosies and similar products.

Linoleum

Traditional linoleum floor coverings were produced by appropriately coating a woven or non-woven fabric structure. Today, traditional linoleum has been virtually totally replaced by PVC-coated materials, which have very much higher durability and 'cleanability', and which are usually produced by coating one or more layers of filled, high-abrasion-resistant PVC plastisols onto a woven or non-woven glass scrim with surface printing or texturing, or colouration being introduced by appropriate techniques.

Luggage

A wide range of handbags, purses, spectacle cases, wallets, cheque book covers, credit card holders, suitcases, hold-alls, and so on, are produced from artificial leather cloth, which is produced from either PVC- or polyurethane-coating of fabric by the transfer coating technique (Section 13.5.12).

While fabric sports bags do not need to be ‘breathable’, they do need to be waterproof. Coating not only allows a waterproof agent to be applied, but also provides a degree of stabilisation, allowing lighter-weight and lower-cost fabrics to be used.

Mattress tickings

Conventionally, mattress tickings have been Jacquard woven fabrics, which are relatively expensive because of the relatively heavy fibre weight and the slow speed of production. Within the USA, this market has almost entirely changed over to woven, warp-knit or stitch-bonded fabrics coated with a mechanically foamed acrylic resin system and post-printed to give the same optical appearance in the finished product, but produced at a much lower cost because of the lower fabric weight and much higher production speeds. By incorporating fire retardants, the ticking can be made non-flammable. By suitably formulating and adjusting the coating conditions, it can also be made waterproof.

This trend is being followed elsewhere around the world and already significant quantities of coated mattress tickings are being produced in Europe and certain other markets.

Pillow cases and duvet covers

To prevent the escape of down, feather and fibre, or small particles these materials, from passing through pillow cases and duvet covers, the inside surface is coated with a mechanically foamed acrylic, which collapses in the heat of the oven and produces a micro-filter system in the same way as for filter fabrics (see above).

Roofing systems

Many industrial and domestic roofs incorporate coated fabrics in order to create a waterproof layer beneath the roof tiles or slates. These materials are generally based upon bitumen-coated glass or similar materials, frequently incorporating fire-retardant additives.

Similar products are extensively used for the thermal insulation of air conditioning ducting where a fibreglass or Rockwool slab will also be incorporated into the product.

Sails

Today, many sails are made of light-weight, high-strength fabrics that are coated with relatively hard resins to give particular surface effects to enhance the performance of the boat. Other sails are made from laminates of films and foils with themselves or textiles, in order to achieve the particular characteristics sought by the designer.

Sports balls

The use of real leather for the production of balls is today very rare, and most footballs, rugby balls, and other sporting balls are made from artificial leathers produced by appropriately coating fabrics with polyurethanes or PVC.

Surgical dressings

Traditionally, surgical sticky plasters have been produced by coating fabrics or films with an adhesive applied from solvent (frequently petrol). However, not only is this a somewhat hazardous coating process, but the product has to be dried under very careful conditions to ensure the total elimination of the petrol, otherwise skin allergies can result. Recently suitable acrylic adhesive systems have been developed that are now replacing the solvent-based materials, and which have none of the disadvantageous characteristics. Furthermore, by mechanically foaming the compound it is possible to further reduce the adhesive weight without any reduction in performance, and this allows both a reduction in cost and an improvement in the breathability of the product.

Upholstery

Conventional uncoated upholstery fabric has to be relatively strong, heavy and expensive, in order to withstand the treatment that it will receive. If the fabric is back-coated with suitably formulated acrylic or SBR (styrene butadiene rubber) systems, a significant reduction in the fibre weight and the finished product cost can be achieved, without any reduction in the performance of the product in use. This is achieved because the coating stabilises the fabric, preventing the movement of the warp and weft yarns relative to each other, and therefore enhances the performance of the fabric.

Back-coating of the fabric is also important in overcoming 'seam slippage', which can be a serious problem on certain constructions of fabric if no back-coating stabilisation has been applied.

Where fire-retardant fabrics are required (BS 5852 Parts 1 and 2, for example), there are three possible methods of achieving the desired results:

- (1) non-flammable fibres can be used, but these are expensive;
- (2) cellulosic fabrics can be impregnated with suitable fire-retardant chemicals, but these have an adverse effect upon the colour and strength of the fabrics, resulting in a need to produce a heavier-weight fabric in order to achieve the required strength characteristics;
- (3) all fibre systems and fabric types can be back-coated with suitably formulated acrylic or SBR latex systems incorporating the appropriate fire retardants. This will not only achieve the fire retardancy standards required, but the overall performance properties of the fabrics are improved, permitting a fibre weight reduction.

Umbrellas

Umbrella fabrics are coated to improve performance.

Wallcoverings

The majority of wallcoverings comprise printed paper that may have a coating on it to confer 'washability' and to improve the durability of the product. However, a considerable market exists for textile wallcoverings – taking the form of warp yarns, woven or knitted fabrics, or flock – all of which will usually have been coated and laminated either to paper or to a non-woven fabric, in order to give dimensional stability to the product, and facilitate its adhesion to the wall.

Wiping cloths

A wide range of artificial chamois leathers, sponges and wipes exist, which are usually produced by impregnating a relatively thick non-woven fabric with a suitable resin system. This is then coagulated as described above in order to create a sponge-like product that has high water absorbency and good dimensionally stability because the coagulated resin binds all the fibres together. The microporous structure that results can be used to take up considerable quantities of water.

Waterproof sheeting

Conventionally produced by coating rubber solution onto fabric, waterproof sheeting is today most commonly produced by either polyethylene film extrusion coating of non-wovens, or by coating PVC, water-based acrylics or silicone elastomers onto woven fabrics, depending upon the application and durability required in the finished product and the cost that can be afforded.

13.3.3 Industrial applications

Table 13.11 summarises the applications of coated and laminated fabrics in industry.

Table 13.11 Industrial applications of coated and laminated fabrics

Industrial field	Application of coated/laminated fabric
Abrasion products	Sanding discs, belts, etc. produced by depositing appropriate particle size of abrasive material (glass, Carborundum, aluminium oxide) into coating of adhesive on pre-coated and stabilised fabric
Aeronautical applications	Aviation fuel carried in multi-ply coated fabric flexible tanks in aircraft wings ≤ 38% of weight of commercial jet liners, and ≤ 70% of modern military aircraft, made of coated fabrics. Wings, wing flaps, tail sections, nose cones, passenger compartment floors, internal panels, etc., all made from epoxy-resin-coated glass, carbon fibre, Kevlar and

Table 13.11 continued on next page

Table 13.11 *Continued*

Industrial field	Application of coated/laminated fabric
Aeronautical applications continued	other speciality fibres alone or in combination – achieves required performance characteristics with significant weight reduction compared to metal Bodies of executive jets and helicopters can be made almost entirely of these materials
Automotive fabrics	Bulk of air-bags produced using solvent-based synthetic rubber (USA) or 100% silicone elastomer (Europe and Japan). Seats, door panels, headliners, carpets, pillar trims and acoustic insulation in cars, trucks etc. are coated and laminated to achieve required characteristics
Awnings and tarpaulins	Awning fabrics in domestic and industrial applications coated to improve durability and reduce soiling rate. Tarpaulins for trucks, lorries, railway wagons, etc. and for protection of bulk storage of grain
Bags and sacks	Industrial bags and sacks (e.g. as used by Post Office) and dry bulk storage bags (e.g. for transportation of cement, sugar, grain, fertilisers) made from coated fabrics
Banner fabrics	Coated to improve durability and stability, and to minimise fray
Book-bindings	'Leather' book-bindings are today almost all coated fabrics
Building materials	Much coated/laminated material incorporated into industrial and domestic buildings for thermal and acoustic insulation and waterproofing
Bulk liquid carriers (dracones)	Multi-ply rubber-coated tanks used extensively to transport water or other liquids, mounted on lorries or towed behind vessels (towed tanks can be several hundred metres long, and contain thousands of tonnes of liquid)
Composites	Most composites are, by definition, coated fabrics
Conveyor belts	Mostly based upon nylon or polyester fabrics coated with PVC, polyurethane or silicone elastomers, or PTFE, depending on application and processing conditions of production line
Dirigibles, hot air balloons	To minimise weight and maximise efficiency, most are made by applying light-weight, airtight coating onto light-weight, tightly woven ripstop nylon fabric
Electrical goods	Large quantities of coated fabrics incorporated into electrical goods, cables, etc.
Filter fabrics, for removal of particles from discharged air	Many applications e.g. in coal-burning power stations. Filter fabrics produced as for domestic use (see Section 13.3.2)
Fire-retardant protective aprons, screens, etc.	Fabric coated to create non-flammable material with good thermal insulation characteristics to protect wearer/object
Geotextiles, used in construction	Fabric coated to enhance stabilisation, and to limit particular passage through textile, as in filter fabric
Hoses	Most hoses incorporate coated fabrics

Table 13.11 continued on next page

Table 13.11 *Continued*

Industrial field	Application of coated/laminated fabric
Hovercraft skirts	Based upon heavy-duty coatings on fabric substrates
Marine applications	Inflatable boats, protective and foul weather clothing etc. made from coated/laminated fabrics Life jackets primarily produced by coating suitable fabric structure with a polyurethane system Sail fabrics made from very tightly woven flat base fabric coated to create required characteristics for efficient wind catchment Sail boards, dinghies, ocean racing yachts and minesweepers increasingly being constructed from prepgres made from epoxy-resin-coated glass, carbon and Kevlar-based fabrics
Military textiles	Covers for protection of military equipment against weather, photography etc., camouflage, groundsheets, sleeping bags, tarpaulins, tents made from coated/laminated fabrics
PVC film coated with pressure-sensitive adhesives	For packing, electrical insulation, nuclear constructions, gas industry, etc.
Printing blanket	Excellent durability and uniformity of thickness achieved by multi-pass coating of the base substrate
Seals and gaskets	Often made by coating textile with appropriate compound
Insulating products	Electrical, acoustic and thermal insulating products – frequently coated

Table 13.12 Medical applications of coated and laminated fabrics

Medical area	Application of coated/laminated fabric
Surgical dressings	Coated with adhesives
Surgeons' gowns and hospital drapes	Coated to confer protection against passage of blood and bacteria. Increasingly, market is being met by use of water-vapour-permeable but liquid- and virus-impermeable fabric laminates – expensive but higher performance and can be re-sterilised many times, making overall cost lower than for disposable products
Biocidal wipes	Produced using micro-encapsulated sterilants on substrate
Plaster of Paris	Coating on a fabric substrate
Waterproof products	Primarily produced by coating an appropriate substrate

13.3.4 Medical applications

Medical applications of coated and laminated fabrics are summarised in Table 13.12.

13.4 COATING COMPOUNDS

Before 1940, almost all coating compounds were naturally-occurring materials usually dissolved in solvent and applied by fairly laborious and inefficient techniques. Natural rubbers, nitrocellulose and waxes were just about the extent of the coating compounds available, and were used in one form or another for virtually all of the limited range of coated products produced at that time.

Similarly, what little lamination was undertaken utilised in the main either solvent-based natural rubber or water-based starches. Since then, an enormous expansion in the range of products available has occurred, and a steady movement from solvent-based systems to the use of compounds in other forms has been forced on manufacturers by virtue of the increasing cost of solvents and the legislation requiring the elimination of solvent discharge into the atmosphere.

Undoubtedly, the Second World War from 1939 to 1946 (when the war in the Pacific finally ended) led to the development of many new chemical systems in order to meet the demands of the Military. After the war, chemical companies were keen to expand and exploit the range of products produced for industrial and commercial reasons, and this gave rise to an extensive range of new polymers – mostly, but not exclusively, derived from oil feedstock – which today play an essential part in our everyday lives.

The pressures for change from the pre-1940-type materials to those more normally utilised today comprised a combination of the need to move away from the relatively expensive solvent systems because of commercial pressures and because of the dangers associated with the use of solvents, together with the legislative pressures for the protection of the environment. (For further details of these pressures, see Section 13.12).

The following are the more important categories of coating compounds, laminating and flocking adhesives, and prepregging resin systems:

13.4.1 Natural and synthetic rubbers

There can be little doubt that both natural and synthetically produced (from oil feedstock) rubbers comprise one of the most important groups of coating compounds. Furthermore, there is little likelihood that they will be replaced, because there is scant chance that alternatives will be produced with the combination of chemical and physical performance properties that has made synthetic rubbers in particular such an important group of compounds.

Synthetic rubbers include:

- (1) butyl = polyisobutylene;
- (2) styrene butadiene rubber (SBR);
- (3) nitrile = butadiene acrylonitrile;
- (4) neoprene = polychloroprene;
- (5) hypalon = chlorosulphonated polyethylene;
- (6) viton = fluorocarbon;
- (7) silicone elastomers.

13.4.2 PVC plastisols and emulsions

There is currently some considerable debate about the potential environmental problems associated with the use of the PVC compounds because of their chlorine content and the presence of plasticisers that partially evaporate during the coating process, and which can subsequently leech into materials with which they come into contact. Considerable controversy continues to be waged between pro- and anti-PVC lobbies, but it is unlikely that PVC could be outlawed until and unless some suitable alternative compounds became available at comparable cost levels. There are now certain acrylic compounds that have been developed specifically to replace PVC plastisols and which are satisfactorily achieving the required results in certain applications. The significantly higher costs of acrylic systems compared to PVC do make it necessary that lower coat-weights achieve equal performance, and although this cannot be described as universally achieved, it is possible in certain applications such as the coating of tablecloth fabrics, aprons and shopping bag fabrics – and one may hope that at some not-too-distant future date, tarpaulins and other industrial-type fabrics could also utilise such newer materials in place of the PVC systems that currently predominate.

13.4.3 PVAs – polyvinyl alcohols

PVAs are water-based materials, generally used as laminating adhesives not only in the textile industry but also extensively in the paper and timber markets, where their relatively low-cost characteristics make them attractive and their lack of resistance to washing and dry-cleaning are essentially irrelevant.

Although chemically different from polyvinyl alcohol, polyvinyl acetate is used in very much the same way and in the same applications.

13.4.4 Phenolic, urea formaldehyde, melamine formaldehyde, and so on

This group of resins, although not widely used in the textile coating market other than as small percentage additives in other compounds, are extensively used in the production of paper or glass fabric-based industrial laminates, decorative surfacing laminates and printed circuit boards. While some of the materials may be applied by impregnation techniques, surface coating techniques are also relevant.

13.4.5 Acrylics

Acrylics were most extensively used in solvent-based solution for the coating of light-weight nylons, for example, in the production of low-cost waterproof fabric for tenting and so on in the 1960s and 1970s. With the advent of similar acrylic resins in aqueous dispersion, a lot of the solvent-based materials have been replaced and this movement from solvent- to water-based systems has opened up very large sections of new market for acrylic systems in the coating of:

- (1) curtains, curtain linings and black-out fabrics;
- (2) vertical, roller and pleated blinds;

- (3) shower curtains;
- (4) air-permeable mattress tickings, duvet and pillow slip covers impermeable to dust and microfibre penetration;
- (5) filtration fabrics for a wide range of applications from coal-fired power stations down to domestic vacuum cleaners;
- (6) a wide range of pressure-sensitive adhesives for electrical, surgical and other industrial and domestic adhesive tapes;
- (7) as a binder resin for fire retardants for the back-coating of upholstery and curtaining fabrics, for example, achieving both stabilisation and fire retardancy in the finished product.

13.4.6 Polyurethanes

Again, the majority of polyurethane resin systems became available first in solvent solution, and were extensively used in the late 1960s and early 1970s for the production of the higher-performance, higher-cost waterproof fabrics and artificial leathers.

Considerable effort has been applied by many polyurethane resin manufacturers to devise suitable water-based products, but until recently most of the products that have been launched in the market have failed for one technical reason or another, and have been withdrawn. Recently, however, some significantly good quality products have been accepted into commercial use, and as the pressures to move away from solvent-based systems grow, the importance of water-based polyurethanes will increase. However, as with other chemical systems, there is further pressure to move away from the water-based materials, and polyurethanes are one of those compounds now beginning to become available as 100% solids liquids or powders. These can be applied to fabrics and other substrates by conventional blade coating techniques (in the case of heat-cured or UV-cured 100% solids liquids), or by extrusion coating (in the case of hot melt 100% solids resins) or by powder coating techniques using cryogenically ground materials. (Cryogenic grinding is a technique where lumps of polymer are reduced to fine particle sizes by subjecting the material to appropriate grinding techniques while held at very low temperatures in a liquid nitrogen bath.)

One of the most important recent developments has been the successful design and production of a group of materials known as PURs. The polyurethane PUR is a chemically reactive hot melt polyurethane adhesive, which reacts with moisture in the substrate to which it is applied and/or water vapour from the air to produce a crosslinked network. Very small quantities of moisture are required (0.3–1.0% typically) to cure the PUR. The speed of cure or crosslinking can be increased or decreased by the use of special catalysts, which, while not affecting the thermal stability of the molten adhesive, do increase or decrease the reaction rate. A wide range of properties can be built into the adhesives, such as extended open time, appropriate viscosity, green wet strength, final bond strength, elastic modulus, wash resistance, antistatic characteristics, fire retardancy, and so on.

While the use of these materials is still in its infancy, there can be little doubt that they will play a very important role in the coating and lamination market, not only in textiles, but in an extensive range of other markets. This is because, although the base chemical cost is high, the

usage rate is exceptionally low, resulting in a technically excellent product at cost levels that may well under-cut those achievable by other more conventional coating and laminating techniques, such as flame and other adhesive systems.

13.4.7 Silicones

Initially, silicones could be applied to textiles only as solvent solutions. Silicone resins were applied by dipping techniques to coat glass and other fabrics to produce electrical insulating tapes, cable braids and rovings. Silicone elastomers dissolved in solvent were applied by blade coating and by dipping techniques to produce not only electrical insulating products, but also conveyor belting and various gasketing and sealing materials.

As with other polymer systems, research has led to the development of both aqueous silicone emulsions and 100% solids silicone elastomers, which can be applied by various different coating techniques to fabrics and other substrates. Such systems can be heat-cured, UV-cured, or reaction-cured using appropriate catalysts or – in some cases – agents such as peroxides, which achieve the necessary crosslinking and further extend the range of applications into which the silicone polymers can be employed.

13.4.8 Fluorochemicals

Fluorochemical compounds are widely used as surface treatments for metals and as coatings for fabrics to create non-stick, high-temperature-resistant conveyor belting, and architectural textiles used extensively in the light-weight flexible roofing structures employed in a number of airports and sports arenas. The fluorochemical compounds are normally applied onto glass, Aramid, or other high-temperature-resistant fibres by a multiple dip followed by dry process, building up an appropriate thickness of the polymer, which can then be fused at around 400 °C to achieve the required finished product properties.

The same basic fluorochemical polymer can also be produced as a film, which forms the basis of the moisture-vapour-permeable ('breathable') waterproof membrane now extensively used in many garment applications.

13.4.9 Epoxy resins

Epoxy resins – best known to most of us as the two-pack domestic adhesive, or the resin system used for the construction of glass-reinforced plastic canoes and so on – are an extremely important group of polymers, finding widespread application in the construction of an increasing number of elements for commercial and military aircraft, minesweepers, ocean yachts, and a wide range of different marine products.

The epoxy resins are typically applied from solvent solution, but as the pressures increase against the use of solvents, an increasing range of these products are becoming available as 100% solids liquids or powders, which can be applied by the appropriate technique, and heat- or UV-cured, or applied at hot melts so that on cooling they become solid once again.

In most instances where the epoxy resins are being used as prepregging compounds, they will be only partially crosslinked during the coating/impregnating stage and then kept in a deep freeze at -30 °C or below, until such time as the prepreg is laid up in the mould. At this time, a degree of flow between the layers is required, followed by final crosslinking to form the thermoset end-product.

New low-temperature-curing solvent-free epoxy resin systems have recently been granted airworthiness certificates for use in both military and civil aircraft, and one may anticipate a further growth in the importance and usage of these materials.

13.4.10 Polyesters

Although chemically different from epoxy resins, polyesters are also widely used in very much the same applications as epoxies, and are applied in much the same way. The selection of an epoxy or a polyester will largely be based upon the performance requirements of the finished product, and the cost implications.

13.4.11 Powders

Mention has been made above that some of the polymers described are available in powder form. There are in fact other polymer systems that are only available in powder or hot melt form, but which are extremely important compounds in the overall coating market.

- (1) Low-density polyethylene (LDPE) is extensively used for the coating of fusible interlinings and automotive carpeting because of its relative inertness and low cost.
- (2) High-density polyethylene (HDPE), with its higher softening/melting temperature, combined with its inertness and relative low cost, is used for the majority of shirt collar and cuff interlinings coated onto the woven or non-woven fabric by the appropriate 'powder point' or 'paste dot' coating techniques (see Section 13.5.15).
- (3) Ethylene vinyl acetate (EVA), while being similar in cost to the polyethylene-based materials, has a higher degree of tack, which therefore makes it particularly suitable as a low-cost laminating adhesive in applications such as footwear, where it is extensively used throughout the world.
- (4) Polyamides (PA) and co-polyamides with other materials are a more expensive resin form but, with a higher melting temperature than the foregoing, and with considerable chemical inertness, make excellent adhesives in the interlining industry, and they are increasingly important laminating adhesives in those industrial applications where solvent- or water-based adhesives are being replaced with thermoplastic powders.
- (5) Polyesters (PES) and co-polyesters are also expensive materials, but – because of their high-performance characteristics – are becoming increasingly important as solventless and waterless adhesives in industrial applications, including automotive seating fabrics where their high-temperature stability gives them excellent performance properties at relatively low coat-weights.

It should be noted that new variants of polyamide and polyester resins are coming to the market incorporating blocked crosslinking agents, so that while the material is truly thermoplastic at normal processing temperatures, once the product has been heated beyond a certain critical point, it becomes thermoset.

- (6) Polyurethanes (PUs) are, as stated above, now increasingly available as powders and at 100% solids materials, either liquid at room temperature, or liquid at elevated temperatures, and can be applied in such form by blade coating or extrusion coating. A group of polyurethane resins incorporating moisture crosslinking reactants (PURs) are also offering considerable advances in adhesive performance properties having extreme resistance to washing and dry-cleaning, while at the same time being very soft and extensible. However, the cost of these materials is currently very high and further work seems to be needed to ensure that these materials not only meet the necessary toxicity requirements, but also become commercially viable.

In some of the above applications, powders are the only means by which the required end-product can be produced. In other cases, powders – by virtue of their low energy requirement and relatively small-size/low-cost machine demand – are technically and commercially very attractive alternatives to some of the older processing systems.

13.4.12 Fire retardants

To prevent a textile fabric and associated filling materials from suffering from extensive fire damage when subjected to an ignition source, one of the following precautions must be taken.

- (1) The textile fibre can be inherently non-burning. However, these fibres tend also to be extremely expensive, and therefore they are not widely used.
- (2) The textile fibre can be impregnated with suitable fire retardants. However, this only works on cellulosic fibres and even then, the presence of these impregnants has an adverse effect upon the handle, colour and strength of the fibres.
- (3) The textile fabric can have a coating applied to it, which, when heated by the initial ignition of the fabric, will give off certain chemicals that extinguish the flame and any residual afterglow. These chemicals are usually halogens such as decabromo diphenyloxide or variations on this, incorporated into a coating compound with a PVC or halogenated acrylic binder, and with additives such as antimony trioxide, or antimony oxichloride, aluminium trihydrate (which liberates its waters of crystallisation to quench the flame) and phosphorous or boron compounds.

13.4.13 Foamed compounds

Mechanically foamed

The technique of mechanically foaming a compound is well known to anybody who has ever beaten an egg white to make a meringue. The technique, however, has only relatively recently

been introduced to the textile industry. Since its introduction, though, it has become a most important technology applicable to virtually any water-based compound except silicones, and it would certainly be reasonable to suggest that more coating compounds are applied in mechanically foamed form than in non-foamed form today. (All foam-backed carpets are coated with a mechanically foamed natural or synthetic rubber; almost all fire-retardant upholstery and curtaining fabrics are back-coated with mechanically foamed acrylic resins or synthetic rubbers; and an increasingly wide range of other products are produced with lower costs and better technical performance as a result of the introduction of mechanical foaming of the coating compound immediately prior to application to the substrate.)

During mechanical foaming, the density of the compound is reduced by introducing a controlled quantity of air in the form of controlled-sized air bubbles. The effect of this is not only to increase the thickness of compound that can be applied for any given coating weight, but also to thicken the compound up, so that its penetration into the fabric is more controllable. As a result, it is now possible as never before to control both the coat-weight and the degree of penetration of the coating compound into the fabric. Furthermore, because the density has been reduced, it is frequently possible to apply a lower total weight of compound with either no loss of performance properties, or in certain circumstances an actual improvement in performance properties, at the same time as reducing the overall cost per square metre. (For example, surgical adhesive tapes can be produced with a significantly reduced weight of adhesive, but an increased adhesion, by applying a mechanically foamed water-based acrylic adhesive to the substrate, the foam being stabilised so that it is stable at ambient temperature but collapses in the heat of the drying oven.)

Chemically blown

Chemically blown coating compounds have been in the market for rather longer, and utilise a gas-liberating additive in the coating compound. At a certain critical temperature, this additive evolves a gas (usually nitrogen), which creates a cellular structure in the product. Thus, most PVC-based artificial leather utilises a nitrogen-liberating additive dispersed in the PVC plastisol which, at the curing temperature or just below, causes the production of the cellular structure associated with this product.

The difference between chemically blown and mechanically blown compounds is essentially the method by which the cellular structure is achieved, and the time at which it is achieved. Chemical blowing has the disadvantage that in order to achieve the cellular structure an additional chemical and hence cost is required, and that the blowing does not occur until the coating has been applied and is in the oven. This therefore means that none of the advantages of using the reduced density product apply, and we are now seeing moves towards the replacement of chemical blowing with mechanical foaming, which gives a more consistent bubble size and a more controllable finished product.

13.5 COATING METHODS AND MACHINES

13.5.1 Blade-over-air coating

The oldest and simplest coating technique is to use what is known as a blade-over-air coating technique, in which the fabric is supported from below on either side of a suitably shaped doctor blade, which presses strongly into the upper surface of the fabric, so that the coating compound is caused to enter the interstices of the fabric, but almost none is left on the surface (Figure 13.1). By this technique, one is able to apply very low coat-weights such as those employed for making very light-weight fabrics totally impermeable – for example, for anoraks, hot air balloons and similar applications. Coat-weights as low as 7 or 8 g m⁻² are regularly produced by this technique, and millions of metres per year are so coated.

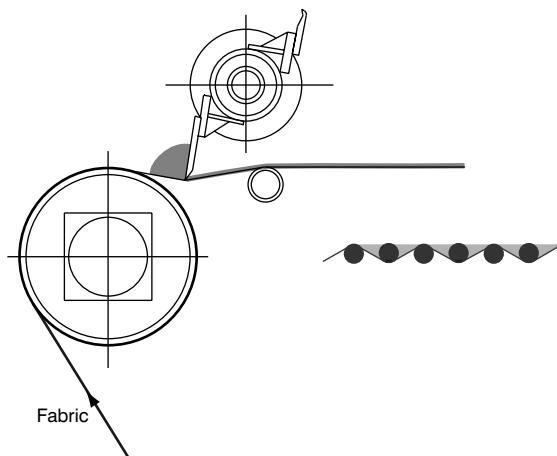


Figure 13.1 Blade-over-air coating

13.5.2 Blade-over-roll coating

A lot of fabrics, however, require to have the interstices sealed first, and then a smooth overall coating applied onto the surface structure of the fabric, in order to increase the abrasion resistance and general performance of the finished product. This is done by the blade-over-roll coating technique, which is in itself the single most important and widely employed method of coating (Figure 13.2).

Here, a suitably profiled doctor blade is located at an accurately controlled gap over a very high precision back-up roller, so that the weight of coating applied is directly related to the gap between the bottom of the blade, and the fabric.

Until fairly recently (around 1970), almost all of the back-up rollers were rubber-covered, which allowed knots, slubs, and other objects of greater-than-the normal fabric thickness to be

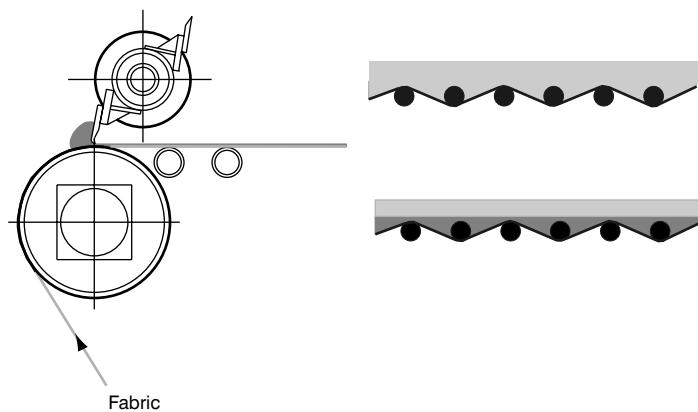


Figure 13.2 Blade-over-roll coating

absorbed into the rubber surface ensuring the passage through the coating blade gap. Unfortunately, however, a rubber roller can only be ground to a maximum tolerance of ± 1 thou. ($25 \mu\text{m}$) and this results in a coat-weight variation of ± 1 oz per sq yd (34 g m^{-2}), which is clearly totally unacceptable in many applications.

The use of a hard chromed back-up roller can reduce this inaccuracy ten-fold, and for that reason, most modern coating heads incorporate such a roller. As a result, in practice, coating uniformities as accurate as $\pm 1 \text{ g m}^{-2}$ are often achievable. In many cases the accuracy is in fact not dictated by the coating head itself, but by the much greater variations in the thickness of the substrate being coated.

13.5.3 Doctor blade profile

While considering blade-over-roll coating, it is appropriate to discuss the importance of the doctor blade profile. In no other coating technique is such a diversity of different profiles employed, and such importance attached to the profile, with regard to the particular characteristics of the coating compounds and the end-product.

Literally hundreds of different profiles have been produced. Admittedly, many of them are, in the author's opinion, totally ridiculous, but one can certainly justify at least three different types of doctor blade, each of which can be sub-divided into a number of different specific characteristics – again according to the nature of the coating compound and the application.

Blade-over-roll coating can be carried out with the coating head being located in front of the drying oven and stenter, or – in the case of stretchy knitted fabrics that would be difficult or impossible to coat at that point – the coating head may be located within the parallel section of the stenter, in such a way that the fabric is held stable at the point of coating, and this then allows an accurately controlled weight to be applied in the previously described manner.

As mentioned earlier, the blade-over-air coating technique is used to apply low coat-weights. In this, one would normally use the first type of blade referred to above – a very sharp blade

chamfered on the outgoing side to create a point, ranging from the sharpest that can be achieved (a 0.5 mm diameter) up to perhaps 4 or 5 mm diameter. The sharper the point, the lower the coat-weight – but the sharpness is not the only consideration. By appropriately angling the blade, and by selecting the degree of depression into the fabric in the blade-over-air application, one is also able to influence the amount of compound that is pushed into the structure of the fabric, and that which is prevented from going forward with the fabric (Figure 13.3).

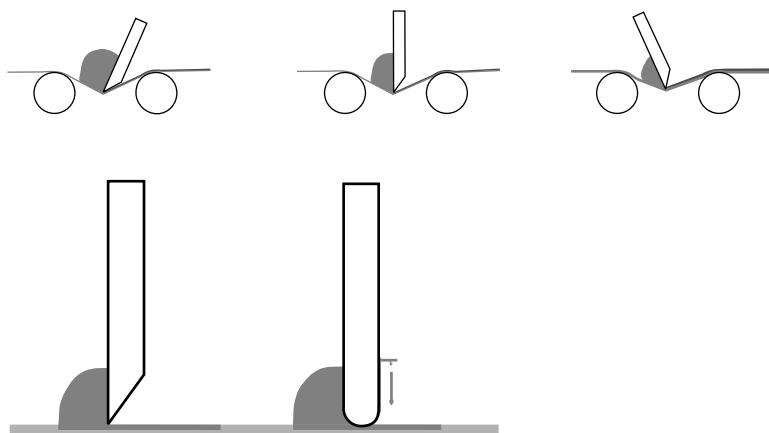


Figure 13.3 Effect of angle change and blade type on coating characteristics

If a blade is chamfered on both sides, the chamfering being in fact a rounding of the blade, one is actually producing a small diameter roller. This is the second type of blade. The wedge effect achieved by the rounded shape results in a considerable hydraulic force to push the coating compound into the structure of the fabric to a greater extent than would occur with the sharp blade, and hence to get a heavier weight coating. This sort of technique is employed where one is using a woven polyester or nylon fabric – as in, say, a tarpaulin, or an air house used to cover a tennis court, for example – and where the first coating must achieve a very high degree of fabric penetration into the tightly woven structure, in order to have good mechanical adhesion to the fibre bundles. Heavy/high-viscosity rubber solutions will also be coated by this method, where one is seeking to achieve multiple coats, each of very low weight, as in the production of printer blankets and other similar structures.

The third group is known as a ‘shoe blade’, because it basically looks very like a piece of footwear. The front of the blade is basically straight, although it may be radius to a certain extent. The base is, however, extended for anything from 2 to 30 mm, and the ‘toe’ is cut away very sharply to form the point, which will be closest to the fabric in the actual operating situation. The position of the doctor blade in relation to the back-up roller, and the angle of the blade, will create the precise coating conditions necessary to achieve the required results; thus, if the ‘heel’ is elevated by virtue either of the blade angle or the position of the blade relative to the top of the roller, the wedge so formed will be filled with coating compound under considerable hydraulic pressure, which will result in considerable penetration of the compound

into the base fabric, if this is possible (Figure 13.4). If, however, the fabric has previously been sealed by blade-over-air coating or previous blade-over-roll coatings – or if the substrate is in fact an impermeable layer such as paper, film or foil – the hydraulic pressure will result in a high-quality surface on the coating emerging from the tip of the blade.

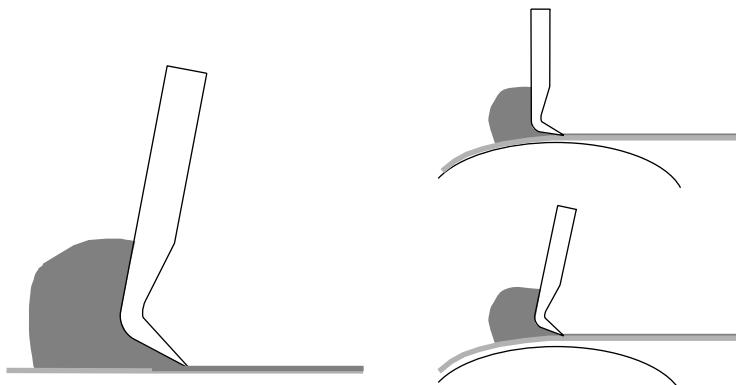


Figure 13.4 Effect of variable blade angle on coat-weight profile, for a 'shoe blade'

This aspect is in itself more than justification for the use of the shoe blade principle, but there is in fact another and even more important reason in certain cases – namely, there are coating compounds such as PVC plastisols and some of the recently developed 'breathable' polyurethane (PU) compounds that will, through their particular surface tension characteristics, climb up the back of a round- or sharp-nosed blade, to fall off onto the surface, giving the appearance of handfuls of rice having been thrown onto the surface, which is of course an entirely unacceptable situation. The sharp cut-back at the toe of a shoe blade makes it impossible for the coating compound to do this, and hence, all PVC plastisol coatings must employ this type of blade.

Additionally, where one is seeking to carry out blade-over-air coatings to achieve light-weight depositions of the above mentioned breathable PUs, one is also forced to use the same shoe principle, although here of course the length of the shoe must be as short as possible, in order to achieve the lowest possible coat-weight. One may infer from this that the coat-weight achieved with a shoe blade is related to the length of the foot. If in a given application, after adjusting the position and angle of the blade, there is still too much penetration or too heavy a coat-weight, reducing the length of the foot of the blade will also reduce the coat-weight and penetration. Reducing the wedge angle underneath the foot will achieve a similar result. Going to a sharp angle on the ingoing side, instead of a radiused angle, achieves the same result, although at a relatively small coat-weight differential.

Consideration of the position of the blade over the crown of the roller (Figure 13.5), and its angle, relates to the same factors, with the following exception: if the doctor blade is at a point after the crown of the roller, and the gap is set according to the coat-weight required, it will result in the fabric pressing up against the under-side of the blade, and an unsatisfactory blade-over-air coating situation will result. This in fact has to be taken advantage of, if one is trying to

coat a fabric with a very heavily three-dimensional surface (the under-side, of course, in the coating process at most times), since if regular blade-over-roll coating techniques are employed, the thickness of coating will be the mirror image of the three-dimensional surface. In that situation, the blade must be set at the appropriate gap above the fabric (not above the roller), so that there is an air gap between the under-side of the fabric and the back-up roller, equivalent to the pile height variation, or slub variation, as the case may be. For this system to work, of course, one does have to have a coating compound that is not in itself going to cause the fabric to be depressed, and this means that the fabric coating must be done by a mechanically foamed compound, which is of relatively light weight, and can be held back above the point of the blade, and this then results in an extremely accurate and uniform coating being achieved (Figure 13.6).

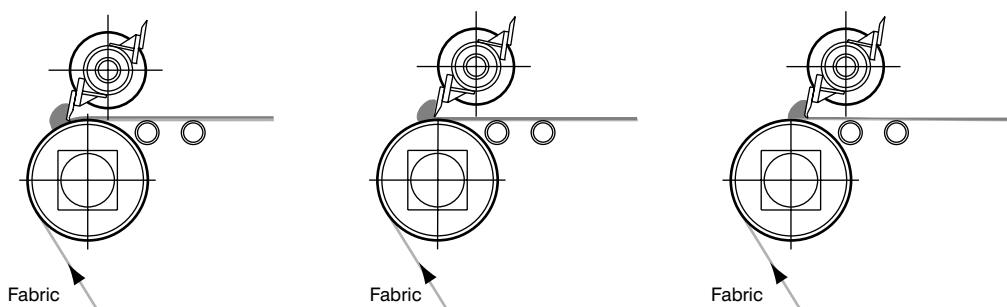


Figure 13.5 Adjustment of blade position in blade-over-roll coating

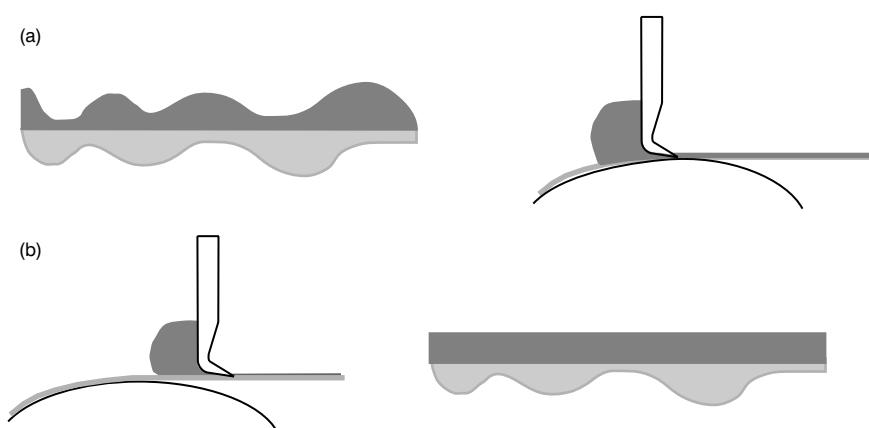


Figure 13.6 (a) Effect of variable thickness fabric coated blade-over-roll and (b) how to get a uniform thickness

13.5.4 Reverse-roll

The reverse-roll technique is extremely important for the application of very low coat-weights at great uniformity onto impermeable substrates, or for the maximum compression of coating compounds into fabric structures. As a result, reverse-roll coating is most frequently employed for paper, film and foil coating and rarely in the textile industry – partly because it is not generally appropriate, partly because the coating head is more expensive, and partly because it is more difficult for the average operator to successfully understand, and hence operate (Figure 13.7).

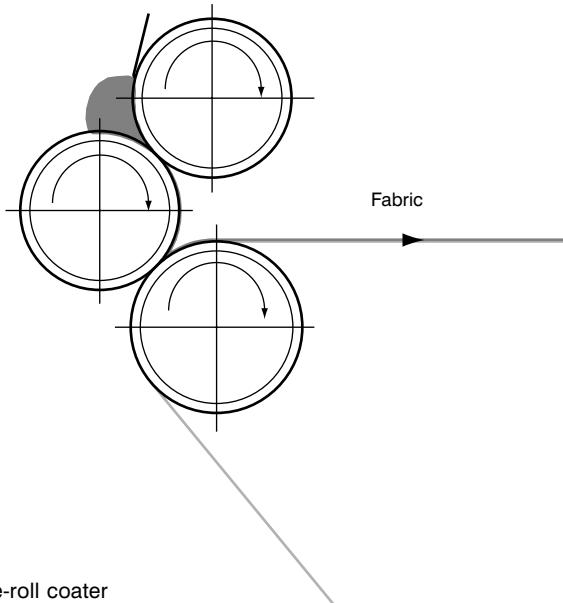


Figure 13.7 Reverse-roll coater

The exact configuration of the rollers one to the other and the precise number of rollers can vary according to the nature of the coating compound being applied, the substrate to which it is being applied and the general processing conditions in terms of coat-weight, line speed and so on. In textile applications, the three-roll 'inverted L' configuration is the most common form, but in the coating of paper, film and foils, it may well be that a four- or even a five-roll stack is employed, and these rollers can be arranged in different configurations according to the particular application details. The reason for this increased number of rollers and layout is generally related to the fact that, in textile coating, relatively heavy weights are applied by comparison to those applicable in the paper, film and foil markets.

Historically, the three rollers were all of a similar size, and would be driven by a common drive motor with gearboxes allowing differential speeds between the various rollers to be achieved. This system has however now been totally displaced by the use of independent DC drive motors on each of the rollers, which results in very much more accurate control of the relative speeds of the rollers and an assurance of total synchronisation as line speed changes, without the risk of getting gear chatter marking in the finished coating.

13.5.5 Meyer bar coating

Here, a wire-wound bar passes into the substrate being coated, and the space between the wires is the volume of coating compound that can remain on the substrate (Figure 13.8).

This very simple technique is widely used in the paper industry, but almost totally inapplicable to textiles.

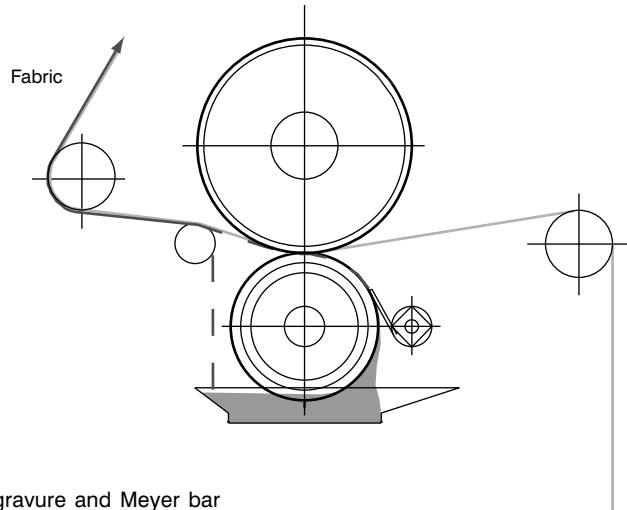


Figure 13.8 Rotogravure and Meyer bar

13.5.6 Rotogravure

Rotogravure is a method by which very low coat-weights of compound can be applied very accurately onto not only paper, film, and foil (where the technique is very widely employed) but also onto textiles and films such as PVC, polypropylene, polyester, and so on, where unless the primer is applied, the subsequent coating compound will not adhere.

With films, the solvent must be evaporated prior to the next coat being applied, but with textiles, because one is applying at such a low weight by the rotogravure technique (typically 1 g of a 10% solids solution, meaning 9 g of solvent only), one is able to go directly from the rotogravure station to the main coating station without any intermediate drying (Figure 13.9).

13.5.7 Blade-over-blanket

This technique is hardly ever used these days, because other easier methods are available, but it was formerly a very widely employed technique for applying a fairly low coat-weight onto dimensionally unstable substrates, or onto a substrate with a pile surface. Quite a lot of PVC film is coated by this technique for surgical dressings, and the early polyurethane-coated fabrics of the 'vistram' type used this technique to apply the polyurethane onto the pile surface of a brushed cotton fabric (Figure 13.10).

The problem is that correct setting of the unit to achieve the required results is quite difficult, and skilled operators are needed. If any damage occurs to the belt, or any dirt gets on the inside surface of the belt, an immediate irregularity of coat-weight will result.

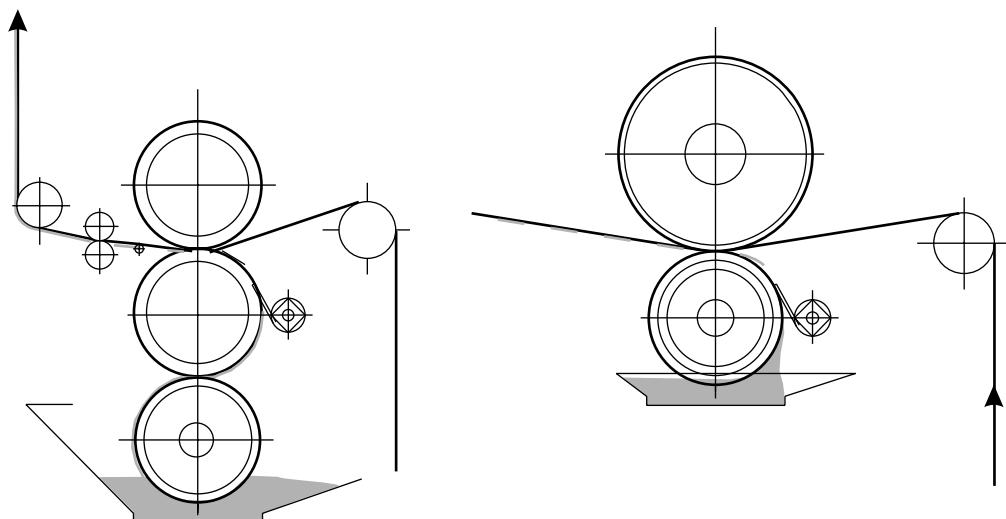


Figure 13.9 Three-roll rotogravure with Meyer bar and polishing roller

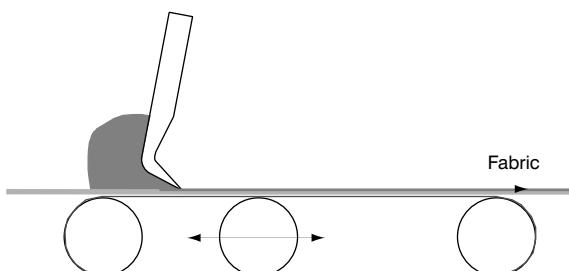


Figure 13.10 Blade-over-blanket coating

13.5.8 Rotary screen

Rotary screen coating systems are of universal application for single- and multi-colour printing, but have found application in certain very specific coating processes (Figure 13.11).

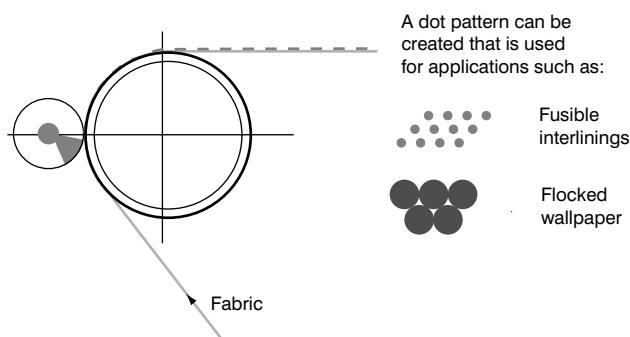


Figure 13.11 Rotary screen coating

In the paper, film and foil field, it is possible to use a screen rather more easily than in the textile field. This is because the paper, film and foils are impermeable materials, and as a result lower viscosity coating compounds can be delivered through the screen, and will themselves be able to flow laterally to create an overall coating.

In the textile industry, however, this is generally speaking the opposite of what is essential for the achievement of the required product. A low viscosity coating compound would flow into the fabric structure, whereas what is actually required is that it stays on the surface. The viscosity therefore has to be increased either by thickening, or mechanical foaming, and either of these techniques results in a material that, when passed through the screen, forms a series of hemispheres on the material surface, which cannot flow together to give a continuous layer. This series of dots with air spaces between is highly desirable in one or two applications:

- (1) in the production of flocked wallpaper, where one needs to be able to let the air escape from between the wallpaper and the wall during the hanging operation;
- (2) in the production of fusible interlinings, where the spots of adhesive must not join up – otherwise it will have an adverse effect upon the handle and drape of the product;
- (3) in the application of non-foamed fire-retardant compounds onto the back of certain specific and generally very light-weight upholstery fabrics, where it is inappropriate to use collapsed foam-coating techniques, but where a discontinuous layer of coating must be employed, in order to achieve air permeability in the finished product.

In most other applications, the rotary screen technique has to be followed by a smoothing blade, which makes the individual hemispheres join up to form a single layer. However, such a system is really using a very expensive rotary screen to apply the compound in front of a blade, where a bucket or more elegantly a pump would serve much the same function.

A rotary screen can be fitted on the coating head in front of the blade position, as shown in Figure 13.12, for single-colour printing, or other discontinuous application techniques, but this

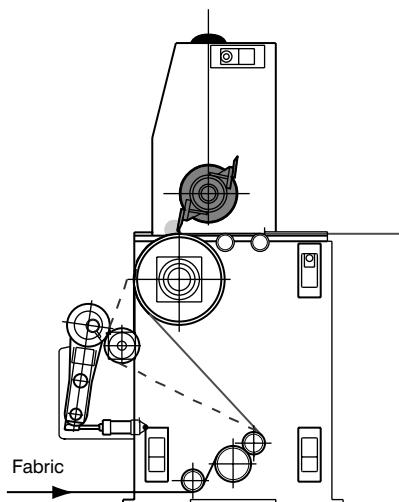


Figure 13.12 Blade coating head with standard rotary screen

would not be used in conjunction with the doctor blade being in operation, except where the screen is applying a logo, and the blade is immediately thereafter applying a clear coat on top of the logo, to seal it in. Here, of course, the blade is having no effect upon the screen-applied colour, but is itself performing an entirely separate and different function.

In the foam-coating of upholstery fabrics, it is, however, important that the fabric be travelling in a horizontal plane at the moment of coating to avoid excessive penetration into the fabric structure, which occurs if the fabric is passing around the circumference of a roller at the moment of deposition (Figure 13.13).

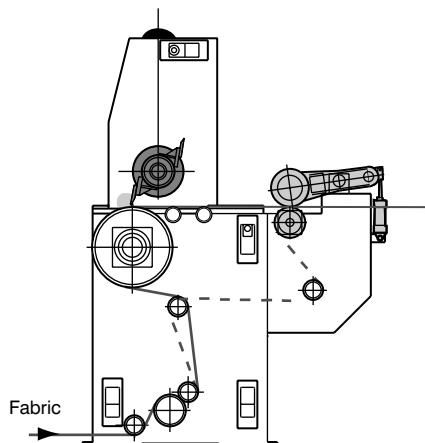


Figure 13.13 Blade coating head with rear rotary screen

13.5.9 Slot die coating

In certain applications, the viscosity of the compound by virtue either of its rheological characteristics or its solids content, is too high to be applied by any of the above techniques, and one then needs to look for alternative systems. If the material is to be retained in liquid form, be it at ambient temperature or as a hot melt normally 100% solids material, it will most usually be appropriate to apply the coating by a 'slot die coating technique'. In this, the compound is fed by a series of gear pumps into a pressurised chamber, from which it can exit through lips of very precisely controlled thickness, being essentially extruded onto the fabric or other substrate passing around the circumference of a rubber-covered or chromed back-up roller with the lips of the die being almost, or actually, in contact with the substrate, and appropriately angled so that a film is created on the substrate with more or less penetration of that film into the substrate, according to the required end-product properties (Figure 13.14).

In the event that a discontinuous coating of low weight is required, this can be achieved by appropriately adjusting the delivery rate of the coating compound through the die, in relation to the substrate speed, and under those circumstances a reticulated pattern of compound lay-down will be achieved.

The precise design conditions of the die itself and the method of adjusting the overall width of the coating (or decal) vary from one manufacturer's unit to another, but the principle remains

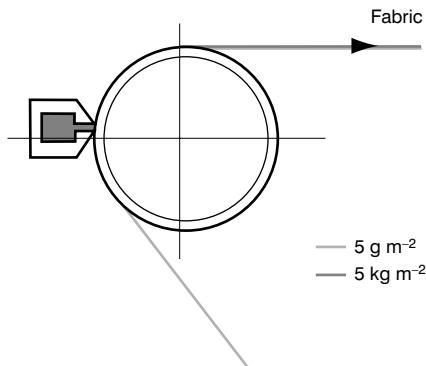


Figure 13.14 Slot die coating

the same, and it is possible by this technique to achieve either very low coat-weights at relatively high speeds (5 g m^{-2} at speeds of several hundred metres per minute) or very high coat-weights of high viscosity materials like atactic polypropylene (applied at 5 kg m^{-2}), but at very low production speeds.

13.5.10 Foam coating

The advent of mechanically foaming a coating compound, by beating it to incorporate air into its structure, has probably had a more fundamentally important effect in the expansion of the coating industry than any other single development (Figure 13.15). By incorporating air into the compound, the viscosity is caused to increase dramatically, but at the same time, the strength and shear characteristics are so greatly changed, that it is possible to apply very accurately controlled weights of the compound, with very precise control over penetration, and onto materials which would be difficult, if not impossible, to coat with non-foamed materials. It has several further advantages in so far as non-uniformity in substrate can be made of less importance, because the coating thickness is of course greater by the degree of density reduction.

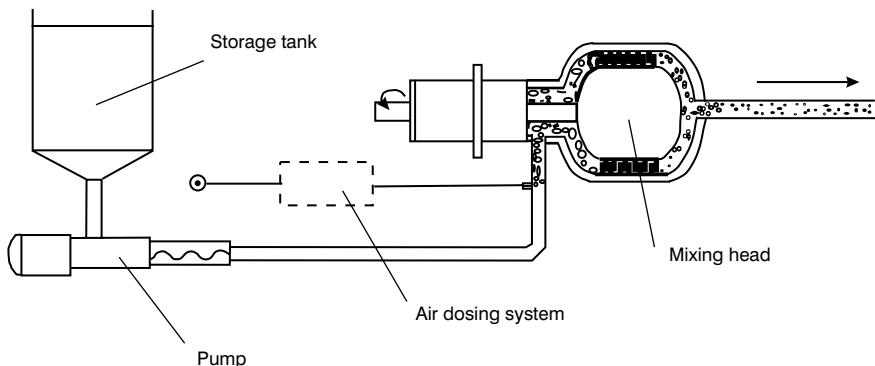


Figure 13.15 Mechanical foam production – schematic

As a result, almost all flocked fabrics today use mechanically foamed adhesives. All thermally lined curtains and black-out fabrics use mechanically foamed compounds. An increasing amount of pressure-sensitive adhesive coatings use them as well, and are in consequence able to reduce the actual weight of adhesive by as much as 50%, and at the same time actually produce a higher adhesion performance in the finished product. The majority of back-coating of upholstery fabric, be it fire-retardant or not, uses a non-stable foam formulation that collapses in the heat of the oven, to give a fully air-permeable layer.

13.5.11 Spray coating

The application of compounds by airless or air-assisted spray techniques is not widely practised in the textile or allied coating fields, because of the extreme difficulty in achieving the uniformity generally required in the application, and the considerable wastage and contamination that occurs because of overspray. However, there are applications where spraying is the standard method of preparation, and this is becoming increasingly associated with the deposition of hot melt adhesive systems applied by highly accurate and pattern-controlled spray techniques, replacing the use of solvent- or water-based systems.

The development of this spray technology must inevitably go hand-in-hand with the development of suitable hot melt adhesive systems with an adequate open time, but because of the uniformity problems associated with any multi-head spraying technique, such spray systems tend to be limited to applications where a relatively small area has to have the adhesive applied to it, such as in the disposable sanitary products market (baby nappies, for example), where the barrier film is laminated to the body of the product using a very low weight of thermoplastic adhesive applied as a hot melt by a spray system.

Wide-width lamination using spray techniques is not generally found to be successful because of the problems of overlap or underlap between adjacent spray heads, and the almost inevitability of occasional blocking of spray nozzles resulting in an area lacking in adhesive.

13.5.12 Transfer coating

In all of the foregoing techniques, the coating compound has been applied directly to the fabric to which it is to be ultimately anchored. There are, however, some fabrics which, because of their dimensional instability or openness of structure, cannot satisfactorily be coated in this 'direct' way. For such fabrics, the technique known as 'transfer coating' was developed, initially for the production of products such as PVC-based 'leathercloth', but now also applicable to polyurethane-based coatings and one or two other chemical systems typically being used to produce a surface film coated or laminated onto a fabric structure, in order to create a finished product typical of which is artificial leather (Figure 13.16).

In this technique, the coating – which may consist of one or more layers of the same or different specification compounds – is laid down onto a silicone or other type of release paper, and the product dried or gelled as appropriate, until the substrate that forms the support

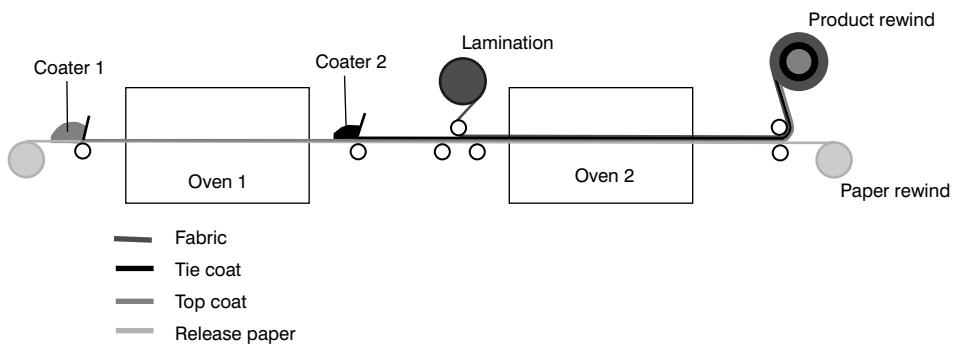


Figure 13.16 Transfer coating

structure for the finished product is introduced by a standard laminating technique immediately prior to the final drying oven.

At the end of the production line, the coated fabric so produced can be peeled from the release paper, and both materials rewound. The release paper after appropriate inspection can be re-used subject to careful handling for perhaps 10–15 times, making the process cost-effective.

This technique is widely employed for the production of PVC- and polyurethane-based artificial leathers, and increasingly for the casting of films of thermoplastic or thermosetting polymers for subsequent lamination to fabrics. In a slightly modified form, it is also used for the ‘enhancement’ of the generally unattractive and inexpensive inner leather splits of leather, which by such a coating technique can be converted into a product closely resembling the high-quality, high-value outer leather product.

13.5.13 Coating for lamination

Above, we have looked at different techniques of applying coatings onto fabrics, where in a finished product the coating typically forms one side of the finished composite structure, and the fabric substrate the other. There are, of course, a number of applications where the coating is a means to anchor a secondary material to the primary substrate, the most important two of which are outlined below.

Adhesive coating

Here, the coating (alternatively referred to as the ‘adhesive’) is applied to the surface of the primary substrate by whichever of the previously described techniques is most applicable to the characteristics of the adhesive and the substrate. The secondary fabric is then brought together with that adhesive layer on the primary fabric, and the two materials are laminated together to create an essentially three-component composite structure. This process can, of course, be repeated endlessly, producing multiple layers of the same or different materials held together by the inter-ply adhesives. Thus, in the simplest form there are many products in the garment and

shoe industries that utilise two- and three-component structures, but products such as conveyor belts, timing belts, dracones, printer blankets, aircraft fuel tanks, and so on, are made up of multiple layers of the same or different fabrics bonded together by appropriate adhesive layers to produce a complicated composite structure meeting all the physical and chemical requirements of the end-products.

Flocking

Here, the adhesive is applied to the primary substrate and flock is applied into the coating to create a flocked fabric resembling an artificial velvet (Figure 13.17). ('Flock' comprises precisely and finely controlled lengths of fibre that have been correctly chemically processed to make them receptive to an electrostatic charge.)

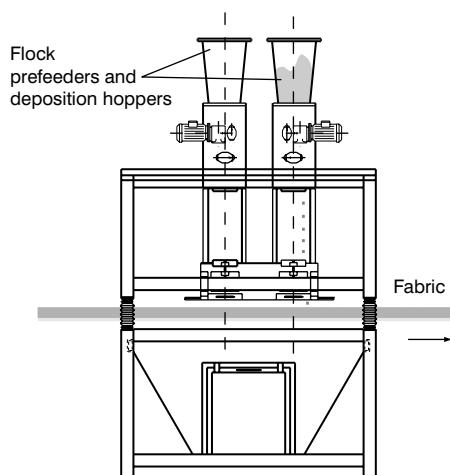


Figure 13.17 Electrostatic flocking

13.5.14 Drying

In all of the above coating techniques we have concentrated on the method of application of the coating compound to the fabric, but this is of course only a part of the story, since in most cases it is necessary to evaporate from that applied coating the water or solvent in which the coating is dispersed. Correct drying is critical, and must be carried out in the right way to avoid 'pin-holing' or solvent-retention (Figure 13.18).

Thus, the coated fabric must be processed through an oven in which the temperature and air velocities are very accurately controlled, and which need to be different from zone to zone, according to the nature of the products employed. If temperature is too high, or the air velocity too great, the surface of the coating will be dried before the under-lying layers have lost all of their solvent or water, which will then only be able to escape by literally vaporising and bursting through the dry skin, to leave a 'mini volcanic crater'.

The secrets of satisfactorily drying a coated fabric depend on impinging upon the upper and lower surfaces of that coating the appropriate velocity of air at the appropriate temperature

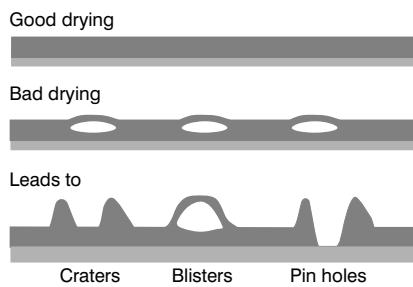


Figure 13.18 Good drying; bad drying

(Figure 13.19). If the velocity or the temperature is too high, the volatile component will be caused to evaporate from the surface at a rate faster than it can migrate through the thickness of the coating, resulting in the 'skinning' and 'pin-holing' problem described above. Thus, in any drying oven there is a vital need to divide the length of the oven into a series of zones in which the temperatures and air velocities can be accurately and precisely controlled in order to achieve the required rate of evaporation.

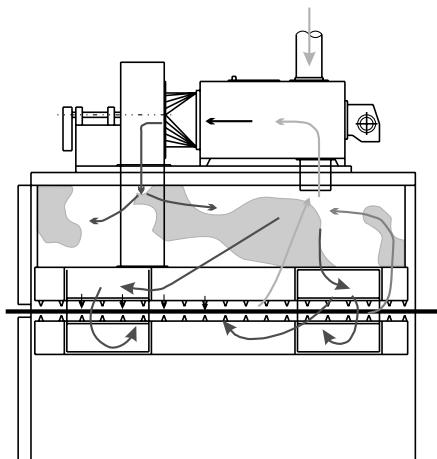


Figure 13.19 Oven circulation

Where solvents are involved, consideration must also be given to the possibility of a fire or explosion (Section 13.11).

However, in addition to satisfactorily drying the fabric, one must also consider what one does with the material evaporated. In the case of water-based systems, it may be possible just to discharge the water to atmosphere. However, in many cases there will be certain chemicals contained within that water, which need to be removed from the discharge in order to avoid pollution.

The same applies when processing such materials as PVC plastisols, which although theoretically 100% solids, do contain plasticisers, a percentage of which will be evaporated during the gelation and curing of the PVC, and which certainly should not be allowed to just

enter the atmosphere, but which should rather be precipitated out of the discharge air by the use of appropriate scrubbers or electrostatic precipitators.

Solvents, quite apart from being toxic and explosive, are of course very expensive, and it really is crazy to simply throw them away. Ideally, the oven system should incorporate automatic solvent concentration monitoring equipment, which will allow the oven to be safely operated at up to 50% of the lower explosive limit of the solvent employed (a very considerable energy saving in itself). The solvent is then taken to an incineration system (more cost-effective these days than solvent recovery), where it is burned to eliminate pollution. The energy so liberated is then used, via steam or circulating hot oil, to heat the ovens on the coating line from which the solvent was evolved. In fact, so rich in energy are most solvents that the burning of the solvent from one line will probably produce enough heat to operate two such lines – so the problem is, generally speaking, not whether or not there will be sufficient energy, but whether you can take advantage of all of the energy available from the incineration process.

To avoid the complications and costs of drying water-based systems and incinerating solvent-based materials, there has been a steady trend to develop products that can be applied as 100% solids materials, without any volatiles being liberated during the process. In some cases this has been achieved with pure 100% solids liquids, which just need to be gelled or cured by the application of heat or UV light.

13.5.15 Coating with 100% solids materials

Because of the problems associated with environmental pollution, drying and the penetration of liquids into fabrics, a steady trend towards the use of 'dry' coating compounds has occurred since around 1960, and today this represents an important sector of the coating and laminating market. The main application techniques that apply are outlined below.

'Powder scatter' coating

Here, the powder in a controlled particle-size range is contained within a hopper at a constant level and packing density. It is discharged from that hopper by an appropriate delivery roller and caused to fall onto the substrate passing beneath (Figure 13.20).

By the correct design and operation of the equipment, extremely high levels of distribution uniformity can be achieved (typically $\pm 2\text{--}3\%$ on width and length), which then passes into an appropriate infrared fusing oven from which it will emerge to be calendered or to be used as the laminating adhesive to stick a secondary material to the primary substrate. This technique is widely used for the production of fusible interlinings, and laminates for the shoe and automotive seating and headliner industries.

'Powder point' coating

Here, the powder (again contained within a hopper) is fed into the engraved cells of an applicator roller, which itself is maintained at a precisely controlled temperature (Figure 13.21).

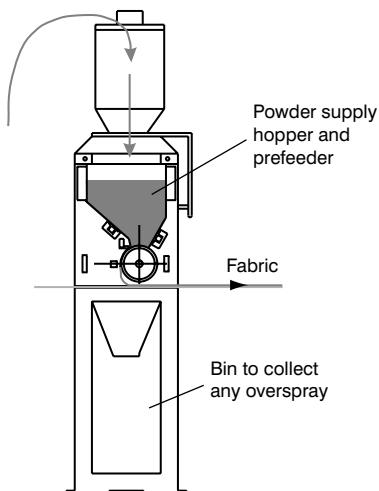


Figure 13.20 Powder coating

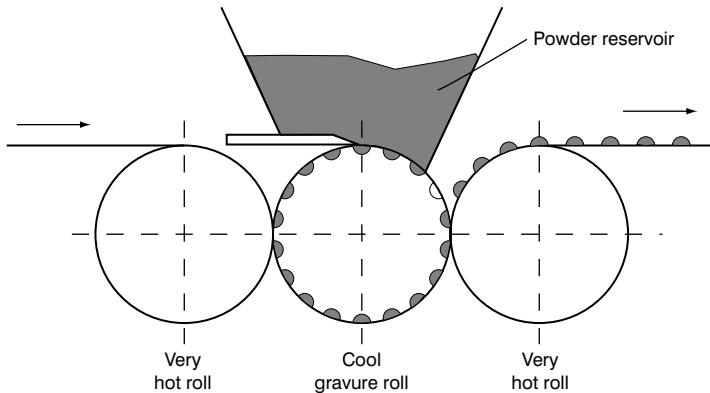


Figure 13.21 'Powder point' coating

The fabric passing around approximately 50% of the circumference of this roller is subjected to considerable heating from oil heated rollers located on either side of the applicator roller, such that the heat passing through the fabric is sufficient to partially melt the powder on the engraved roller, and cause that powder to adhere in droplets onto the surface of the fabric. The fusing process is completed in the passage of the fabric through a short infrared oven prior to calendering or lamination, as appropriate. This technique is the primary system used for the production of fusible interlinings particularly for shirt collars and cuffs, and is also employed for the lamination of filmic materials to fabrics.

'Paste dot' printing

Here, the rotary screen system previously described (Section 13.5.8) is employed to deposit an aqueous slurry of fine-particle-size thermoplastic powder onto the fabric to create a regular

pattern of the thermoplastic adhesive, which, after the water has been evaporated, is fused in the same manner as described above (Figure 13.11). This technique is particularly applicable to the production of fusible interlinings on non-woven substrates, because it allows certain liquid additives to be incorporated into the paste that would not be possible by the 'scatter coating' or 'powder point' techniques.

Hot melt dot coatings

The engraved roller system described above for 'powder point' coating can be employed for the deposition of hot melt adhesives onto fabrics, provided that the hot melt has itself adequate stability against oxidation at elevated temperatures. The basic technique has been attempted on a number of occasions over the past 50 years, but until relatively recently the oxidation rate of the polymer was so rapid that within minutes, the engraved roller became enveloped in a film of degraded polymer, necessitating clean-down. Recently, polyesters and polyamides, as well as certain other polymer systems, have become available with appropriate anti-oxidants, allowing this technique to be satisfactorily employed without the need for complicated and generally unworkable nitrogen blankets everywhere.

However, although the initial bond achieved with these materials is satisfactory, the crystallisation of the resin systems over a period of time (generally a few weeks), is such that the adhesion deteriorates to an unacceptable level and as yet it is not possible to use such systems in the majority of applications where their performance would be desirable.

There are in fact at least five methods of application of hot melt coatings:

- (1) roller coating – cheap, simple, but generally not suitable for textiles;
- (2) gravure roll – almost as cheap and simple, and most suitable for textiles;
- (3) slot die – expensive and complicated;
- (4) spray – 25 mm or 100 mm width spray bands, very expensive, problems associated with individual spray nozzles blocking and with overlap and underlap of adhesion, giving rise to serious and excessively frequent faults;
- (5) hot melt rotary screen – very expensive and complicated.

One must obviously select a technique that is appropriate to the characteristics of the compound employed, the substrate(s) being processed, and the properties required in the end-product. Cost of the equipment will also be an important factor in any decisions, since some of the hot melt systems do require very expensive equipment to produce them satisfactorily.

13.6 LAMINATION METHODS AND MACHINES

13.6.1 Adhesive systems

Solvent-based adhesives

Solvent-based natural and synthetic rubbers and polyurethanes were extensively used in the laminating industry until commercial and ecological pressures caused a movement towards

alternatives. Thus, apart from hand-sewn shoes, almost all footwear was produced on solvent-based adhesive systems, but these systems have now been almost universally replaced by hot lasting techniques using thermoplastic adhesives pre-applied to the component parts.

Water-based adhesives

Originally, water-based adhesives were mainly based upon starch and other naturally occurring products, but now they are almost exclusively based upon either PVA or acrylic resin systems. Water-based products were an extremely important category of laminating adhesives up to the 1980s, from which date their importance has steadily diminished.

Flame lamination

The technique of flame lamination was originally developed in the USA, and licensed around the world under patents granted to the Reeves Corporation of the USA. At its heyday, flame lamination accounted for thousands of millions of square metres of laminated fabric per year, produced in the USA, Europe and many other countries. The main applications were for garments, curtains, footwear, ironing board covers, and various industrial applications.

The process relies upon the impingement of a gas/air mixture flame upon the surface of a polyurethane foam, causing that surface to both melt and to undergo a reduction reaction creating a high-tack adhesive layer on the surface of the polyurethane foam. Fabrics being brought into contact with that sticky layer immediately after its formation are caused to adhere to the polyurethane foam, and hence two- and three-ply laminates are produced in a single pass through a twin burner machine (Figure 13.22). Very high production speeds (up to 120 m min^{-1}) are not uncommon.

However, the process is dependent upon the use of the polyurethane foam, and this is adversely affected by sunlight and elevated temperatures, particularly in combination with high humidities. Thus, the durability of curtains and many garments made from flame laminated fabrics was not particularly good, and the technique and the end-products fell from favour. Today the flame laminating process is primarily restricted to the lamination of automotive seating, headlining and door panel products in the industrial market, with 'baseball' and 'American football' caps being the single largest market for the product in the apparel field.

During the flame laminating process, a quantity of noxious gases is evolved, which has created problems for flame laminators under the increasingly rigorous environmental protection regimes being established in most countries. However, techniques have become available that will remove the majority if not all of these toxins from the exhaust stream discharged from the flame laminating machine, which may result in a continued viability for the process. This would clearly be to the advantage of the existing processors who do not wish to make relatively expensive and sophisticated machinery redundant, unless there is no option but to do so.

Powder adhesives

Where environmental or commercial pressures are making life difficult for users of solvent-

based, water-based or flame laminating techniques, the movement will be towards the use of powder adhesives. LDPE, HDPE, polyamides, polyesters and copolymers (Section 13.4.11) are becoming increasingly important alternatives to more conventional compounds, because there is virtually no environmental pollution by-products from these systems, the energy requirements are low, the machine size and hence cost is normally a fraction of that associated with solvent- or water-based machinery, and much of the existing flame laminating machinery can be relatively simply and inexpensively converted to the use of powder laminating techniques.

Hot melt adhesives

In certain applications, the powders are not in a physical form suitable for application to the substrates. In that situation it may be more appropriate to use the same polymer, but applied either as a hot melt adhesive applied by spray or lick or extrusion deposition, or by using a thermoplastic film version of the same polymer laid between the substrates to be laminated, which is heat reactivated by an external heat source.

Where thermoset compounds can be employed, the new PURs (reactive hot melt polyurethane compounds that react with moisture in the substrate and/or water vapour in the atmosphere to produce a crosslinked network structure), are finding increasing importance and uptake in the market because of their extremely high performance, elongation, soft handle, wash resistance, dry-clean resistance, and cost per square metre in many applications.

13.6.2 Application techniques

Blade-over-roll/rotogravure

Most conventional solvent-based or water-based adhesives are either applied by blade-over-roll or by rotogravure coating techniques (Sections 13.5.2, 13.5.6) in order to achieve a continuous or a discontinuous lay-down of adhesive onto one of the substrates, which is then combined with the second material in order to produce the laminate.

Rotary screen

There are applications where a water-based emulsion or an aqueous dispersion of a thermoplastic powder needs to be applied in a regular dot pattern through a 'rotary screen' (Section 13.5.8). This technique is the same as that employed for rotary screen printing, except for the construction and design characteristics of the screen itself.

'Powder scatter' coating

This is the oldest technique for the application of thermoplastic powders, and is still probably the most important in total volume terms. Improvements in the uniformity of deposition and the automation of control have occurred over the last few years, and it is estimated that today

scatter coating of thermoplastic powders accounts for some 20–25% of all lamination undertaken.

The reservoir of powder in the hopper (Section 13.5.15) is automatically maintained at a constant level and packing density, by a side-to-side traversing pneumatic powder feeder system. An appropriately constructed roller in the base of the powder hopper delivers the powder onto the substrate passing beneath. The width of powder deposition is limited by internal dividers within the hopper. The rotational speed of the applicator roller can be automatically synchronised with the line speed, so that once the pre-determined coat-weight has been established, it can be automatically maintained. A weight monitoring system can make automatic adjustments if necessary, and log the processing conditions on a minute-by-minute basis.

Flame lamination

A natural gas or propane or butane flame mixed with the appropriate volume of air is impinged upon the surface of the polyurethane foam (Figure 13.22). An interface temperature of around 860 °C is achieved in the flame, and this brings about a melting of the surface of the polyurethane foam and a reduction reaction to create the adhesive layer on the surface of the foam.

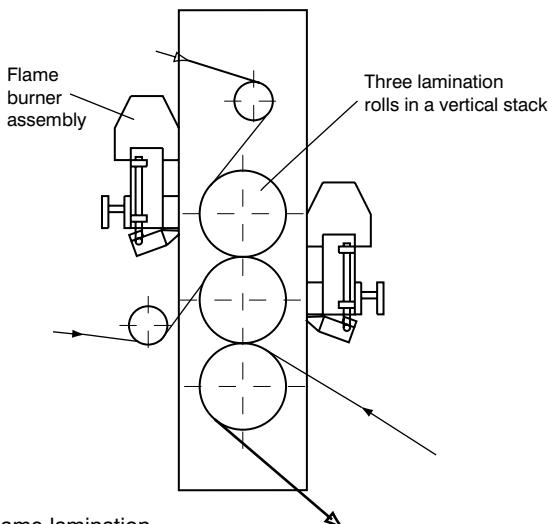


Figure 13.22 Three-ply flame lamination

The same technique can be applied onto polyethylene foam, in which case the polyethylene foam may be laminated to itself or to other materials.

Spray

Spray coating of water-based or solvent-based adhesives has been virtually eliminated in the laminating industry, but still represents an important technique with hot melt spray-applied

adhesives, particularly in the disposable products and non-wovens industry, where very low weights of finely dispersed adhesive are adequate for the bonding of the materials together. In this, a stream of hot air is mixed in with the atomised hot melt adhesive to lay down an appropriate pattern of adhesive, which retains its tack for sufficient time to bring the secondary substrate into contact, and achieve adhesion.

Extrusion die coating

An overall layer or lines of hot melt adhesive can be applied onto a substrate through a slot die coating head, which operates at high internal pressures and causes the lay-down of a controlled weight/thickness of adhesive onto the primary substrate (Section 13.5.9). The substrate is supported at the point of coating by an appropriate back-up roller, which may be either water-cooled chromed steel, or covered with silicone rubber (Figure 13.14).

However, in this situation, the adhesive lay-down is typically in a continuous form and this may give rise to an overly stiff end-product, having no porosity. Where these characteristics are undesirable, a modified extrusion coating technique can be employed – ‘starved die extrusion coating’ is achieved by feeding the coating compound to the lips of the die at too slow a rate to achieve an overall coating of the substrate passing the lips; this then achieves a ‘spider’s web’ effect that is accurately and easily reproduced at any given delivery rate/line speed combination.

13.6.3 Applications for laminated products

As stated above, the largest single volume of laminated fabric produced today is employed in the construction of caps sold in the USA and increasingly world-wide for ‘baseball’ and ‘American football’ club supporters. However, there are many other industrial, domestic and medical applications for laminates including those in Table 13.13.

13.7 NEW TECHNOLOGICAL DEVELOPMENT IN THE LAMINATING MARKET

All of the previously described methods of lamination suffer from certain disadvantages.

- (1) Solvent-based systems obviously create a fire- and explosion-hazard as well as the majority of solvents being toxic or having other undesirable physiological characteristics.
- (2) Water-based adhesive systems, generally speaking, require relatively high-energy input in order to evaporate the water and to polymerise the residual polymer.
- (3) Powder adhesives, while not suffering from any of the problems associated with solvent- or water-based systems, do have limited applications because of the particulate nature of the materials, the thermoplasticity of the majority of the polymers, and the tendency for dust pollution in the working area around the machine.

Table 13.13 General applications of laminated fabrics

Area	Application	Laminate
Automotive	Seating fabrics Headliners Door panels Sun visors A and B pillars (between windows) Dashboard (fascia) Car carpet Boot (trunk) carpet Acoustic mat in engine compartment	Generally face fabric / foam / lining fabric or film Generally face fabric / foam / thermoformable membrane Generally fabric or vinyl / polyolefin foam Generally vinyl film / foam Generally fabric or vinyl / polyolefin foam Generally fabric or vinyl / polyolefin foam Generally tufted or non-woven carpet / PE thermoplastic / non-woven Generally tufted or non-woven carpet / acoustic layer / rigid layer / non-woven Generally acoustic absorber encapsulated in oil-resistant film
Domestic applications	A wide range of lingerie products Protective clothing: high visibility clothing, workwear A wide range of sporting garments Medical products including operating gowns and drapes, incontinence products, dressings Shoes, boots, slippers Ironing board covers Swimming pool covers	
Industrial applications	Conveyor belting Dracones Fuel tanks Timing belts Printing blankets	

- (4) Filmic adhesives, although having certain obvious advantages, are extremely expensive per square metre of finished product, and therefore, generally speaking, represent the 'last resort'.
- (5) Flame lamination gives rise to significant quantities of toxic fumes of an extremely hazardous and injurious nature, such that current legislation requires that none of those fumes be discharged into the working environment around the machine or to the outside atmosphere. This can only be achieved using expensive carbon-absorption systems, which need frequent and costly maintenance in order to continue to be effective.
- (6) Thermoplastic hot melt adhesives, while satisfactory in some applications are by-and-large not suitable for the majority of textile products because the adhesive remains thermoplastic and therefore generally fails to give the long-term durability of adhesion required.

13.7.1 Reactive moisture-cured hot melt polyurethanes (PURs)

In the last few years, a new family of adhesives has become available to the textile laminating industry. In what is probably one of the most important technological advances to have reached the textile coating and laminating industry for several decades (along with the process of mechanical foam generation in the coating sector), PUR adhesives offer the prospect of replacing many of the currently employed laminating systems with a material of comparable cost, enhanced performance, and virtually no environmental or other health and safety problems.

PURs first became commercially and industrially available around 1990, but at that time the polymers were too reactive to be employed in the textile lamination market, and were restricted to applications such as footwear assembly, the lamination of acoustic and thermal insulating materials in panel products, and so on, where the PUR was delivered from a closed system to the substrates and exposed to the atmospheric air for a matter of a few seconds only. Longer exposure, as would be necessary in the majority of textile applications, would have given rise to problems of oxidation, thermal degradation and excessively rapid curing.

By 1996, improved stability products were beginning to be employed in the textile market, but the level of stability was still such that the machines could only operate on a non-stop basis to prevent yellowing and set-up of the materials on the applicator systems. In addition, they needed relatively frequent clean-downs in order to maintain satisfactory operating conditions and consistency of laminate properties and performance.

By 2001, further significant improvements in the chemistry of the products made it possible for the adhesives to be kept on the machines for hours without degradation taking place, thereby allowing significant simplification and cost reduction of the machinery as well as a rapid expansion of the applications for which the PURs are now viable adhesives.

Although PURs are still relatively expensive materials per kg, the extremely high levels of adhesion they produce, combined with excellent resistance to washing and dry-cleaning, make it possible to achieve the required results with very low weights of adhesive ($5\text{--}15\text{ g m}^{-2}$ is frequently adequate in many applications). Therefore, the final cost per square metre of product is competitive with, or cheaper than, many of the older systems that PURs are replacing.

Dependent upon the particular polymer characteristics as well as the non-polyurethane additives often incorporated into the commercially available PUR adhesives, the adhesive suppliers are able to tailor the performance characteristics to include:

- (1) very high levels of adhesion to most substrates including PTFE-based materials, although certain olefinic films, foams and fabrics may require to be corona discharge treated prior to lamination (corona discharge treatment is the impingement of a very high voltage electrical discharge onto the surface being treated which causes molecular re-arrangement of its atomic structure, giving it a much greater reactivity to the coating or adhesive about to be applied);
- (2) elongation between 300 and 550%;
- (3) excellent resistance to dry-cleaning procedures;

- (4) excellent resistance to washing and even – in the case of certain of the polymers – resistance to hospital steam sterilisation procedures, which frequently call for 50 cycles of washing, drying and autoclave steam sterilisation at 134 °C;
- (5) very soft handle;
- (6) resistance to thermal degradation up to around 160 °C in the finished laminate;
- (7) very low levels of environmental pollution.

Although a very small quantity of isocyanate is present within the formulation, the amount liberated into the environment is minimal. The author, who has been sensitised to isocyanates from 40 years of working in the textile coating and laminating industry, can operate these machines on a continuous daily basis without suffering any discomfort, demonstrating the very low level of isocyanate content within the material and the minimal discharge of that isocyanate from the material into the environment around the machine. However, machines should incorporate an appropriate extraction system from the associated drum melter and in the area of the adhesive applicator.

Curing is effected by the absorption by the adhesive of small quantities of moisture from the substrates being laminated and from the atmosphere around the machine. Typical absorption levels required to effect full polymerisation are 0.1–1% of moisture on a weight/weight basis. Carbon dioxide is the only discharge product from the reaction. Once cured, the adhesive is fully thermoset and no softening or deterioration will occur.

By the use of PUR adhesives, new components can often be incorporated into laminates making it possible to create a 100% recyclable product where previous manufacturing techniques prevented this. If, for example, a laminate were to utilise a polyester face fabric, a polyester needlefelt and a polyester lining fabric with a PUR adhesive at both interfaces, the resultant product would – both because of the very low weight of PUR employed and the chemical base of that PUR – be 100% recyclable to make, for example, a further polyester needlefelt.

13.7.2 Methods of application of PURs

While PURs can be applied by roller coater, gravure roll, slot die, spray and rotary screen, the majority of applications within the textile industry, where roll-to-roll goods are being laminated, are best served utilising a gravure roll adhesive application system, which allows very accurate coat-weight control, coupled with a relatively low-cost and simple-to-use application technique.

In the laminate manufacturing process, the PUR is normally delivered to the laminating machine in 180 kg drums, which are placed within an electrically heated drum melting unit. This pumps the molten compound, at temperatures typically ranging from 90 to 130 °C according to the polymer formulation, to the adhesive applicator group on the laminating machine where an automatic level control system monitors the size of the adhesive bank and controls the rate of delivery of the adhesive from the drum melter (Figure 13.23). Today's

adhesives no longer require dry air, nitrogen or argon to be in place around the adhesive applicator, which, as a gravure roll system, will incorporate a heated applicator roll and doctor blade, and the other appropriate rollers and laminating facilities, generally as shown in Figure 13.23.

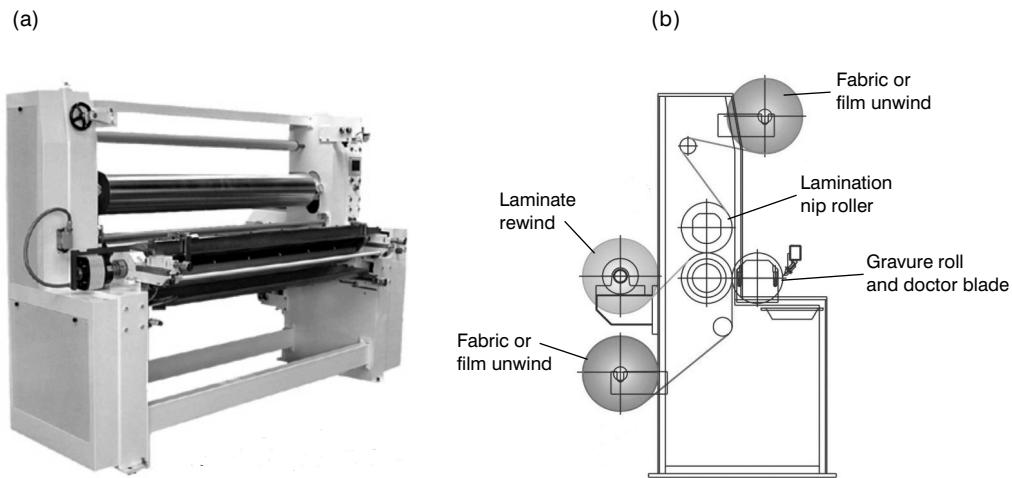


Figure 13.23 PUR adhesive laminating machine

Further developments in PUR polymers and the adhesive formulations based upon them can be expected from the chemical manufacturers over the course of the next few years, further increasing the performance characteristics of these products and expanding the importance of PUR lamination technology in the marketplace, replacing older and less desirable technologies.

13.8 BONDING

Bonding can only just be justified in this chapter, on the basis that it is not truly a finishing technique, but a method by which fibres can be stabilised by the application of appropriate chemical systems, albeit often producing a finished product that is homogeneous in nature. The main applications that can be considered as being bonding, rather than coating, are described in the sections that follow.

13.8.1 Anti-fray applications

Pocketings, labels, and other fabrics need to be treated to avoid fray or seam slippage that would otherwise occur, and which would result in defective finished products. This anti-fray anti-slippage is achieved either by coating the fabric by the blade-over-air technique with a low weight of appropriate chemical compound, or by impregnating the material in the same manner in order to achieve inter-fibre adhesion, and hence to prevent fraying and seam slippage from occurring subsequently.

13.8.2 Upholstery

Much upholstery fabric is back-coated with an acrylic or a styrene butadiene rubber (SBR) system in order to prevent fibre slippage, which in the finished upholstered article would rapidly give rise to product failure. The presence of the back-coating prevents the movement of one fibre relative to another, and hence creates a stable fabric structure that withstands the usage conditions applied to it. In fact, this back-coating process normally allows a significant weight of fibre to be removed from the upholstery fabric, resulting in a cost saving in the finished product, despite the expense of the back-coating process and chemicals.

If fire-retardant compounds are incorporated into the back-coated resin, the upholstery fabric can be rendered fire-retardant as well.

13.8.3 Non-wovens manufacture

The production of non-wovens is perhaps the largest area in which chemical bonding is utilised. Non-wovens can be produced by the following techniques.

Chemical bonding

Chemical bonding involves the carded web being coated or sprayed on one or both sides, using a water-based binder (typically an acrylic) that, after drying and curing, gives a good stability to the finished product, albeit making the surface of the non-woven relatively flat. In the case of light-weight non-wovens such as coverstock for disposable sanitary products, the product will be bonded right the way through its thickness. By contrast, heavy-weight waddings used as thermal insulation in anoraks, duvets, and so on are spray bound on both surfaces, but the spray applied adhesive does not penetrate into the structure of the non-woven, and hence the upper and lower surfaces can be pulled apart.

Thermal bonding (by calendering)

This process involves passing the non-woven web (composed predominantly or entirely of synthetic thermoplastic fibre) through a pair of high-temperature calendering rollers, one of which at least has an engraved pattern on its surface, so that the thermoplastic fibres are melted at the high spots on the roller, and fused together to stabilise the fabric structure.

Thermal bonding (by oven)

If a non-woven web incorporates 5–10% of a low-temperature-melting thermoplastic fibre (generally polypropylene) uniformly distributed through its structure, the web can be passed through a high-temperature oven supported on a conveyor belt with hot air being drawn through it. This melts the polypropylene fibre, so that it acts as an adhesive to bond the entire structure into a homogeneous batt. An upper belt may be provided above the non-woven batt to appropriately compress the overall thickness of the material. This technique has largely replaced

chemical bonding for the production of thick insulating non-woven waddings for use in anoraks, quilts, and so on.

Powder bonding

In place of the polypropylene fibre in the description of thermal bonding above, an appropriate thermoplastic powder can be incorporated into the non-woven. If this powder is caused to melt, it creates multiple bondings in the non-woven, and gives it the required strength. By repeatedly melting the powder and immediately calendering the product into a thin layer, and then re-melting it and calendering it, the number of points of adhesion can be progressively increased, thereby gradually increasing the strength of the material. The finished product is normally sold in the compressed state to minimise transport volume and cost, and is 're-lofted' once sewn into the finished garment and delivered to the point of sale.

Although powder bonding is the most expensive of the above techniques, there are certain product areas where the technical properties achieved by this method justify its utilisation.

13.9 FLOCKING

The process of flocking essentially consists of laying down a layer of fibres onto the surface of a substrate held there by an adhesive and thereby producing a pile or 'velvet-type' effect. A well known application of the effect is in 'flocked wallpaper' used in restaurants and other establishments, but in fact flocking is an extremely important technique both in domestic and industrial applications. It is applied not only to the processing of continuous-roll goods, but also to discreet objects where the essential techniques are the same. However, this section will only deal with the specifics relating to the processing of roll goods.

Flocking has been carried out for at least 200 years, until fairly recently using purely mechanical techniques. With the introduction of electrostatic flocking systems, and the significant improvement in the processing conditions for the flock and the flocking adhesive that have occurred since around 1980, the range of applications and the market size for flocked products has significantly increased as the technical quality of the finished product has improved.

13.9.1 Applications

The major applications into which flocked products are supplied, include the following.

Flocked blankets

Extensively used in the USA, the flocked blanket comprises a two-ply layer of polyurethane foam laminated together with an open mesh polyester scrim between to confer the necessary tear strength and dimensional stability to the product. Both sides of this laminate are coated with a discontinuous pattern of adhesive and flocked, using a 3.3 decitex, to produce a very soft,

thermally insulating, light-weight, non-flammable blanket. The US market is currently estimated to consume some 10 000 million m² of such fabric per year.

Curtain velours

The UK currently consumes approximately 5 million m² per year of flocked curtain velour made by flocking a 3.3 decitex fibre (or finer), 1.2–1.5 mm length, nylon flock onto a woven cotton or cotton/polyester base fabric using a mechanically foamed acrylic adhesive. The resultant product resembles a velvet, but because of the production techniques and speeds, its costs are lower and its technical performance is extremely good.

Garments

A significant quantity of garments is produced using flocked fabrics. In this instance, it is usually a viscose fibre that is used in order to give softness of handle. Typically a 1.1 decitex (or finer), 0.5 mm fibre is employed, adhered to the appropriate substrate using a mechanically foamed acrylic adhesive to give the softness of handle and the washability required in the end-product.

Discontinuous lay-down of flock can be achieved to produce light-weight sari type fabrics, which may be based upon light-weight open-structure woven or knitted fabrics. Similar constructions can be employed for curtaining nets and laces.

Industrial products

Flock is applied onto a number of industrial fabrics in order to improve the technical performance of the product. For example, many drive belts are made of multi-ply rubber-coated fabrics that are flocked to improve the inter-ply adhesion.

Packaging and display materials

A large volume of flocked fabric generally based upon rayon flock applied onto paper or a non-woven substrate is used in the window dressing, packaging and display markets. A very similar product is used for the lining of cases, handbags, briefcases, and so on.

Painting pads and rollers

These are produced by flocking a relatively long fibre length flock onto a polyurethane foam pad or roller, to produce an absorbent surface that will hold the paint and allow it to be transferred to the wall or other substrate being painted.

Thermally-lined curtains, curtain linings and black-out fabrics

The market for two-piece curtains, comprising a plain or printed face fabric lined with a woven curtain lining, is steadily being replaced by a market in which the curtain lining is entirely eliminated. Instead, the face fabric is back-coated with a mechanically foamed and partially

crushed acrylic foam, onto the surface of which approximately 10 g m^{-2} of a ground or precision-cut viscose or ground cotton flock are applied, giving the feel and appearance of a textile material.

In its simplest form, with a single layer of white or off-white acrylic foam-coating, the product will transmit a considerable amount of light. However, if a two- or three-coat product is produced in which one of the layers incorporates a quantity of carbon black, a 'black-out' or 'sun block' product is produced.

This product has grown over the past 30 years to a world market estimated to exceed 1000 million m^2 per year world-wide, and offers the advantages of technically high quality performance combined with low cost, because of the high production speeds that are possible.

Upholstery velours

A significant market exists around the world for upholstery velours, which are produced in essentially the same way as curtain velours, utilising 1.7, 2.2 and 3.3 decitex, 1.25, 1.5, 1.6 and 1.7 mm length nylon flock applied onto a cotton/polyester open-structure base fabric with a mechanically foamed acrylic adhesive, which is usually coloured and fire-retardant to the standards required in the marketplace into which it is to be sold.

As with the curtain product, the technical performance of the material is very high by comparison to more conventionally produced velours, and because of the high production speeds the overall cost is low. In consequence, it is currently estimated that the UK consumption of these products is running at around 15 million m^2 per year with a world-wide consumption in excess of 200 million m^2 per year and growing.

The finished product can be used plain or can be post-patterned or printed by wet or transfer printing techniques to further enhance its aesthetic characteristics. It may also be embossed to give a three-dimensional structure, or simultaneously embossed and transfer printed.

Wallpapers

Flocked wallpapers can take the form of either an overall deposition of rayon flock onto a paper or non-woven substrate, which is usually embossed to give an appropriate patterned effect to the finished product, or a discontinuous pattern of flock on a plain or printed background. The latter product is produced either with a single colour of flock, usually utilising a self-coloured flocking adhesive, or can be produced as a multi-colour finished product. The multi-colour effect is achieved by applying a number of different colours of flocking adhesive, by gravure or off-set gravure printing techniques, with a white flock being deposited into them, resulting in the production of a multi-coloured pastel effect finished product.

13.9.2 Flocking techniques

Machinery

The design and construction of the flocking machine has been significantly improved over the past ten years. Previously, the process was fairly inaccurate, and not in any way scientifically

controllable. Today, with a significantly better understanding of the electrostatic process and sophisticated electronics and control systems, the flocking process can be defined as a partially scientific technology, which requires very precise and accurate control of the conditions in and around the flocking machine and of the raw materials used in it.

The flock is held in pre-feed hoppers, where it is constantly stirred to prevent cavitation. It is delivered from these storage hoppers into the flock deposition zone in frequent, small doses, in order to maintain a constant level of flock within the zone (Figure 13.17).

In the flock deposition zone, a multiple-row brush is caused to rotate at an appropriate speed, and as it does so, a controlled quantity of the flock passes through an electrostatic sieve where the flock takes on an electrical charge appropriate to the voltage applied to the sieve. The maintenance of a constant quantity of flock within this hopper is of extreme importance: any variations will result in a fluctuation in the flock coat-weight on the substrate. Changing brush speeds, mesh size and the open area of the screen also affect the deposition weight.

Where heavy weights of flock are being applied (as in curtain and upholstery velours – 50–100 g m⁻²), the hoppers are normally connected in pairs with a minimum of three and perhaps a maximum of ten such pairs being used, each one connected to its own electrostatic generator with the output voltage progressively rising as the fabric passes through the machine in order to achieve the dense piles required.

Beneath, a series of square or triangular bars are beating against the under-side of the fabric in order to cause a vibration within it and to bounce any flock that is not adhering into the adhesive back to the electrostatic grid.

For the production of velours, it is also desirable that the fabric should be held flat in its passage through the machine by a light-duty pin frame in order to ensure that all of the fibres are laid perpendicular to the substrate at all points. The height of the sieve above the substrate is critical, and will vary according to the voltage being applied to the individual screens.

The electrostatic generators used outside of the USA normally produce a DC current of around 0.2–2.5 mA, with a potential difference of between 30 000 and 100 000 V, dependent upon the usage rate and flock type. In the USA, a number of AC generators operate under similar voltage conditions, but with significantly higher currents (perhaps as much as 2.5 A). UK 'Electricity at Work' and Health and Safety Regulations do not permit the usage of AC electrostatics because of the higher currents and greater risks attached.

For safety reasons, the whole of the electrically live machine must be enclosed behind interlocked access doors, which prevent an operator having access to the live areas until the current has been switched off, and all current discharged to earth.

The complete electrostatic flocking machine must be enclosed within a flock house, the primary function of which is to maintain a constant temperature (22–25 °C) and relative humidity of 72–75% within the flocking zone.

Any flock remaining on the surface of the product as it leaves the flock house will be sucked off by extraction slot units, and any poorly adhering flock will be brushed from the fabric after drying and curing, to ensure that there is no loose flock left in the finished product.

Ongoing research, in which the author is involved, has so far established important

improvements in the design characteristics of the equipment, allowing significant advances in the quality of the end-product with a reduction in the number of hoppers required, and hence in the cost of the equipment. This research programme may be anticipated to offer further enhancement to the technology as it continues over the next few years.

Flock type

Ground cotton and ground viscose are the cheapest materials for flock, but because of the variation in length, they are only suitable for those applications where the flock is serving a subsidiary role at relatively low weight.

Precision-cut viscose, generally ranging from 0.5 up to 3 decitex, and 0.5 mm length up to 1.5 mm, is used where a heavier-weight of flock is to be deposited, and where the product requires a verticality of the individual flock fibres.

For high abrasion resistance applications such as curtain and upholstery velours, a nylon 6.6 at 1.7, 2.2 and 3.3 decitex is employed at lengths from 1.5 up to 1.75 mm.

Polyester flock is used for the coating of extruded rubber profiles for the sealing around car windows. Coarser denier nylon flocks will be employed in carpeting and paint pad and brush applications.

Regardless of the type of fibre employed, all flock needs to be prepared in a highly scientific manner if the resultant end-products are to be of consistent quality and performance.

Precision-cut flock is cut on guillotines where the cutting blade needs to be maintained in a highly sharp condition – this requires re-sharpening perhaps every 15 min in order to avoid variable length or non-square cut ends. A highly compressed wet block of fibres, perhaps amounting to as much as 10 million decitex, is squeezed out of the compression slot and advanced by the appropriate length between each cut.

The fibres so cut are processed in a wet finishing vessel where a quantity of humectant (generally sea salt) and an electrostatic charge-retaining chemical (generally an amine) are applied. If the flock is to be supplied in coloured form it is dyed simultaneous to the application of these finishes.

After hydroextracting to remove as much water as possible, the flock is dried to a controlled moisture content in a fluidised bed dryer, and then stored in sealed bags at the pre-determined moisture level until used.

Flocking adhesives

Undoubtedly, the vast bulk of flocking adhesives are based upon appropriately formulated acrylic resins with fillers, pigments, fire retardants, and foam stabilisers incorporated, in order to produce the required multiplicity of end-product performance. In some applications, PVC plastisols or PVC emulsions may be employed. For clucking onto metal or fibreglass, epoxy resins or non-flammable solvent-based epoxy or polyurethane adhesives have been employed, but this is a relatively insignificant volume compared to the acrylic sector. Under no circumstances may flammable solvent-based adhesives be used because of the high electrostatic voltages that are present in the flocking machine.

There are still a few applications where the adhesive is applied without mechanical foaming; however, this is now almost entirely replaced in all garment, upholstery, curtain and most other applications with the use of a mechanically foamed compound in order to bring about a number of significant technical and commercial advantages.

By mechanically foaming the adhesive, the thickness of adhesive is increased without increasing the weight, or the thickness is maintained with a commensurate reduction in the weight of adhesive applied. This gives an improved uniformity of adhesive thickness as well as a reduced adhesive cost, and an improvement in the handle, softness, drape and air permeability of the finished product. The abrasion resistance and scuff resistance are also improved, compared to the same product produced with a non-foamed compound.

Adhesive application

The flocking adhesive is most commonly applied by a blade-over-roll coating technique where an overall flock layer is to be applied, or by rotary screen or rotogravure where a discontinuous pattern is required (Sections 13.5.2, 13.5.6).

Drying and curing

The coated flocked fabric must be dried and cured. In the case of partially crushed flocked curtains, curtain linings and black-out fabrics, the water must be evaporated to leave a residual 8–10% at the end of the drying oven so that the crushing between fixed gap nip rollers can be carried out and be retained. The balance of water is then removed in the curing oven where the resin needs to be subjected to a temperature of 150 °C for 5 min, 160 °C for 2.5 min, 170 °C for 1.25 min, and so on subject to the maximum temperatures that the fabric and the flock will withstand.

Post-processing

The finished flocked fabrics can be embossed, pattern sheared, or post-printed by wet printing or transfer printing techniques, according to the technical and aesthetic requirements of the end-product application.

13.10 PREPREGGING

13.10.1 Applications

The prepregging of fabrics is a very new technology, but one that has grown very rapidly over the past three decades, stimulated by military demands for lighter and more efficient materials, but with the benefits being felt across a wide sector of the industrial, commercial, and leisure industries. The overall market for preps is currently estimated to be in excess of 1000 million

US\$ per year world-wide, and although there is a reduction in military requirements, this is rapidly being made up for by an increase in almost all sectors of non-military application.

Some military fighter aircraft utilise as much as 70% of their total weight in the form of prepreg materials. Some commercial aircraft utilise as much as 38% by weight of preps. Most current generation helicopters utilise entirely prepreg structures for the body and rotors. Minesweepers and many other types of small naval vessels, as well as the majority of racing yachts, sailboards, surfboards, and so on, are made from preps. Formula One racing car bodies are made from preps. Tennis rackets, squash rackets, golf clubs, fishing lines, and many other sporting goods are constructed almost entirely from preps. Protective garments including helmets for the military, motor cyclists, horse riders, and so on are primarily made of preps. Moulds are increasingly made of prep materials instead of metal, being easier to machine and more dimensionally stable at fluctuating temperatures.

13.10.2 Substrates

Preps can be produced from two types of substrate:

- (1) uni-directional (UD) tapes, where bundles of warp yarns are processed so as to produce a single-fibre thick sheet, which is then impregnated with the resin system;
- (2) woven, knitted and non-woven fabrics are impregnated by various techniques.

13.10.3 Fibre types

While the vast bulk of fibres employed in preps are glass, because of the relative low cost of this material, in value terms carbon fibre, Aramid fibres, ceramic fibres and other high-tech fibres play an important part, sometimes on their own and sometimes incorporated into glass fabric structures.

13.10.4 Resin systems

The bulk of the resins employed in prepregging are based upon epoxy systems, which are applied from solvent solution in order to produce an air-bubble-free prepreg, or in the form of aqueous dispersions, or as 100% solids materials applied either at room temperature and post-cured by heat or UV systems, or applied at hot melts. In all cases, the epoxy resin is a two or more component mix that will polymerise at pre-determined speeds at appropriate temperatures. The open time of the resin system is relatively short, and for this reason the application temperature is kept as low as possible with the polymerisation being allowed to proceed only to a certain point prior to refrigeration of the product, so that the prep can subsequently be laid up and caused to flow, creating a multi-ply homogeneous structure that is then fully crosslinked into the final moulded form. In this state, it can then be further machined as appropriate.

A certain quantity of pre-cast epoxy resin film is also used, being laid up between the fabric structures in the mould and caused to flow into the fabric structure in the moulding process under the influence of heat and pressure.

13.10.5 Prepregging machinery design and techniques

The very highly specialised nature of the majority of prepreg applications is such that there are very many different designs of machine required to meet the individual processing conditions for the specific end-products. The more common machine designs and application techniques are outlined below.

Solvent impregnation

For solvent impregnation, it is normally necessary to effect the prepregging in two stages.

- (1) The fabric or UD tape needs to be pre-wet using an extremely dilute solution of the resin system being applied, just applying a sufficient quantity of the low-viscosity, solvent-based resin to wet the surfaces of the fibres within the individual fibre bundles or strands, so that when the subsequent application of the higher-solids, higher-viscosity material is undertaken, a thorough impregnation and wet-out of the fibres with the resin is achieved. This main resin application is normally effected in an impregnating bath in which the fabric is so handled that the air is eliminated from the fibre structure and replaced with the solvent-based resin system. The required final weight of resin pick-up is achieved by passing the material between metering rollers set at a precise gap and usually rotating at a slow speed in the reverse direction to the web path (Figure 13.24).

The material then passes vertically upwards through a drying tower where the solvent is evaporated. On the down leg from the tower, the resin is partially polymerised by the application of the required temperature/dwell time relationship. The material is then rapidly cooled and wound up with release paper or, more probably, release film applied on either side, and placed into a deep freeze.

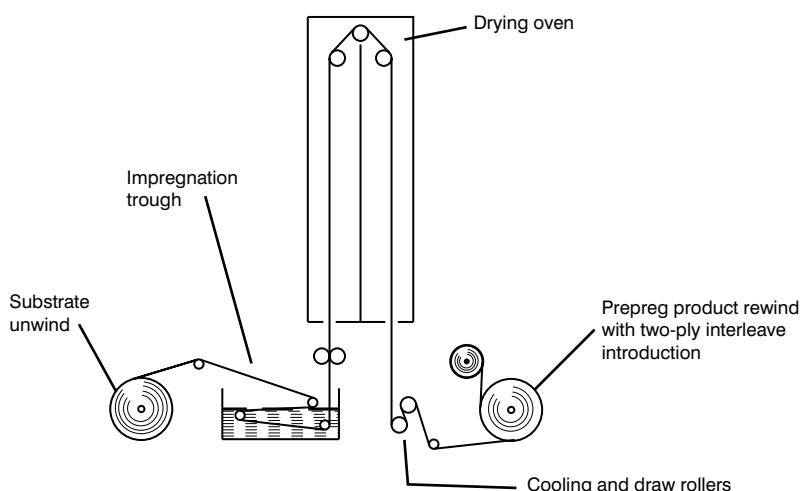


Figure 13.24 Vertical tower prepregging machine

- (2) Solventless resin systems are typically applied by blade-over-roll coating techniques, either directly into the fabric supported on a release paper, or by first coating the release paper and laying the fabric into the coating, followed by the appropriate 'massaging' of the fabric/resin system to achieve a uniform impregnation of resin into the fabric. The fabric is again rewound with appropriate inter-ply films and papers, before being placed in the deep freeze storage section.

Marine construction

In the marine construction field, particularly where large structures are being produced, prepregging and lay-up of the prepreg into the mould can be carried out simultaneously with a traversing prepreg unit being located along the length of the mould, so that the resin is applied into the fabric structure. The fabric is then directly applied onto the mould to build up the appropriate thickness of prepreg in the various points of the finished product construction.

13.11 OVENS

Two types of oven are required in most coating, laminating, flocking and prepregging applications: drying and polymerising.

13.11.1 Drying ovens

The drying of a coating on a fabric is not the same as the drying of water from a wet fabric after typical finishing processes. Because the solvent or water is present in a relatively thick layer of the coating compound on the surface of the fabric, and unless the drying conditions are very carefully controlled, the solvent or water is caused to vaporise within the coating layer faster than it can migrate through that layer, giving rise to bubbles, blisters and pin-holes that will make the finished product technically unacceptable.

Figure 13.18 shows progressive slow drying of a coating, giving rise to a pin-hole-free film of reduced thickness at the end of the drying process ('good drying'). The figure also shows what happens when the processing conditions within the oven, in terms of temperature and air velocity, are wrong – there is a volatilisation of the solvent or water and blistering and pin-holing of the film results ('bad drying').

To avoid this happening, the drying oven must comprise a multi-zone unit in which the coating is subjected to a progressively increasing temperature while the air velocity is kept low enough to prevent the formation of a skin on the surface of the film. The migration rate of the solvent or water through the film to the surface must exceed the rate of evaporation of that liquid from the surface if the satisfactory drying effect is to be achieved.

In practice, this means that air velocities must be kept down to around 15 m s^{-1} during the drying process with air temperatures being maintained well below the boiling point of the individual solvents to be evaporated within each section. In a typical multi-solvent coating, the

lowest boiling solvents must be evaporated before the higher boilers are allowed to evaporate in any significant quantity.

The maximum efficiency of drying is achieved if the appropriate temperature and velocity of air is caused to impinge upon the upper and lower surfaces of the material as it passes through the oven (Figure 13.19). It is important that the percentage of air can be adjusted between the upper and lower plenums, and in certain circumstances it may be necessary for the temperature of the air to be differentiated between the upper and lower plenums. This is, however, an extra cost that is avoided where possible. In most ovens the air is recirculated by a fan through the heat exchange battery or flame chamber in order to minimise energy consumption, and a controlled percentage of the evaporated solvent or water is constantly extracted from the oven in order to maintain both safe and efficient processing conditions. An appropriate heat recuperation unit may be installed in the extract ductwork which, when designed and operated to maximum efficiency, can recover close to half of the energy that would otherwise be thrown away, by preheating the make-up air required in the oven.

Absolute elimination of all solvent or water is practically impossible, but in those applications such as surgical dressings and electrical insulating tapes where an absolute minimum of residual solvent is required, a final section within the drying oven is needed where the processing conditions are such that the final traces of solvent can be almost eliminated.

Where solvent-based coatings are being processed, the concentration of evaporated solvent within all parts of the oven must be maintained at a safe working limit. All solvents have a concentration range below which they are unable to ignite or explode. This is known as the 'lower explosive limit' (LEL), and will vary for each solvent. Above the LEL, there is a band where – if the solvent-laden atmosphere is subjected to any spark – expressive ignition will take place with usually serious consequences of mechanical damage and fire.

An 'upper explosive limit' exists above which the concentration of solvent is too great for ignition and explosion to be possible.

Under normal processing conditions, therefore, it is necessary that the concentration of the solvent or solvents be maintained at around one quarter of the LEL unless some suitable failsafe solvent concentration monitoring equipment is in operation. In recent years, this type of equipment has been refined so that the actual concentration of solvents can be very accurately monitored on a continuous basis. In the event of the concentration rising above a predetermined point, appropriate alarms are triggered, the machine can be shut down and appropriate exhaust systems or extinguishers activated at a point prior to any explosive risk.

Although this equipment is not cheap, it normally results in cost savings both in terms of reduced insurance premiums and a significant reduction in energy consumption because the plant can be operated at higher solvent concentrations, and hence there is a reduced volume of air needed to be heated. The operation of solvent recovery or incineration systems is enhanced.

13.11.2 Polymerisation ovens

Once the coating has been dried, it is frequently necessary to effect polymerisation in order to

achieve the required long-term performance characteristics in the resin. These typically require the film to be held at a certain temperature for a certain duration. Normally, for every 10 °C temperature rise, the dwell time may be halved.

Polymerisation can therefore be carried out in an oven with very low air flows and extraction volumes, but where the air distribution system is such that good temperature uniformity is achieved across the full width of the product (Figure 13.25). Thus while horizontal single-pass ovens with or without stenter frames are technically fine, less cost and space is required in multi-roll or festoon baking ovens where the fabric passes up and down around a series of rollers, so that typically 75 m of fabric can be contained within a polymerisation oven measuring only 2–3 m in length, dependent upon the available height.

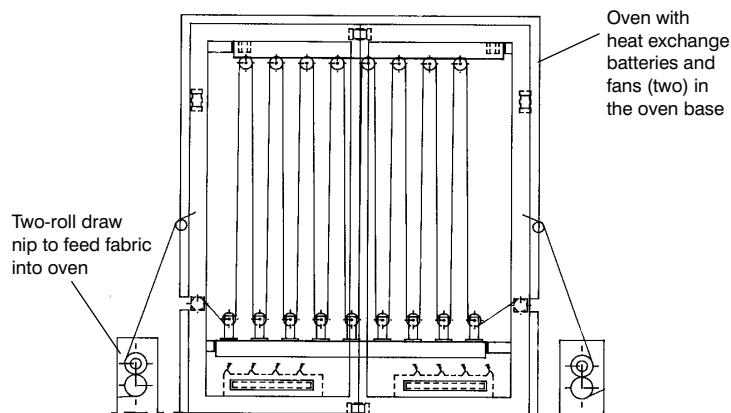


Figure 13.25 Polymerisation oven

In designing a drying oven for a coated fabric, one must take very special care to ensure that the following primary parameters are correctly calculated and that the machinery allows the correct levels and control of these parameters to be achieved.

Air temperature

The attainment of good drying is not dependent upon having a particularly high temperature. Indeed, too high a temperature will cause far more problems than too low a temperature. The temperatures must be set and graded along the length of the drying oven so as to ensure the evaporation of the water or solvents without drying the surface of the coating. Where a mixture of different solvents is present, this temperature control is of even greater importance to ensure that the lowest boiling solvent is evaporated first, and that higher boiling solvents are progressively evaporated one after the other.

Air velocity

The velocity of the air impinging upon the coating's upper surface and lower surface is equally

important. Too high a velocity will lead to a drying/skinning of the surface of the coating and the consequent problems associated with volatilisation of the solvent or water within the coating as described above.

However, an adequate velocity is necessary to ensure that the evaporated material is rapidly removed from the surface of the coated substrate. A variability of the air velocity is necessary unless the machinery is to be used always for the same product. Similarly, a variability from one zone to another is necessary in order to achieve the correct drying rates at different levels of solvent or water retention.

Air volumes

Air can only carry a finite quantity of any material (22.4 l of air at NTP are required for 1 g mol). In practice, of course, one cannot afford to operate under normal circumstances with saturated air, and therefore in the case of the evaporation of water or non-flammable solvents, one needs to determine the maximum concentration of the volatile material in the air at which one wishes to operate, having regard for all aspects of the drying process.

Where flammable solvents are being used, it is necessary to ensure that the total volume of air being extracted from the oven will maintain the concentration of the solvent or solvent mix at one quarter of the lower explosive limit for that solvent or solvent mix, if no automatic solvent concentration monitoring is being employed. If it is in use, then the solvent concentration can be allowed to rise to 40% or even 50% of the lower explosive limit, according to the legislation applicable in the location involved.

Air-flow patterns

Not only is it necessary to ensure that the correct temperature, velocity and volumes of air are provided into the oven, but also to ensure that the movement of the air is so arranged as to achieve the maximum efficiency. The air, once it has impinged upon the surface of the material, must be quickly removed and not impede the arrival of the further quantities of air from the air distribution plenums. Thus the design and construction of the entire air delivery system is an extremely critical area, which can have a significant effect upon the drying efficiency of the oven.

Fume removal

Having evaporated the volatiles from the coating, these must be removed from the oven by the extraction system, and this must be sized so as to maintain the equipment with only the required and safe concentration of volatiles within the oven. Where flammable solvents are employed, automatic monitoring and failsafe shutdown devices are required by legislation to ensure the safe operation of the equipment. Where non-hazardous processes are being carried out, it is highly desirable from a cost-efficiency point of view to ensure that the oven is appropriately balanced to minimise energy utilisation while at the same time maximising the drying efficiency of the unit.

Bringing all of the above variables together, it can clearly be seen that any efficient drying oven must be arranged so that the individual zones can each be adjusted in respect of air temperature, air velocity impingement upon the substrate from above and from below the web, air volume circulation and extraction from the oven. All of these factors need to be adjustable according to the processes being effected, while the actual air flow paths need to be correct for the volumes, velocities and temperatures involved.

13.12 ENVIRONMENTAL CONSIDERATIONS

Under the various Health and Safety Regulations governing the use of equipment and the carrying out of industrial processes, serious consideration must be given at all stages in the design, construction, installation and operation of the machinery used in the coating, laminating, flocking and prepegging fields.

The designers, manufacturers, suppliers (including agents), owners and operators of machinery owe a duty of care to themselves and to others to ensure that the equipment is designed, constructed and operated so as to avoid causing any hazard to anyone, either by virtue of direct contact with the machine, or from any discharges that may come from the machine. Thus, in respect of the machine itself, it is necessary that a number of precautions be taken to ensure its safe working at all times. These include:

- (1) that all drives, nips, or other hazardous points on the machine are guarded to prevent access to them when the machinery is capable of operation, and that all such guards are 'failsafe' so that their function cannot be overruled to create an unsafe situation;
- (2) that the external temperature of any ovens or heated rollers is such that no injury can befall any person from contact with that surface; this means either adequate thermal insulation or guarding is required to prevent anyone having contact with the heated surface if such insulation is not possible;
- (3) the elimination of excessive noise from any equipment by suitable design or insulation;
- (4) the avoidance of the use of any toxic or in other ways hazardous chemicals, or if they are to be used, to ensure that the equipment is designed so that no operator or other person can come into contact with them or their vapour during the operation of the equipment; this includes the adequate ventilation of the working area around the machine, and the extraction of any volatiles given off during the process in such a way as to ensure that the operators are not subjected to any unsafe concentrations of such materials;
- (5) that the equipment must also be designed, constructed and installed so that it will not cause any interference with other machinery, and that it is itself not subject to interference by any electromagnetic radiations that may impinge upon it.

In addition, the equipment must be installed in conjunction with suitable ancillary equipment to ensure that no pollution of the external environment occurs as a result of any of the processing to be done on the machine. This requires specialised equipment, which can include systems outlined below.

13.12.1 For solvent-based systems

All solvents are essentially hazardous in one way or another, and their discharge to atmosphere is or very soon will not be permitted. To overcome the problem there are a number of options available.

Solvent recovery

By adsorption onto activated charcoal or by condensation, solvents can be recovered and, after recovery and possible purification, can be re-used. This technique is generally most efficient where single solvents are employed, and where no water is being evaporated as well, so that the recovered liquor is the same pure or almost pure solvent that was initially introduced into the process. Where mixed solvents are employed, or where a concentration of water is mixed with the solvent, additional costs for purification, distillation and separation may make the solvent recovery option uneconomic.

Incineration

Here, the evaporated solvent can be burned in a suitably designed and constructed incinerator with the heat from the burning of the solvent being utilised either to heat directly the processing oven, or – more normally – to heat circulating hot oil or hot water, or steam systems, which return the recovered heat to the processing line.

In practice, this option is normally cost-effective, provided that there is a sufficient demand for the considerable amount of heat liberated from the burning of any solvent. Although actual calorific values vary from one solvent to another, the energy liberated from the burning of any solvent is typically 3–4 times the energy required to evaporate that solvent, so that the cost efficiency of an incineration system often depends not upon whether enough heat is liberated, but whether the company has sufficient use for all of the energy derived from the incinerator.

With careful planning and a degree of luck, an incineration system can be very cost-effective, despite the initial high capital cost, and can offer not only a solution to the legal obligations of the process, but can also give a payback of less than two years.

Catalytic oxidation

The catalytic oxidation of solvents is similar in principle to incineration, but the actual burning of the solvent is replaced by a catalytic conversion of the solvent from its initial form into derivatives that do not have an adverse effect upon the environment, and which can be discharged into the environment without problem.

In the conversion process, energy will normally be liberated and this energy can be harnessed as described above.

13.12.2 Water-based compounds

Although water is itself of course not a hazardous material when discharged into the

atmosphere, it is necessary to carefully consider the consequences of discharging the evaporated products from a water-based coating line into the atmosphere because water vapour is a very visible material, and when discharged in large quantities from a chimney gives a ‘false’ impression that pollution is occurring. Also, in practice there may well be certain other volatiles present within the discharged water vapour that *are* hazardous, and which need to be removed before the air is fit for discharge into the environment. There will also be a considerable amount of energy present in the discharge air/water vapour because of the high energy requirement to evaporate water (1 calorie per gram per 1 °C temperature rise plus 540 calories per gram latent heat of evaporation). Thus, it is extremely cost efficient to effect a heat exchange between the outgoing air and incoming air, in order to recover for re-use as much of the energy that would otherwise be discharged to atmosphere, and in the course of reducing the temperature, one is assisting in the removal of other volatile products from the air-stream. These can be further removed by passing the air through either electrostatic precipitators or water spray scrubbers, so that the finally discharged air is free from pollutants.

13.12.3 Flame lamination

In the section on lamination (Section 13.6), it was mentioned that the flame laminating process gives off a number of toxic materials. Until recently the discharge of these into the atmosphere has been permitted, provided that the concentration was reduced to pre-determined levels. This was achieved by diluting the pollutants, rather than eliminating them. New legislation requires that all such pollutants be eliminated to below a pre-determined quantity per unit time, and this has or will have a significant effect upon the discharges from such flame laminating equipment, as well as from all other types of processing machinery.

Satisfactory cleaning of the exhaust from a flame laminating machine can be achieved to current regulation standards by the use of special carbon absorption filters. Incineration and aqueous scrubbing are only partially satisfactory, destroying only a part of the pollutant and converting the pollutant from an airborne to a waterborne state.

13.12.4 PVC

PVC platisols contain a relatively high percentage of plasticisers (di-alphonyl phthalate, di-isooctyl phthalate, and so on), which are partially volatilised during the gelation and curing of the PVC. Until recently the discharge of these materials into the environment has been permitted. However, under current legislation this is no longer permitted, and the volatilised plasticisers must be either incinerated or in some other way removed from the discharge air-stream.

By incorporating heat recuperators to drop the air-stream temperature from the ovens, and then feeding that cooled air-stream into suitably designed and constructed scrubbers, the PVC plasticisers can be condensed. This is more cost-effective than incineration, where relatively large and expensive equipment is required, but from which virtually no heat can be recuperated.

13.12.5 Electromagnetic compatibility

Under current legislation, the giving off of electromagnetic radiation by any machine or the supply services to any machine is considered to be an environmental pollution, because of the adverse effect that it can have upon other machinery. All equipment must now be designed and constructed so that it does not give off such radiation and is itself insensitive to the effect of any such radiation given off by any other equipment.

13.13 TEST METHODS

The production of appropriately coated, laminated, flocked or prepreg fabric needs to be assessed to determine the attainment of the required end-product performance properties, and to establish that these are in conformity with the requirements of the application into which the product is to be supplied. Thus a series of standard and, generally speaking, internationally recognised test procedures have been developed which allow products to be tested. These include:

- (1) abrasion resistance;
- (2) scuff resistance;
- (3) pill testing;
- (4) water-repellency;
- (5) hydrostatic head testing;
- (6) Bundesmann waterproof test;
- (7) spray rating water-repellency test;
- (8) water vapour permeability;
- (9) drape test (Cusick drape tester);
- (10) peel bond strength test;
- (11) wash resistance;
- (12) dry-clean resistance;
- (13) colour fastness;
- (14) fire retardancy;
- (15) flex cracking;
- (16) burst strength;
- (17) temperature resistance (high and low).