6 Machine-washable knitwear — Production routes

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6.1 Introduction

The inherent ability of wool to shrink, or felt, during wet finishing has been used to good advantage for generations to produce a huge variety of products, ranging from woollen spun knitted and woven goods to felts for use either in hat manufacture or as coverings for snooker tables. Whilst this property divides for endless property development potential, it does constitute a major disadvantage in terms of end-product performance, and impacts considerably on the care labelling associated with wool products. Consequently, products made from wool which has not been subjected to chemical treatment may only be labelled as being suitable for either dry cleaning or hand washing.

Techniques for the production of machine-washable wool products have, of course, been a commercial reality for many years, but the importance of this type of finishing has recently assumed greater importance for a number of reasons, the most important of which is the progressive shift by the modern consumer to a more casual lifestyle, which, in turn, has emphasised the need for easy-care properties such as machine-washability.

Environmental issues and concerns have also now assumed greater importance in terms of product marketing, as evidenced by the high profile generic promotion of eco-labelled products, and the inherent machine-washability of a garment often warrants such a label, because of the legislation to which the dry-cleaning industry is progressively being subjected.

The end product which is the primary subject of this article is wool knitwear, and recent years have seen a number of developments in chemical finishing techniques which have been of particular relevance to the production of machine-washable garments. Although the options available to the knitwear finisher for producing machine-washable products might appear somewhat diverse and confusing (Figure 6.1), many of these processes have been developed and introduced with a particular end-product or market in mind; in most cases, therefore, only one or two options realistically need to be considered.

When deciding upon the finishing route to be used, the primary consideration is the nature of the product, since, whereas the production of a washable worsted spun product will feature techniques designed to prevent facing-up, woollen spun products will require a route which includes a milling cycle in order to produce a typical woollen finish.

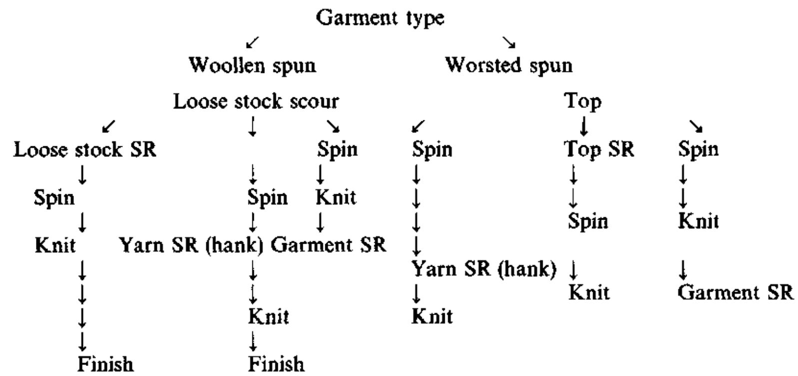

Figure 6.1 Options available for producing machine-washable products; SR = shrink-resist treatment.

Milling, the process by which yarns are burst to produce a raised finish, is a controlled form of felting, and clearly this procedure must be carried out before the shrink-resist treatment is applied; consequently, such products are most effectively produced using garment treatment techniques. Worsted spun products may be produced either from continuously treated top or via garment treatment routes, although yarn treatments in hank form may also be considered.

Woolmark specifications in terms of washability vary according to the nature of the product, with garments worn next to the skin, such as underwear, hosiery and shirts, requiring a higher performance standard than, for example, trousers or knitwear (Table 6.1). The specifications for knitted sweaters cover both felting and relaxation shrinkage, the primary distinction between them being that only felting shrinkage is irreversible.

Table 6.1 Woolmark shrinkage specifications for machine washable knitwear

	IWS test method	Sweaters and cardigans
Relaxation shrinkage		
% Extension—width maximum		5
% Shrinkage—length maximum	31	10
% shrinkage—width maximum		8
No. and type of wash cycle		1 × 7A*
Felting shrinkage		
% Area shrinkage—based on dimensions after 1 × 7A* wash		8
No. and type of wash cycle		2 × 5A**

* 1 × 7A Cycle is equivalent to 1 Woolmark Machine Wash Cycle. ** 1 × 5A Cycle is equivalent to 10 × 7A Cycles.
IWS = International Wool Secretariat.

The maximum area felting shrinkage permitted is 8% after a total of 20 Woolmark machine wash cycles (40°C), whereas the dimensional changes occurring during relaxation shrinkage encompass the possibilities of length and width shrinkage as well as width extension.

Relaxation shrinkage is normally introduced during finishing by oversize framing, i.e. stretching, immediately prior to steam pressing, and is effectively removed during the first wash cycle. Although, from a production point of view, it is important to be able to differentiate between, and measure, both components of shrinkage, it is of course of little consequence to the customer, whose only concerns in terms of garment performance are those of after-wash appearance and toal shrinkage.

6.2 Garment treatments

6.2.1 *Equipment*

Although the treatment route, or process, chosen depends upon a number of different factors related to the aesthetics of the product, e.g. handle required, colour combination/design, etc., an equally important consideration is that of the equipment available in which to treat the garments. However, before any form of shrink-resist finish is carried out, the garments must first be scoured and, for woollen spun products, milled to give the characteristic woollen aesthetics.

Numerous types of equipment are used for the scouring and milling of woollen spun knitwear, and many of the earlier models were based upon industrial washing machines featuring central rotatable drums. Such machines have a relatively severe mechanical action, and later models have incorporated a number of useful features such as high-speed hydro-extraction and a high degree of automation over heating and drum rotation speeds.

Another machine type which has been successfully modified for the scouring and milling of wool knitwear is the Pegg dyeing machine, in which the liquor is circulated by an impellor situated under a perforated false bottom. The garments are circulated in a spiral (toroid) fashion and, because it operates so slowly, it allows garments to be easily inspected without either draining or stopping the machine. However, because the action of the machine is so gentle, the milling times are somewhat longer than for horizontal, rotary drum-type machines.

Worsted-type products are generally processed in machines with a gentle action such as a side-paddle or overhead-paddle machine and, without doubt, the most widely used type of equipment for the shrink-resist finishing of wool knitwear is the side-paddle. The degree of sophistication and control associated with these machines varies considerably from those which feature a single-speed paddle to models, such as those from Flainox, which feature

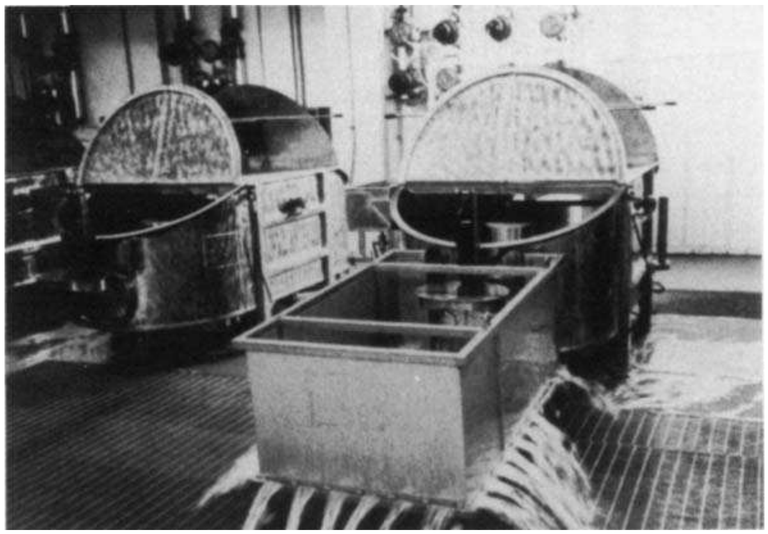

Figure 6.2 Flainox side paddle.

programming facilities, variable-speed paddle drive, chemical addition facilities, temperature control and automatic emptying (Figure 6.2).

Side-paddle machines operate at a liquor ratio of approximately 25–30:1, and because they exhibit a characteristically gentle mechanical action, are ideal for obtaining even and consistent results during both shrink-resist finishing and dyeing. However, the major disadvantage of this equipment lies in the relatively large volumes of water consumed. Overhead-paddles, which are usually used for garment dyeing, may also be used for the finishing of knitwear but, because the mechanical action of these machines is even less severe than the side-paddle, the process times are extended still further. Furthermore, the degree of liquor exchange operating is also substantially less than that operating in a side-paddle which, for critical processes such as shrink-proofing, may lead to unsatisfactory results.

Most of the major developments in knitwear dyeing and finishing equipment in recent years have been associated with front-loading machines, which offer the advantage of lower liquor ratios (10–15:1) and a high degree of automation and, furthermore, integral hydro-extraction facilities provide for much more rapid and efficient rinsing facilities. However, it is precisely because of the low liquor ratios which are a feature of these machines that they are not entirely suitable for shrink-resist finishing, and those companies which do operate this type of equipment may utilise its higher productivity only for certain parts of the production route, e.g. scouring and milling of garment dyeing, following piece chlorination in a side paddle.

6.2.2 *Scouring and milling procedures for woollen spun knitwear*

The scouring and milling of woollen spun products is an extremely important part of the finishing routine, and many companies have developed their own in-house techniques to produce the aesthetics typically associated with their products. Woollen spun products contain relatively large amounts of oil, which must be removed either before or during milling; this is normally achieved by using anionic or nonionic detergents under mildly alkaline conditions, e.g. sodium bicarbonate or carbonate, and a typical procedure would be as follows:

Scour	Set bath at 40°C Add 3–6% detergent Run 3–15 min Drain bath
Mill	Set bath at 40°C Add 1–3% detergent Run 3–40 min Drain bath Warm rinse (3–5 min) Drain bath Cold rinse (3–5 min)

In preparation for shrinkproofing it is essential that a maximum oil level of 0.8% on weight of wool (o.w.w.) is achieved (DCM Extract). The scouring procedure adopted to achieve this level will depend upon the nature of the lubricant used in yarn production and, although most modern woollen spinners use low levels of synthetic, water-soluble lubricants which are easily removed during scouring, higher lubricant levels which contain vegetable or mineral oils may still be encountered. Products of this type may only be removed efficiently by scouring under alkaline conditions using sodium carbonate, but, wherever possible, this procedure should be avoided because it can result in yellowing and also impair the handle of the wool. Such conditions may also result in the removal of dyestuffs leading to shade change or, when processing high colour-contrast designs, backstaining on to pale shades or undyed areas. However, several auxiliaries are now available which, provided that the amount of dyestuff removed is not excessive, can effectively prevent this from occurring.

A temperature of between 35 and 40°C is recommended for both scouring and milling because it is within this temperature range that the detergents are most effective and, because most of the residual oil is removed during the scouring cycle, the detergent concentration can be normally reduced by half in the milling cycle. Some companies do in fact scour and mill their garments in a single operation and, although the use of modern spinning lubricants does make this option more viable, its use as a preparation for

Table 6.2 Typical scouring and milling times for different types of equipment

		Process time (min)	
Machine type	Liquor ratio	Scouring	Milling
Rotary	12:1–20:1	3–10	3–10
Paddle	30:1–40:1	10–15	20–40
Toroid	10:1–20:1	5–10	10–20

shrink-proofing should first be carefully assessed before committing garments to production. As a general recommendation, the minimum scouring–milling time used should not be less than 3 min, to ensure efficient cleaning of the garment. Efficient scouring is a particular concern for the commision shrink-proofer, especially for woollen spun products where the level and type of lubricant used in yarn manufacture may vary significantly depending on the yarn source. Under these circumstances, solvent scouring techniques have been found to be an extremely effective option. Solvent milling may also be carried out following scouring by the selective introduction of a mixture of water and emulsifier into the machine, but in practice a superior handle is often obtained using aqueous milling techniques and it is not uncommon for an aqueous mill and shrink-resist finish to be applied following solvent scouring.

The extent to which woollen spun products such as lambs' wool and Shetland garments are milled can vary considerably, and this is particularly the case with lambs' wool, since certain markets now require a clean finish which is more reminiscent of a worsted spun product. For machine-washable products the degree of finish obtained during scouring and milling must be reduced to compensate for the additional milling which may occur during subsequent shrink-resist finishing, and the reduction in the length of the milling cycle will of course vary, depending on a number of different structural factors and the type of equipment being used. Typical scouring and milling times for different types of machine are shown in Table 6.2, but for a fixed milling time the degree of finish achieved will increase with increasing fibre fineness, increasing yarn count, reduction in yarn twist, reduction in cover factor, and even the colour of the wool, since dark, heavy shades can often require milling times of up to three times as long to achieve the same finish as that obtained on a pastel or pale shade. However, once these parameters have been established for a particular product and machine combination, reproducible results in terms of finish and handle may be readily obtained.

6.2.3 *Scouring and anti-cockle procedures for worsted spun knitwear*

The criteria which must be satisfied in the production of worsted spun products differ considerably from those of woollen spun products, since a clean finish in which the knit structure is clearly visible is required and every effort is therefore made to prevent milling or facing-up of the garments during processing. However, worsted spun products can often exhibit a phenomenon termed as cockling, which is described as 'an irregular surface effect caused by loop distortion'. This effect, which occurs most often in plain knit structures, is due to the relaxation of mechanical strains introduced during spinning or knitting, and almost invariably occurs when the garment is relaxed in water leading to a three-dimensional distortion of the knit structure. This effect occurs either at the rib–panel interface, near panel edges or, in severe cases, randomly distributed over the whole garment (Figure 6.3).

Provided that these effects are not too severe they can be eliminated, or at least significantly reduced, by carrying out an anti-cockle process. This is designed to set the yarn in the knitted configuration, and the normal wet-finishing routine adopted for processing worsted spun garments is therefore as follows:

Anti-cockle → Scour (optional) → Shrink-resist treatment

Again, because the processing aids used in the production of worsted spun yarns are applied at such low levels and are also often water-soluble, the scouring requirements are minimal, and in fact the anti-cockle procedure itself is normally sufficient to reduce the residual oil level to a value which is compatible with the application of a shrink-resist finish.

The conditions operating in the anti-cockle treatment will reflect the nature of the cockling which has been observed and, if it is not too severe, a mild treatment may be used as follows.

- Set and maintain the bath at the boil with the paddle operating at a speed which is just sufficient to prevent the garments from sinking.
- Add the garments individually to the bath and allow them to static-soak for 10 min, occasionally operating the paddle for 10–20-s periods.
- Cool the bath slowly to 40°C by adding cold water, again with the paddle operating at minimum speed. It should be noted that rapid cooling can cause permanent creases to be set into the garments.

This procedure often provides sufficient stabilisation to allow the garments to survive conventional shrink-resist finishing; however, if the cockling performance is particularly poor or if the garments are to be piece-dyed, a higher degree of set may be required. This is achieved by adding sodium metabisulphite or sodium sulphite (3–5% on weight of wool) to the anti-cockle bath immediately before adding the garments. This procedure will improve the performance considerably but, because some dyestuffs are sensitive to reducing agents, an effective compromise in terms of shade change and cockling may be obtained by treating at 80°C rather than at the boil. In both cases, the sensitivity of the dyestuffs being used must be tested before committing garments to bulk production.

The factors responsible for producing cockling in worsted spun knitwear are extremely varied and have been discussed at length in the literature

(a)
(b)
(c)

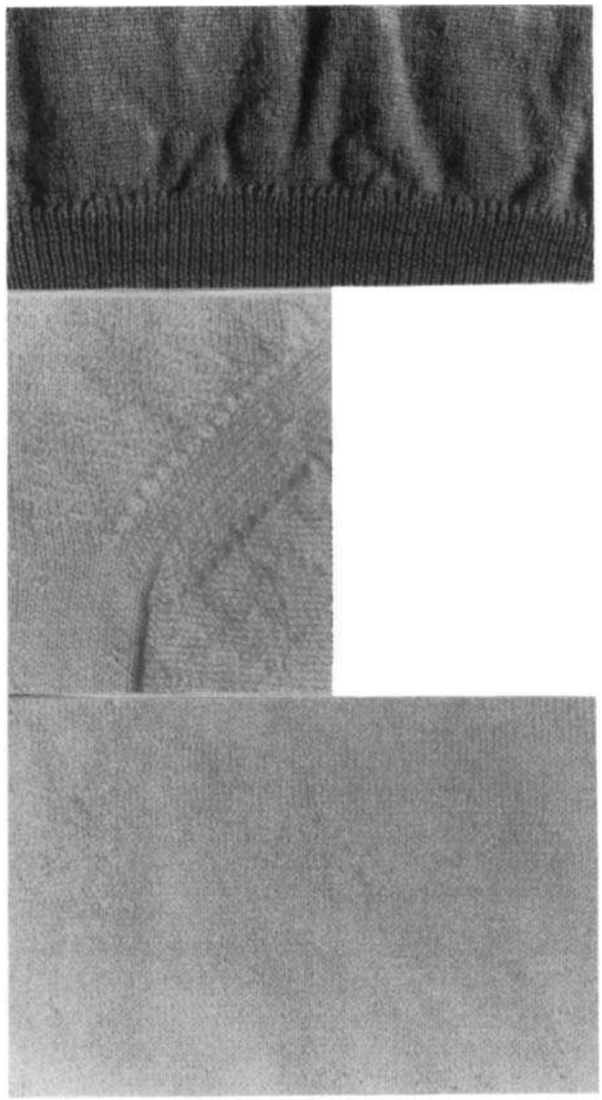

Figure 6.3 Examples of cockling: (a) cockling at the junction between the rib and plain knit area; (b) severe cockling near to the panel edge at fashioning points; (c) an example of severe random all-over loop distortion.

(Robinson *et al.*, 1965), but there is little doubt that its primary origin lies in the evenness and consistency of the yarn and ultimately those factors which can influence these properties. The quality of wool used in the production of a particular yarn is a major contributory factor and, as a general observation, the tendency of yarns to cockle reduces with decreasing fibre micron. The fibre micron range used can also influence cockling, and attempts to reduce manufacturing costs by diluting a blend with coarser fibre often leads to an increase in yarn rigidity, which in turn leads to yarn irregularity and ultimately cockling.

The degree of set imparted to yarns prior to knitting can also exert an influence since, if yarns cannot be reset in the knitted configuration, one might therefore expect an inferior result. The performance of package-dyed yarns in terms of cockling therefore tends to be inferior to an equivalent yarn which has been dyed either in hank form or produced from top dyed wool.

Where most of the garment is not affected, cockling may still occur at the rib–panel interface and at panel edges where loops are stretched during fully fashioned knitting. Both can be significantly improved by using conventional anti-cockling procedures, and further improvements at the rib–panel interface might also be expected by adjusting either the tightness of the rib or the cover factor of the plain knit area such that, on relaxation, the dimensions of both are similar; additional improvements may also be obtained by doubling when transferring the rib to the fully fashioned machine.

Panel edge cockling is more difficult to overcome but can be reduced by minimising the rate of width change during knitting, i.e. by reducing the angle between the line of the panel edge and the vertical wale lines.

Other properties such as yarn regain and tension control during knitting have also been implicated in the occurrence of cockling, albeit to a lesser extent than some of the other factors considered, but there is little doubt that the primary causes are those associated with yarn quality, and when these issues are addressed an anti-cockle procedure may not always be required, even when garment dyeing.

For garment finishers who do not routinely use, or have access to, yarns of this quality, the factors responsible for cockling are of little importance, unless action based on this knowledge can be taken to improve the situation. The primary concern of the finisher is to produce a garment which is of a commercially acceptable quality, and interest lies therefore in techniques and procedures which will allow this aim to be achieved. In most cases, an acceptable product can be obtained by carrying out an anti-cockle treatment and/or adressing some of the other points discussed in this context. However, when cockling is particularly bad, it may even occur in garments which have been stored prior to wet-finishing. Under these circumstances it is essential that the garments are subjected to an anti-cockle treatment as soon as possible after knitting, and if the necessary equipment is available, garments should also be steamed and framed immediately before treatment. Such a procedure would clearly only be used where no other option was available and is designed to deal with the symptoms rather than the cause of the problem. However, if an acceptable product may ultimately be produced by adopting these techniques, exposure to water should of course be avoided and the care label in the garments should therefore specify dry-cleaning only and not hand-washing.

6.2.4 *Garment shrink-resist treatments for knitwear*

Batch techniques for the treatment of knitted garments are by far the most versatile route for the production of machine-washable knitwear, since not only do they provide for the option of processing both woollen and worsted spun products, but they also allow the production of garments in a variety of shades and colour combinations and provide considerable scope in terms of handle modification.

Although there are many processes available to the modern knitwear finisher, in practice the options available are very much dictated by factors such as the nature of the equipment available, the type of garment (woollen or worsted), the shade or colour combination, the handle required and the inclusion, or omission, of dyeing in the finishing cycle.

Most batch processes for knitwear, in common with all other shrink-proofing treatments, feature an oxidative pretreatment in combination with the application of a suitable polymer, although two processes have been successfully used which feature polymer application only, namely Synthappret BAP (Bayer) and DC 109 (Dow Corning/PP(T)), the latter being applied from solvent in a modified dry-cleaning machine.

The relative merits of the batch routines currently available are considered in the following sections.

6.2.4.1 *Oxidation/polymer systems.* The oxidising agents most commonly used in the treatment of knitwear are either dichloroisocyanuric acid (DCCA) or potassium peroxymonosulphate (PMS). The former is available from BASF (Basolan DC) and PP(T) (Dylan Auxiliary), and the latter from BASF (Basolan 2448), PP(T) (Dylanise Salt), Interox (Curox), Dupont (Oxone) or Degussa (Caroat). Although an oxidative pretreatment alone will impart a degree of shrink-resistance, the extent of which will depend upon the application level used. Its primary function is to prepare the surface of the fibre for polymer application, and the combined effects of both lead to the production of a full machine-wash finish.

Both products are well-established in the field of knitwear finishing but each exhibits advantages and disadvantages which must be taken into consideration when deciding on which process is to be used. For example, DCCA treatment often results in a degree of yellowing, the extent of which will depend upon a number of factors including the treatment level used and the conditions under which it is applied; consequently it is unsuitable for the treatment of garments that feature pastel shades or high colour contrast designs. PMS treatment, however, imparts a mild bleaching effect and there are therefore fewer restrictions in terms of the colours or colour combinations that may be treated.

The potential for knitwear to shrink is influenced by a number of different factors and, as a result, some products are much more difficult to stabilise than others. For instance, worsted spun products are more difficult to stabilise than woollen spun products, because the finer quality wools which are often used in their production exhibit a higher tendency to shrink and also the tighter cover factors which are a feature in such products can prevent complete penetration of the oxidising agent into the yarn or knit structure. Of the two products, DCCA is far superior in terms of shrink-resist efficiency and, as such, is equally effective on a wide range of products. PMS is much less effective in this respect and its use is therefore restricted almost exclusively to the treatment of woollen spun products.

Another, and more fundamental, difference between these two oxidising agents is that, whereas DCCA treatment imparts shrink-resistance progressively as it reacts with the wool, this is not the case with PMS, which by itself imparts no resistance to felting whatsoever. Shrink-resistance with Caroat treatment is only subsequently achieved by after-treating (developing) the oxidised wool with sodium sulphite under alkaline conditions (Sweetman and McLaren, 1965). The degree of shrink-resistance imparted by this route increases progressively with increasing pH in the development stage, but in practice a maximum pH value of 8.0 is normally adopted. Such conditions can result in the removal of loosely bound dyestuffs and dyed soluble proteins which are generated as a result of the oxidative treatment, in which case their redeposition on to the garments can result in back-staining. The procedures adopted to minimise this effect will vary depending on the severity of the problem and the nature of the design.

Clearly, if large amounts of colour are removed during this stage of the process then a similar situation would have been observed during scouring and the dyeing procedure itself would ultimately have to be addressed. For solid shades, the consequences of treating such garments would then merely be a change in shade as a result of dye loss, but for high colour-contrast designs the situation following scouring may well be irretrievable. Where dyestuff loss is less apparent, back-staining can be prevented by including in the bath a proprietary auxiliary designed to hold dyestuff in solution, typical products being Milliclean IBA (PP(T)), Croscour SA25 (Crosfields) and Tinuvetin LB (Ciba). Further improvements may also be achieved by using a lower pH during the development stage following Caroat treatment, but this procedure realises only a proportion of the potential shrink-resistance imparted by the oxidative pretreatment, and therefore relies more on the shrink-resist efficiency of the polymer to achieve full machine washability.

Although a variety of polymers is used in combination with an oxidative pretreatment, not all products are compatible with both PMS and DCCA pretreatment. The polymers that may be used in combination with DCCA include Basolan SW and Basolan MW (BASF), Hercosett (Hercules) and Polymers RSM and GE (PP(T)), the latter being the polymeric component of the Dylan GRB process, by far the most widely used route for the treatment of knitted garments. All of these combinations are equally effective on both woollen and worsted spun garments, although the pretreatment level required varies depending upon the type of product and the polymer being used. Some polymers, namely Polymer GE and Hercosett, do require the application of a suitable softener to achieve an acceptable handle. Neither Polymer GE nor Hercosett is compatible with PMS treatment, but silicone-based products such as Basolan MW (BASF) and Ultrasoft (PP(T)) are used to good effect in the production of soft handling woollen spun lambs' wool. Further, non-silicone-based products, namely Polymer RSM and Polymer TM (PP(T)), are also suitable for use in the treatment of woollen spun products.

The reason for the difference in terms of shrink-resist efficiency between the two oxidative treatments is not immediately apparent, since both result in the production of a high concentration of sulphonic oxides at the fibre surface which, in turn, provide sites for the attraction of the cationic polymers during the subsequent exhaust treatments. It has been suggested that protein crosslink density, and ultimately the ability of such proteins to swell and prevent scale interaction, can influence the degree of shrink-resistance obtained with oxidation-only treatments, and this is consistent with the observation that DCCA leads to a lower protein crosslink density, and higher swelling capacity, than PMS treatment (Byrne *et al.*, 1990). However, of much more significance is the observation that, whereas chlorination produces a marked increase in wettability which ultimately leads to improved polymer spreading and increased wool/polymer adhesion (Bereck and Reincke, 1989), PMS has little or no effect in this respect (Byrne *et al.*, 1979). Consequently, only those polymer systems which exhibit a surface energy below that of PMS-treated wool, namely silicones, will spread and adhere to PMS-treated wool, whereas those polymers exhibiting a higher surface energy, such as Hercosett and Polymer GE, are only compatible with chlorine treatment.

However, there is one exception to this rule, namely Basolan SW, which is compatible with both PMS and DCCA treatment and which may be applied equally effectively to both woollen and worsted spun products. This product is perhaps the most efficient shrink-resist polymer available and as a result, the pretreatment conditions necessary to produce full machine-washability are not nearly as critical as with other polymer systems. In practice, this means that the development pH required following PMS treatment is much lower than that required for other polymer systems, and this observation has led to the development of a one-bath process in which PMS treatment is followed by simultaneous development and polymer application at pH 6.0 in the presence of sodium metabisulphite, features which all but eliminate any potential for back-staining, while also reducing water consumption and increasing productivity.

6.2.4.2 *Garment dyeing.* Shrink-resist technologies impact considerably on the dyeing process, not only because of the influence of the chemical treatment on the dyeing properties themselves, but also because of the higher dye fastness requirements. These specifications do impose some restrictions on dyestuff selection but, as a general observation, there are few shades which cannot be produced to a machine-washable standard. Dyestuff selection is beyond the scope of the article and for further information on this subject, either the International Wool Secretariat (IWS) or the dyestuff manufacturers themselves should be contacted.

The colour fastness of Woolmark products produced by garment, yarn, stock or top dyed routes must meet the IWS Machine Washable Colour Fastness Specifications. These are illustrated in Table 6.3.

Garment dyeing may be incorporated into a conventional shrink-resist finishing route, although the potential for facing-up or milling is much greater because of the extended processing time and high temperatures involved and, as with conventional shrink-resist finishing, the procedure adopted will depend very much upon the nature of the product and the type of equipment available.

The ideal route in terms of preventing excessive milling would be to dye immediately following a full oxidative/polymer shrink-resist process, but this option has not been widely adopted because any unevenness in terms of polymer distribution, which is cationic in nature, is invariably reflected in an uneven dyeing. The recommended procedure therefore is to rely upon the chlorination stage to stabilise the garments against felting during dyeing and, to this end, somewhat higher treatment levels are used than in conventional garment shrinkproofing (Ryder and Lavocah, 1984). However, chlorination also radically affects the dyeing properties of wool and, once again, any unevenness in treatment can lead to uneven dyeing, notably in terms of seam penetration. Particular care must therefore be taken to ensure that all areas of the garment are evenly treated.

Table 6.3 Colour fastness requirements for machine-washable knitwear

Colour fastness to	IWS test method	Minimum fastness rating		
Light	TM 5	3 at 1/12 standard depth and below; 4 above 1/12 standard depth		
		Change in shade	Staining of wool and nylon	Staining of other fibres
Washing	TM 193	3–4	4	3–4
Wet alkaline contact	TM 174	3–4	4	3–4
Rubbing wet and dry	TM 165	—	—	Wet/dry 3/3

6.2.4.3 *Equipment for garment dyeing.* Not surprisingly, the equipment recommended for garment dyeing is much the same as that used for shrinkproofing and, again, the side-paddle is the most widely used machine. The trend in all garment dyeing is towards the use of rotary machines because of the high degree of control and increased productivity that they provide, but when processing wool garments the low liquor ratios which operate in this type of equipment effectively increase the rate of chlorination, leading to an uneven and inconsistent treatment and ultimately poor quality dyeings. Consequently, in order to take advantage of the increase in productivity associated with such machines, one option is to carry out the chlorine pretreatment in a side-paddle and transfer the garments to the rotary machine for dyeing.

6.2.4.4 *Bright pastel shades.* Although the action of a side-paddle is gentle, milling and facing-up can be reduced still further by turning the garments inside out and operating at a paddle speed which is just sufficient to maintain constant movement of the garments through the liquor. The latter procedure may also be useful in controlling the rate and evenness of chlorination, but these parameters are more commonly controlled by adjusting the pH and temperature of the liquor. Where the water temperature varies considerably throughout the year, and cooling is not an option, consistency in terms of treatment time may be obtained by carrying out the chlorination stage at the maximum ambient temperature and heating the bath to this temperature when necessary. In addition, the rate of reaction may also be controlled by adjusting the liquor pH, with the rate of reaction decreasing with increasing pH. However, the disadvantage of this approach is that the degree of yellowing obtained also increases with increasing pH and, although this effect is of little consequence when dyeing to dark heavy shades, bright pastel colours cannot be produced unless this problem is addressed.

Because PMS treatment does not yellow wool, it might therefore be considered as a viable alternative to DCCA treatment; however, PMS does not impart sufficient shrink-resistance to enable the garments to survive the dyeing cycle. One solution therefore is to use wool which has been continuously chlorinated in top form; this route offers advantages in terms of evenness of treatment, and therefore dyeing quality, and furthermore the acidic conditions which operate during continuous top treatment minimise yellowing and therefore permit the production of pastel shades.

In the absence of treated top, such shades can be obtained via the batch route by carrying out a combined reductive bleach and antichlor immediately following chlorination, using a stabilised hydrosulphite product.

Additional improvements in terms of colour maintenance are obtained by dyeing at low temperatures (85°C) and by including in the dyeing a dyebath bleaching agent such as Lanalbin B (Sandoz), Erioclarite B (Ciba) or Lufibrol W (BASF). Further improvements in evenness of dyeing are obtained by using specific low-temperature dyeing auxiliaries such as Baylan NT (Bayer) and Lanasan LT (Sandoz), and improved control over dyestuff exhaustion is obtained by the use of acid donors. These products are esters which are progressively hydrolysed with increasing temperature, slowly releasing acid in the process. This produces a gradual shift in the pH from slightly alkaline or neutral pH to acid, and thus enables the dyeing to be started under conditions which provide for uniform dye uptake, i.e. pH 7.5–7.0.

6.2.5 *Polymer-only treatments*

Because most of the practical problems associated with the batch treatment of knitwear originate from the oxidative pretreatment, the ideal process is one which achieves full machine-washability via polymer application only. Two such processes are available for the treatment of knitwear, one of which is applied under aqueous conditions and the other from solvent in a modified dry-cleaning machine.

The aqueous-based route features the exhaust application of the product Synthappret BAP (Bayer), a polymer emulsion which is used extensively in certain markets for the shrink-resist treatment of woven wool fabrics. In this case, application is by padding and the treated fabric is then cured in a tenter at a temperature of not less than 140°C, but for the treatment of knitwear an exhaust application technique is used which relies upon destabilisation of the polymer emulsion using magnesium chloride; this leads to the polymer being taken up by the wool and complete curing is then achieved in the bath merely by raising the pH. The performance of garments processed by this route is excellent in terms of shrink-resistance, shape retention and pilling, but the conditions required to cure the polymer effectively restrict the shade range and, although considerable improvements can be made with microsilicone based softeners, the handle is still not consistent with current market requirements.

The second route features the application of a crosslinkable silicone polymer from solvent, the polymer being DC 109 from Dow Corning/PP(T). Although numerous application procedures can be adopted, the most common technique is to immerse the garments in a solution of the polymer, extract to the required pick-up, then to apply the catalyst by spraying on to the garments as they are tumbling. The process produces a product which, like the BAP route, justifies the label 'high performance' because of its excellent resistance to felting, good shape retention and low pilling performance; furthermore, being silicone-based, it also imparts a degree of enhanced water repellency, and this has led to this product becoming well established in the golf market.

Once again, however, the handle of treated garments is not consistent with the requirements of 'High Street' retailers, and this finish is only seen to its best advantage on woollen spun lambs' wool, with both worsted spun and

Shetland products exhibiting a synthetic, greasy handle. A further negative feature of this process is the legislation which is being introduced to restrict the use and discharge of solvents and, in the light of this, the long-term future of this finish must be in question.

6.3 Yarn treatments

Wool yarn can be effectively shrink-resist treated in hank form although, as with garment treatments, there are a number of factors which must first be considered. The production of piece-dyed machine-washable knitwear requires that the chlorination stage be carried out prior to dyeing to prevent milling or facing-up during dyeing, and although clearly this is not a requirement for hank dyeing, the sequence adopted is just as important and is influenced both by the shade being dyed and the type of machinery being used. Because of the potential for shade change and yellowing which accompanies chlorination, the ideal processing sequence would be to chlorinate prior to dyeing; however, on hank-dyeing machines which feature convential stick supports, the reduced circulation of the stick–wool interface is sufficient to reduce the overall level of chlorination achieved in this area. This in itself is not sufficient to impair shrink-resistance but, because the final shade produced is a function of the chlorination level achieved, this sequence can lead to the production of 'stick marks'. Under these circumstances, chlorination must be carried out after dyeing is complete, thereby leading to restrictions in terms of shade range. If, however, the dyeing machine features stick supports through which the dye liquor may be circulated, such marks can be prevented, and a full shade range may be produced by utilising the dye-bath bleaching techniques used for knitwear.

Because felting is not an issue for hank treatments, another option available to companies with conventional hank-dyeing equipment is to use a PMS-based shrink-resist process. This allows the treatment to be carried out following dyeing with minimal shade change, and therefore permits the production of a much wider shade range without the use of reductive bleaching techniques.

The use of PMS instead of DCCA once again restricts the options in terms of the polymers that may be used, but optimum results in terms of handle are obtained using either Basolan SW or MW from BASF. As with knitwear, the shrink-resist efficiency of PMS-based routes is somewhat lower than that of DCCA treatment, but even so, these processes are more than capable of attaining the machine-washable standards for knitwear. Most, if not all, of the production in this field has been on worsted spun yarns, but there is no reason why woollen spun yarns should not also be processed in this way. The main disadvantage is, of course, that products made from these yarns would have to be milled, in which case a treatment level would have to be determined which gave an effective compromise between milling propensity and shrink-resistance.

6.4 Continuous treatments

Approximately 75% of the wool treated to a machine-washable standard in top form using the IWS/CSIRO Chlorine Hercosett (Feldtman *et al.*, 1967) process, and at present about forty lines are operating throughout the world today. A detailed consideration of this technology is beyond the scope of this chapter, but the importance of this process and, in particular, the use of chlorine in top treatments, more than merit a review of such processes. Wool processed by this route meets the maximum Woolmark specifications for machine-washability and may therefore be used in the production of virtually any product, irrespective of structural considerations such as cover factor or yarn count. Machine-washable worsted spun knitwear may be produced in solid shades using either the top or garment dye routes, although the latter is not a widely adopted technique, because the cationic character of Hercosett resin alters the dyeing characteristics of the wool to the extent that a much higher degree of control over the dyeing cycle is required to ensure that evenness and consistency are obtained. The top dye route is therefore more widely used and obviously provides the option for the production of both solid shades and multicoloured designs. However, such a route does not lend itself to the quick-response philosophy which nowadays plays such an important part in retailing, and other factors, such as minimum lot sizes and high inventory costs, also restrict this route to the larger companies.

Those processors who offer the Chlorine Hercosett technology on a commission basis may often have little or no knowledge of the end-use to which the treated wool is put, in which case the wool is treated and tested to the maximum Woolmark specification. However, it is possible to achieve the Woolmark knitwear specification via a chlorine only treatment in top form, and this is a route which has been used to good effect by some knitwear producers, particularly in the production of garment dyed products. This is not an option which is widely adopted by garment processors using batch chlorination techniques, because the treatment levels required often lead to impaired product performance and excessive yellowing; the normal procedure therefore is to combine a low level of chlorination with polymer application to achieve full machine-washability. The acid conditions featured in continuous top chlorination produce very little discolouration and allow the machine-wash knitwear standards to be achieved by virtue of the improved levelness of chlorination when compared to batch routes, but there are some disadvantages associated with the use of wool treated in this way, notably the sinkage which occurs in the mechanical processing of chlorinated wool, the impairment in handle which is produced, and the additional weight loss which can occur both during dyeing and treatment. The increase in weight loss that occurs during treatment will be a function of the treatment level used, and this in turn will be dictated by the wool quality being processed, but the difference in weight loss observed between this route and Chlorine Hercosett treatment is partly compensated for by the application of 2% Hercosett solids following chlorination. The resin also provides a protective coating to the treated fibre which reduces weight loss during dyeing.

The handle associated with acid chlorination techniques is characteristically dry and is associated with a change in the frictional characteristics of the fibre surface (Makinson, 1979); consequently, the application of a suitable softener is required to provide an acceptable handle. However, the combination of acid chlorination and the application of a microsilicone softener does provide for a very significant improvement in handle, so much so that this combination, albeit using higher levels of chlorination, was used in the development of numerous handle modification treatments for wool top including the IWS Soft Lustre process (Rushforth, 1989).

Processes of this type were developed at a time when not only was the price of fine quality wools at its highest for some time, but they were also in short supply, and the demand was therefore for a chemical procedure that would allow coarser wool fibres to be used in certain end-products without compromising handle.

The forerunner of developments in this field was the Vantean process carried out at Nippon Hi Spinning Mill No. 21 (PCT, 1979). This was a continuous top process which was only carried out on commission, and details of the process are therefore limited to what can be gleaned from the patent literature. The effect of the process is to remove the scale structure completely and this is achieved by applying a transition-metal cation to the wool in a saturated salt solution and then passing it into a chlorination bowl. The former treatment ensures that the application is restricted to the surface of the fibre and this, in turn, leads to rapid surface-specific decomposition and reaction of chlorine, leading to scale removal. Although all efforts were made to restrict the chemical treatment to the fibre surface, this may not have been possible in all cases, and further evidence for this supposition is provided by the fact that a formalin treatment was also an integral part of the process; this presumably acted as a protein crosslinker.

The commercial introduction of this process never extended beyond the company that developed it, and indeed the large amount of equipment required to carry out the process would have precluded its use on conventional shrink-proofing lines. Developments in this field therefore concentrated upon utilising conventional shrink-proofing equipment and, although numerous companies operate processes under a variety of different names, they all feature acid chlorination, at a level approximately twice that applied in conventional top processing, followed by the application of a suitable microemulsion silicone softener. As a general observation the improvement in handle obtained is equivalent to approximately 2 μm, although the actual change in fibre diameter is less than 0.1 μm. As with the Vantean process, the scale structure is effectively removed, although in this case the restriction of chemical damage to fibre surface is a result of the mechanics of the chlorination units rather than the use of saturated salt solutions. The removal of the scale structure also leads to the production of full machine-washability and, as an additional bonus, the comfort properties of the treated wool are also significantly improved, thus leading to significant product development potential in the field of products worn against the skin (Garnsworthy *et al.*, 1988), e.g. sportswear, spring/summer knitwear and underwear.

The main advantage of acid chlorination techniques for the treatment of wool top is the low chemical cost involved; however, in certain markets, notably Italy, many companies continually treat wool top using DCCA via a pad application technique. This treatment is part of a production route that is designed to impart an improved handle to worsted spun yarns produced with fine quality wool, and also features hank dyeing followed by the application of a suitable softener. The DCCA route is somewhat more expensive than conventional top chlorination procedures that use either sodium hypochlorite in combination with sulphuric acid or chlorine gas dissolved in water, but the yarn bulk obtained is considerably higher than with acid chlorinated wool, a feature which is thought to be due to the additional protein crosslinking provided by the cyanuric acid liberated during treatment (Veldsman and Swanepoel, 1971). Many of the high quality Italian yarns that are sold on the basis of handle and colour feature this production route, and although machine-washability is rarely an issue, it can be achieved merely by increasing the DCCA application level. Such yarns supplied in ecru may therefore be used in the production of garment dyed products or, by applying a polymer after dyeing, fully machine-washable products.

Because the production of woollen spun knitwear invariably features a scouring and milling cycle, and because machine-washability and milling propensity are mutually exclusive, machine-washable woollen spun products have been traditionally produced only by batch techniques. These are extremely flexible in terms of the handle that can be produced and the colour combinations that can be featured; however, the design potential is limited by the fact that Jacquard knits cannot be processed because of the high felting propensity of the float stitches.

The solution to this problem is one that has vexed the collective minds of many workers in this field, since clearly the requirement is for a treatment which, while it is sufficient to produce the necessary level of shrink-resistance, can also allow the products to be milled. Such a combination, if it could be achieved, would allow any knitter with basic finishing equipment to produce machine-washable knitwear without recourse to conventional batch techniques, and provide for a dramatic increase in product design and development potential.

Some companies have pursued such a development via the batch treatment of loose stock in dyeing machines and, although some success has been achieved by this route, the evenness, consistency and reproducibility have in general proved to be an insuperable barrier to commercial success.

Clearly the key to success in this field lies in the precise control of the shrink-resist treatment, and this was ultimately achieved via the Kroy loose stock technology (Bourn *et al.*, 1985), which was originally introduced for the treatment of wool used as filling materials in bedding products.

The International Wool Secretariat is working with the two companies operating this technology, and also suitable woollen spinners, and each stage of the production pipeline has been optimised to produce a range of commercially acceptable yarns. At the time of writing, Chuwa of Taiwan are currently supplying yarns via two spinners, and yarn development with Jarmains, UK, is progressing along the same lines.

6.5 Environmental considerations

The environmental profile of all fibre production routes has in recent years attracted a great deal of interest, so much so that the concept of eco-labelling has become increasingly important in retailing. Although a discussion of the relative 'green' credentials of the different fibres is beyond the scope of this chapter, the facts that wool is a natural biodegradable fibre and is produced on land that can rarely sustain agriculture obviously offer advantages over many other fibres. It is the policy of the International Wool Secretariat to ensure that grower country wool is processed using production techniques that ensure minimal environmental impact, and the single most important issue as far as the production of machine-washable products is concerned is the use of chlorine.

Chlorine is not only cheap, it is unique in terms of the effect it has on the properties of the wool fibre, producing both efficient and rapid oxidation of the fibre surface and a high level of wettability. As a result, chlorination of one form or another features in a wide variety of chemical finishing procedures, including shrink-proofing techniques applied to wool in top, loose stock, yarn, woven fabric and knitted garments, as well as handle modification techniques, garment dyeing and printing.

An inevitable consequence of the chlorination of wool in aqueous solution is the release in the effluent of chlorinated organic products, mostly wool proteins, which are collectively termed as absorbable organic halides (AOX) (Waste Water Tax Law, 1987). Legislation has been introduced in some countries, notably Germany, to restrict the discharge of certain organohalides that are known to be, or suspected of being, injurious to health but, because the test method developed to analyse for these components does not differentiate between individual chemicals, the net effect is a blanket restriction of all such products, irrespective of their toxicological profile.

Whether or not AOX legislation will eventually spread to other countries is not yet clear, but even where this has not occurred, the number of restrictions being placed upon chlorine users is increasing progressively; the ultimate requirement is therefore for an environmentally acceptable alternative to chlorine for the chemical finishing of wool.

The most obvious replacement for chlorine in this respect is, of course, PMS, but its performance in terms of shrink-resist efficiency is such that commercial success has only been achieved in woven fabric, knitwear and yarn treatments, with little or no progress yet reported in garment dyeing, top and loose stock treatment, handle modification or printing.

Although much of the work being carried out in this field features the use of conventional wet finishing, other areas such as enzyme finishing and electrical discharge techniques are also being considered. Enzymes have been used in the past on wool to produce either shrink-resistance or handle modifications (Philips *et al.*, 1941; Philips and Middlebrook, 1948), but such techniques were never widely adopted because of the non-specific action of the enzyme, which resulted in an unacceptable degree of damage to the fibre. However, it is to be hoped that the advances that have been made in enzyme technology and manufacture will ultimately lead to the development of products which, either alone or in combination with conventional wet-finishing procedures, can duplicate the effects of chlorination and lead to an environmentally acceptable alternative.

The use of electrical discharge techniques has also attracted considerable attention in recent years, primarily because it is possible to achieve many of the effects of chlorination without either yellowing or chemical damage (Philips *et al.*, 1941; Philips and Middlebrook, 1948). Furthermore, it is a dry technology and, as such, its use is consistent with all of the criteria associated with an environmentally friendly process.

This route lends itself well to the treatment of wool in woven fabric form either under vacuum (glow discharge) or atmospheric conditions (corona discharge). A version of the former technology is used commercially in Japan by Unitika, and it is manufactured by Sando Iron Works of Wakayama, Japan, where it has been used to achieve a variety of different effects, including improved evenness of piece dyeing, to increase the depth of shade obtained with piece-dyed blacks, colloquially described as 'Real Black', and in the production of machine-washable fabrics.

A similar machine is also available from Niekmi of Ivanova in Russia; this is used commercially as a prepare for print on wool fabrics, and has recently been introduced into a mill in Italy (Mascioni). The cost of the Japanese equipment is considerable and, although information relating to the price of the Russian alternative is not readily available, it is likely to be such that its use will be restricted to large vertical companies who can fully utilise the multipurpose finishing capacity to good effect on substrates other than wool. Corona discharge equipment is a much cheaper alternative, because the process is carried out under atmospheric pressure, and results have shown that in terms of dyeing properties, printing and machine-washability, an equivalent effect may be obtained. Equipment of this type may be obtained from Softal of Hamburg.

The equipment referred to does not lend itself to the treatment of wool in any form other than fabric; however, a prototype glow discharge machine for the treatment of wool in top form has been built at The Textile Institute at Łódź, Poland, and a joint evaluation with IWS has again demonstrated the multipurpose finishing potential for this technology. Treated wool has been shown to exhibit significant processing advantages in terms of spinning performance and, when used in the production of woven fabrics, produces a marked improvement in dyeing properties and gives full machine-washability. Treated wool may also be used in the production of machine-washable yarns and knitted goods, although the application of a suitable polymer, namely Basolan SW (BASF), is invariably required.

6.6 Conclusion

Although many routes are now well established for the production of machine-washable knitwear and virtually any product can now be produced to this standard, the challenge to those working in the field is to eliminate the use of chlorine and thereby further improve the environmental profile of the wool production pipeline.

In order to achieve this end, techniques other than conventional wet finishing must also be considered, and the concepts of enzyme finishing and electrical discharge treatment, amongst others, must be firmly embraced by those wishing to progress in the field of easy-care finishing.

In addition, one must also ultimately accommodate a wider interpretation of the term 'easy-care' to include other properties such as stain-resist, stain-repellent, stain-release, water-repellent, anti-pill, tumble-dry, shape retention and so on, thereby ensuring that wool knitwear continues to meet the ever more stringent requirements of the modern consumer.

Shrink-resist polymer compositions

Basolan SW — aziridine terminated polyether
Basolan MW — polyamino siloxane
Hercosett — cationic polyamide epichlorohydrin resin
Polymer GE — proprietary mixture
Polymer RSM — proprietary mixture
Polymer TM — proprietary mixture
Synthappret BAP — carbamoyl sulphonate polyether
DC109 — silicone elastomer

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