

## **4 Physical and chemical effects of domestic laundering processes**

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### **4.1 Introduction**

The manufacture and marketing of household laundry products constitutes a large, profitable and highly competitive business. In 1990 the 'world' market for these products (excluding China and the former USSR) was estimated to be about 16 million tonnes per annum with a value of approximately £15 billion (Karsa, 1990). More recently, the European market alone was stated to be worth £6 billion and the US market \$10 billion (Markus, 1994). Substantial investment in research and development is essential for the major manufacturers, if they are to maintain, or improve, their individual positions in this competitive market. It is therefore not surprising that much research investment has been directed towards gaining a fundamental understanding of detergency processes, with a view to developing products with improved cleaning performance. As a consequence there are numerous publications, including several up-to-date textbooks, which deal comprehensively with aspects of surfactant science relating to the theory and technology of detergency (Cutler and Davis, 1972, 1975, 1981; Cutler and Kissa, 1987).

During the past twenty years or so, manufacturers of domestic detergents have also invested heavily in improving the environmental acceptability of their products and manufacturing processes. The debate over the replacement of phosphates and the need for continuing improvement in the rate and completeness of biodegradation of the surfactants being used has been widely publicised (Brussels, 1987; SDIA, 1989a,b). It is not therefore the purpose of this chapter further to discuss detergency, or the environmental issues surrounding fabric washing products. The aim is rather to consider the physical and chemical effects of the washing process, and washing products, on some of the most frequently washed textile substrates.

From the textile manufacturer's point of view, domestic washing is similar to a mild scouring process which is often carried out in machines which, although smaller, are similar in design to those used for processing piece goods in the textile industry. The physical and chemical effects of such a process, whether applied for preparation of grey goods, or for washing-off dyed and finished articles, do not normally give cause for concern. The cumulative effects, however, of repeating the process, perhaps 25 to 50 times in the first year of use, can be seriously damaging to some textiles. The

investigation of these long-term effects is costly, and does not usually form a part of the quality control procedures employed by textile manufacturers or retailers. Nevertheless, a better understanding of the effects of repeated domestic washing, and of the concerns of consumers for the care of washable textiles, may pay dividends in terms of improving perceived garment quality, for little or no on-cost in manufacture.

The manufacturers of fabric washing products have always tried to formulate their products well within the constraints imposed by textile substrates. Clearly, any product found to cause damage to textiles — no matter how good its cleaning performance — will be pilloried by consumer organisations and rejected by the consumer. For these reasons, products with the potential to damage carry appropriate warning labels. For example, brands containing proteolytic enzymes usually warn the consumer not to soak articles made of wool or silk.

Over the years, the diversity of washable textiles, and in particular machine-washable textiles, has increased dramatically. Not only are there increasing numbers of dye class, fibre type, and fabric finish combinations to wash, but some developments — microfibrils for example — are changing the washing characteristics of previously well-known dye-substrate combinations. Worldwide fashion trends and changing lifestyles have led to increasingly full shades and bright hues in new types of casual clothes and sportswear. These are predominantly of knitted constructions in which dimensional stability, or the preservation of elastomeric properties, is essential to continued 'fitness for purpose'. Furthermore, many textiles now being imported into Europe are dyed to washfastness standards that are adequate only for countries where domestic washing is done at ambient water temperatures of about 10–25°C. When these textiles are washed under typical Northern European conditions (40–60°C) the resulting dye desorption and cross-staining causes considerable problems.

This continual change in the characteristics of typical domestic wash loads has provided new challenges — and opportunities — for the manufacturers of household detergents. Their response is to be seen in the proliferation of brands on supermarket shelves which now offer superlative cleaning at low wash temperatures, care for coloured fabrics, and special care for delicate fibres such as wool and silk.

These are, however, comparatively early days in the development of more caring, specialist domestic laundry products, and it is to be expected that continuing efforts to understand the cumulative effects of repeated washing, on a wider variety of textile substrates, will lead to further innovation in this competitive product arena. It is therefore the aim of the following discussion not only to acquaint the textiles student with some of the more important physical and chemical consequences of domestic laundering processes, but also perhaps to stimulate new thoughts on improved textile aftercare in the minds of the manufacturers of textiles and household detergent products.

## 4.2 Domestic laundry processes—Effects of water, mechanical action and tumble drying

### 4.2.1 Introduction

Whenever and however domestic washing is done, be it on a river bank, in a sink, bowl or bucket, or in an automatic washing machine, the principles of the process are the same. Fabrics are saturated with water and agitated or beaten in the presence of products which are designed to aid wetting, and the breakdown and removal of soils. After squeezing out dirty water, rinsing in clean water (usually several times) and finally squeezing out as much water as possible, the fabrics are dried. Usually at least some of the dry fabrics are finished by pressing or ironing.

In the final rinsing stages, fabric finishing or conditioning products such as softeners, or starch, may be applied, sometimes to selected articles following a common wash process. In most countries, drying is still done mainly by hanging the clothing in the open air, but in Western countries, drying is increasingly being done in tumble driers, where softeners and antistatic agents are often also applied. Thus it is in rinsing, drying and pressing that the domestic launderer seeks to improve the final appearance and handle of the clean washing by applying a variety of finishing techniques.

It is recognised by domestic consumers (as well as in commercial laundries) that the wet rubbing and beating operations essential to effective cleaning are at least partly responsible for the deterioration in textiles that have been washed, and used or worn many times. There is in fact good evidence that washing processes generally contribute more to fabric damage than do use or wear. For example, data from a typical wash and wear trial (Mohamed, 1982) showed 43% tensile strength loss in hospital uniforms (made of 50/50 polyester/cotton) after 25 wash/wear cycles, and 39% strength loss in the 'washed only' control articles. Thus 90% of the total damage was caused by the wash process in this particular case.

The fabric changes that occur during washing, such as shrinkage, distortion, fibre damage, fabrics becoming stiff and harsh, colour fading, and cross-staining by fugitive dyes, are all highly dependent on fibre type, fabric construction, dye class and the fabric finishing processes applied, as well as on the wash process and product. For the purpose of the following discussion, an attempt has been made to separate fabric changes according to:

- (i) The physical effects of water, temperature and agitation on different fibre types, with some reference to fabric construction, and drying method.
- (ii) The chemical effects of individual ingredients of fabric washing products on different fibre types, with some reference to common fabric finishes.

- (iii) The combined physicochemical effects of the wash process and washing product ingredients, on the colourfastness and cross-staining properties of some of the most commonly used dye class/fibre type combinations.

#### 4.2.2 *Physical effects of water, temperature and mechanical action on textile fibres*

4.2.2.1 *Previous history.* The ways in which water, and variables such as temperature and mechanical action, affect fabrics during domestic washing processes, especially during the first few washes, often depend strongly on the previous history of the fibres, yarns and fabrics, as well as on fabric geometry and the physicochemical properties of the fibres themselves. Consequently, factors such as:

- (i) yarn structure and the nature of stresses built into yarns during spinning
- (ii) fabric structure and the nature of stresses built into fabrics during knitting or weaving
- (iii) physical and chemical effects of scouring, bleaching, mercerising, dyeing and chemical finishing processes
- (iv) drying methods, heat setting and mechanical finishing

may need to be considered when studying the performance of individual fabrics or garments. Since the combination of these variables is different for almost every finished fabric, it is only possible here to identify and discuss those factors that are known to be most relevant to the behaviour of important fibre types and fabric constructions under typical laundering conditions.

4.2.2.2 *Combined effects of water and wash temperature: glass transition temperatures, fibre swelling and diffusion rates.* The extent to which water affects the second-order or glass transition temperatures ( $T_g$ ) of textile fibres, depends on their chemical and physical structures. Some typical dry and wet  $T_g$  values for common washable fibres are given in Table 4.1, together with their recommended washing temperatures. For cellulosic and proteinaceous fibres in which the secondary forces between molecules result largely from polar or semipolar interactions such as salt linkages and hydrogen bonds,  $T_g$  may be lowered by 200°C or more when the accessible polar sites are hydrated by imbibed water. In these cases, the wet  $T_g$  is below 0°C and the fibres are in the rubbery state at all possible wash temperatures.

The 50–60°C reduction in  $T_g$  that occurs on wetting typical polyamide fibres is attributed to disruption of hydrogen bonding between the amide hydrogen and carbonyl oxygen atoms in adjacent polymer chains. The resultant wet  $T_g$  is close to 0°C and hence polyamides are also always washed in the rubbery state.

The wet  $T_g$  values for other fibres listed in Table 4.1 fall within the normal range of washing temperatures, but their recommended wash temperatures

**Table 4.1** Principal dry and wet glass transition temperatures for common fibres and their recommended wash temperatures

	$T_g$ (°C) in dry air	$T_g$ (°C) in water	Recommended wash temperature range
Cotton Viscose rayon	None before thermal decomposition at ~200°C	$\left\{ \begin{array}{l} <0 \\ <0 \end{array} \right.$	All temperatures Up to 60°C
Cellulose triacetate			
Cellulose diacetate	~180	~60	$\left. \begin{array}{l} \text{Up to 60°C} \\ \text{Up to 60°C} \end{array} \right\}$
Polyester	~100	~85	
Nylon 6	~56	Close to 0	$\left. \begin{array}{l} \text{Up to 40°C} \\ \text{Up to 40°C} \end{array} \right\}$
Nylon 6.6	~62		
Acrylics	70–90	<0	Up to 40°C
Wool	None before thermal degradation	<0	Up to 40°C

are all below  $T_g$ . The consequences of washing these fibres above the recommended temperatures are discussed in sections 4.2.3.3, 4.2.3.5 and 4.2.3.6. It should, however, be noted here that while the rates of diffusion (in fibres) of water, water hardness ions, and other species present (either in washing products, or in the fibres themselves) increase with temperature according to the Arrhenius equation:

$$D = D_0 \exp\left(-\frac{\Delta E}{RT}\right)$$

there is, at  $T_g$ , a step change in typical diffusion coefficients of approximately two orders of magnitude. This clearly has implications not only for the colourfastness and cross-staining properties of dyed fabrics, but also for the location, and reaction of species diffusing into the fibre from washing product solutions.

The extent to which fibres imbibe water and swell is highly correlated with their wet  $T_g$  lowering. Fibres containing many hydrophilic sites become heavily hydrated; the polymer becomes rubbery; and swelling continues until the free energy of mixing is balanced by the elastic restraining forces imposed by 'fixed' points in the swollen network such as cross-links, entanglements, or crystalline regions not penetrable by water. Equilibrium swelling increases with increasing temperature, and with applied stress, according to well-established relationships (Flory, 1953). For typical fibre diameters of 10–20  $\mu\text{m}$ , equilibrium swelling in water is achieved within less than 30 s given a typical diffusion coefficient of the order of  $10^{-7} \text{ cm}^2 \text{ s}^{-1}$ . Thus, fabrics washed at above their wet  $T_g$ , achieve equilibrium fibre swelling at any chosen wash temperature, but since the stresses imposed by the washing action are likely to change rapidly throughout the wash process, water may be continually

'pumped' in and out of the fibres as the network tries to maintain equilibrium. In highly swollen structures this may accelerate the rate of fibre breakdown, although fibre-on-fibre, and fibre-on-metal abrasion and beating must be considered the prime causes of mechanical degradation.

**4.2.2.3 Mechanical action in washing and tumble drying.** The nature of the mechanical action applied in washing processes varies widely across the range of handwash methods used and the washing machine types available in different countries around the world. It seems reasonable, however, to assume that for any given combination of fibre type and fabric construction, similar changes must occur, but at different rates, according to the mechanical severity of the wash method employed. There have been few comparative studies between different handwash and machine wash methods, but there is certainly sufficient evidence to show that handwashing cannot be assumed to be generally less damaging than machine washing. Indeed, some handwash techniques, such as rubbing fabrics on the ribbed concrete surfaces of the typical wash 'tanques' found in many South American countries, are known to be particularly damaging. Similarly the beating of wet fabrics against rocks or walls, or with heavy wooden sticks or bats, as practised in parts of India and Southeast Asia, is also more severe than any washing machine action.

The mechanically induced changes occurring in textiles during washing and tumble drying processes may result from:

- (i) movement of yarns relative to one another
- (ii) migration of fibres within yarns
- (iii) damage to individual fibres by abrasion and beating

These types of change may be expected to lead to:

- (i) changes in garment shape and size, and in fabric thickness
- (ii) fuzzing, pilling, felting and fibre shedding, and
- (iii) fibre splitting, fibrillation and breakage

Mechanical property changes, and associated visual and tactile changes accompany each of these types of change. Their relative importance for different fibres and fabric constructions are discussed in section 4.2.3.

**4.2.2.4 Effects of washing product formulation on mechanical action.** The chemical effects of individual ingredients of fabric washing products are discussed in section 4.3, but it is relevant here to note that washing products do significantly modify the physical effects of the mechanical action applied during washing. This occurs in two ways.

- (i) Foam, generated by agitating surfactant solutions, cushions fabrics against the beating and rubbing action, thereby reducing fabric damage. The volume and quality (bubble-size distribution and stability) of the

foam generated is of course dependent on the surfactant and antifoam types and levels used in a given formulation, as well as on product dosage, and the mode of mechanical action. It should be borne in mind that excessive foam cushioning reduces soil removal as well as minimising fibre damage. Furthermore, horizontal axis washing machines require particularly low-foaming products to avoid the inconvenience and potential electrical hazards of foam overflow, and to prevent the formation of foam-locks in pumps and pipework.

- (ii) Surfactants adsorbed on fibre surfaces, as either monolayers or multilayers, reduce the frictional forces operating at fibre–fibre and fibre–metal contacts. In the case of water-swollen fibres, the frictional forces that operate at fibre–fibre contacts are particularly high. This is because the true area of contact, for a given normal force, increases as the fibre becomes rubbery and more easily deformed. In addition, the ploughing component of the frictional force also increases as the fibre becomes more deformable. Consequently, the lubrication provided by adsorbed surfactants plays an important role in mitigating against the damaging effects of beating or abrading water-swollen fibres.

#### 4.2.3 *Physical effects of washing on fibres and fabrics*

##### 4.2.3.1 *Cotton and regenerated cellulose fibres*

(a) *Swelling, shrinking and wrinkling.* Cotton fibres swell about 40% by volume in water. This is almost completely accounted for by radial swelling; longitudinal swelling accounting for only about a 1–2% increase in fibre length. This markedly anisotropic swelling behaviour is explained by the fact that the crystalline, microfibrillar structures in cellulosic fibres are not penetrated by water. Swelling therefore occurs only between microfibrillar structures, and consequently their orientation in the fibre determines the swelling anisotropy.

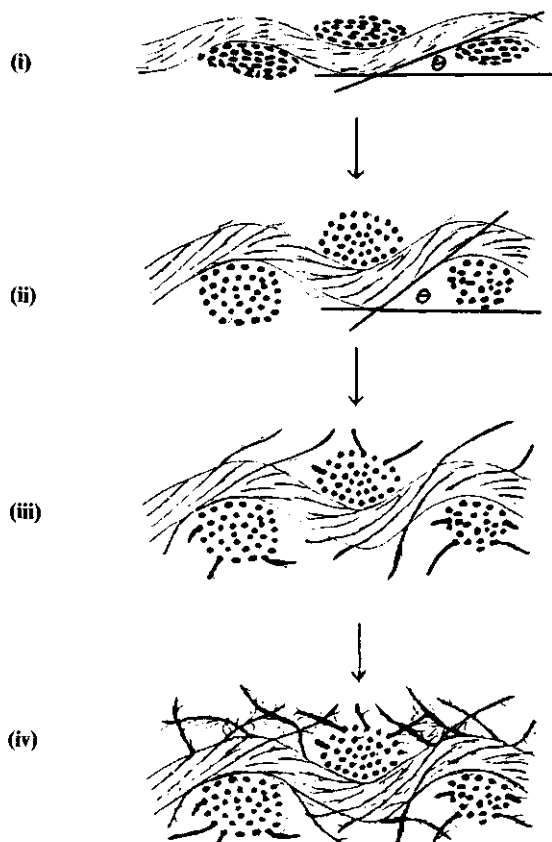
For regenerated cellulose fibres with their generally lower level of crystallinity, but nevertheless high degree of orientation achieved by the drawing process, swelling is typically in the range of 70–130% by volume with only a 3–5% increase in fibre length.

When fibres are disposed in a spiral configuration — as they are in spun yarns — it can be shown that radial fibre swelling with no significant increase in fibre length must lead to a reduction in spiral length, and hence to yarn shrinkage. The shrinkage of wet ropes is a familiar manifestation of this phenomenon; when it occurs in textiles, the changes in fabric geometry are complex.

In woven structures, ‘wet relaxation’ caused by fibre swelling leads to an increase in yarn crimp (weave angle) and a thickening of yarn cross-section.

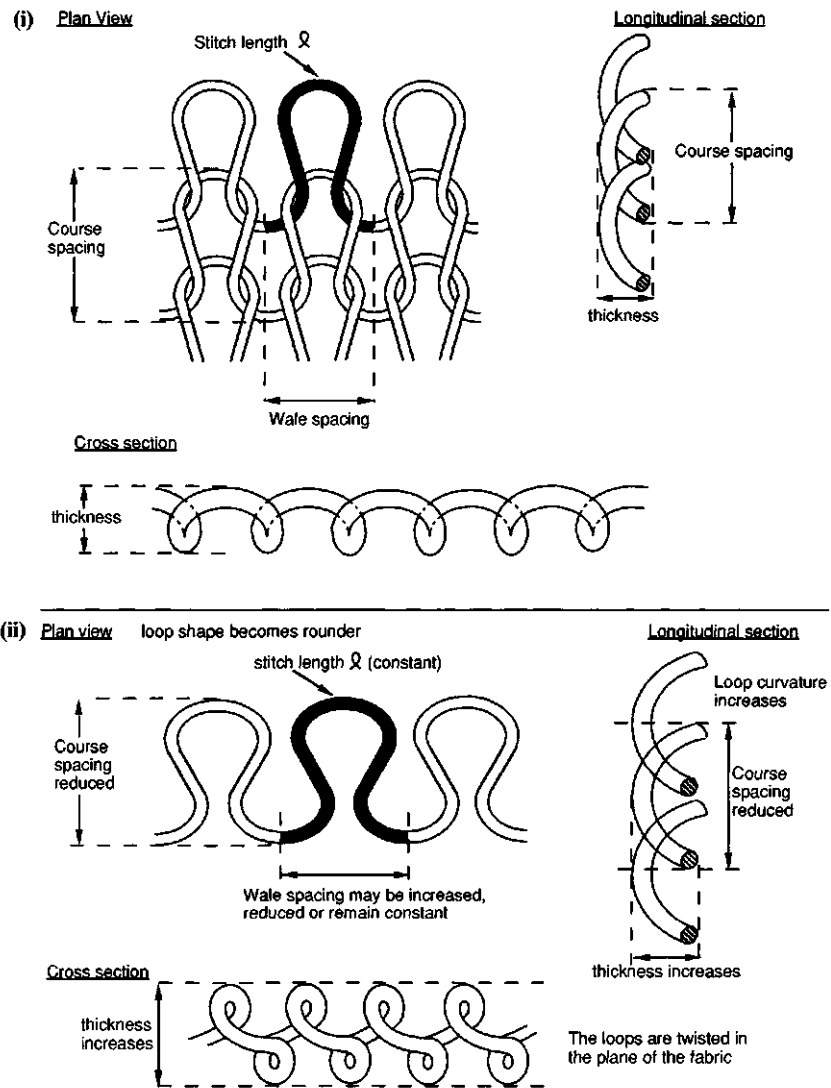
Yarns that have been flattened to an elliptical cross-section by calendering tend to resume a more circular cross-section and the fibres within the yarns become less tightly consolidated after wetting and subsequent drying (see Figures 4.1(i) and (ii)).

In knitted cotton fabrics the shape and orientation of the loops changes as the fibres swell and relax towards their minimum energy conformation. This often occurs without significant changes in knitted loop (stitch) length. The loops usually become rounder in shape (Figure 4.2) causing shrinkage in the wale (length) direction, especially when the fabric has been previously dried under tension. In order to release the stresses imposed by bending twisted yarns into loops, the loops themselves tend to twist out of the plane



**Figure 4.1** Schematic representation of progressive changes caused by repeated washing in a woven cotton fabric: (i) new fabric; (ii) relaxed fabric after one wash/tumble dry cycle; (iii) fibre migration; 'fuzz fibres' appearing after a few washes; (iv) fibre migration and fibre fibrillation damage after many washes.





**Figure 4.2** Schematic representation of relaxation shrinkage processes in a knitted fabric: (i) new fabric; (ii) relaxed fabric.

of the fabric (Figure 4.2(ii)). This causes shrinkage in the course (width) direction, and often produces significant differences in twist level in the two legs of the knitted loops (Anand *et al.*, 1990).

Fibre swelling causes many cellulosic textiles to become 'jammed' in the wet state. This may limit the relaxation that can occur in a single wet treatment, even when considerable mechanical agitation is applied. In woven fabrics, in which the wet swollen yarns cannot move readily, fabric buckling or wrinkling may develop as a means of relaxing the 'swelling stresses' in the yarns. The end results of wet treatments are evaluated on dry fabrics, but the final fabric properties also depend on the nature of the drying process.

Under static drying conditions, drainage and evaporation of water from the fabric causes increasing capillary attraction between fibres and yarns. This tends to hold the fabric in the wet conformation, and as the fibres de-swell and the moisture content falls, strong inter- and intra-fibre adhesions develop as hydrogen bonds reform in the cellulosic matrix. Any wrinkles, folds or creases then become hydrogen-bonded into the dry fabric structure. These cannot easily be removed unless  $T_g$  is exceeded by an appropriate combination of moisture and heat. Thus under hot-pressing, calendaring, or domestic ironing conditions, wrinkles and creases are removed, and the fabric is re-set in a smooth conformation, by breaking and reforming inter- and intra-fibre hydrogen bonds.

In tumble drying, the constant agitation of the fabric structure prevents capillary attraction between yarns and fibres from forming inter-fibre adhesions in the structure. Consequently as the fibres de-swell, there is sufficient mobility in the structure for further relaxation to occur. At tumble-drying temperatures, intra-fibre hydrogen bonds will not reform until the fabric is almost 'bone-dry'. Consequently, as long as cotton fabrics are removed from the drier before they are completely dry, and before the drier cools down, much of the wrinkling and creasing associated with 100% cotton fabrics can be avoided.

(b) *Initial changes in fabric properties.* It will be apparent from the preceding discussion that the first few washes, and the choice of drying method, can cause a variety of changes in the geometry of new cellulosic fabrics. These changes must be expected significantly to affect both fabric mechanical properties, and the perception of fabric handle. In extreme cases, such as gross shrinkage of knitted cotton garments, there may also be visible changes.

Figures 4.3–4.5 illustrate some of the changes in fabric mechanical properties that occurred when a new, plain woven cotton sheeting fabric was washed and tumble dried ten times. It can be appreciated that the measured changes were consistent with the woven fabric geometry changes described earlier, and shown schematically in Figures 4.1(i) to (iii). Increased yarn crimp in the washed fabric led to increased tensile extensibility (Figure 4.3) and

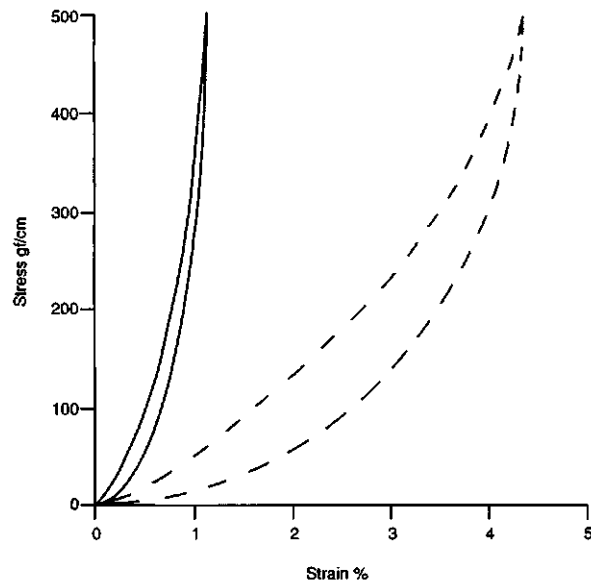


Figure 4.3 Changes in the tensile properties of a cotton sheeting fabric after ten machine wash/tumble dry cycles; —, new fabric; ---, fabric after ten wash cycles.

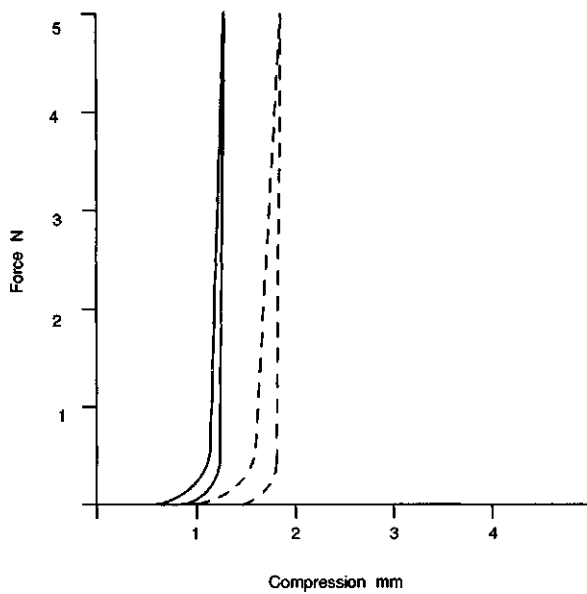
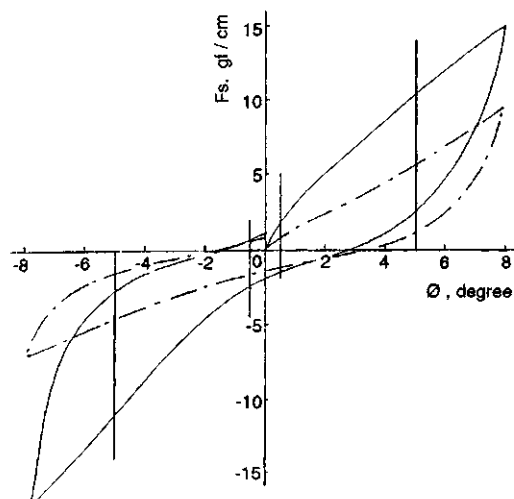


Figure 4.4 Changes in the compressibility of a cotton sheeting fabric after ten machine wash/tumble dry cycles; —, new fabric; ---, fabric after ten wash cycles.



**Figure 4.5** Changes in the shear stiffness and shear hysteresis of a cotton sheeting fabric after ten machine wash/tumble dry cycles; ———, new fabric; - - - -, fabric after ten wash cycles.

increased fabric thickness (resulting from both increased yarn crimp and yarn thickening) led to increased compressibility (Figure 4.4). The reductions in shear stiffness and shear hysteresis in the washed fabric (Figure 4.5) resulted from the reduced number of fibre–fibre contacts at yarn crossover points, and from the generally reduced inter-yarn pressure in the fully relaxed, washed and tumble-dried fabric.

The effects of wash temperature and drying method on the shrinkage of a cotton interlock fabric are illustrated in Figure 4.6. Since fibre swelling, and hence the yarn retraction forces, increase with increasing temperature, it might be expected that wash temperature should determine the final dimensions of knitted cotton fabrics. For the present example, this trend is apparent only after the first wash (line dried). The results of further washing suggest that the wet, swollen structure became ‘jammed’ at about 25% area shrinkage, and that these dimensions became ‘frozen-in’ under static, line-drying conditions. Since mechanical agitation during tumble drying prevented inter-fibre adhesion, the structure approached a more relaxed conformation as the fibres began to de-swell (but still remained above  $T_g$ ) and this led to further shrinkage.

It is notable that between five and ten wash/tumble dry cycles were required to attain the fully relaxed fabric dimensions, and this is believed to be typical for knitted cotton fabrics. The final percentage shrinkage of any fabric is of course a function of its original ‘new’ fabric dimensions. In this particular

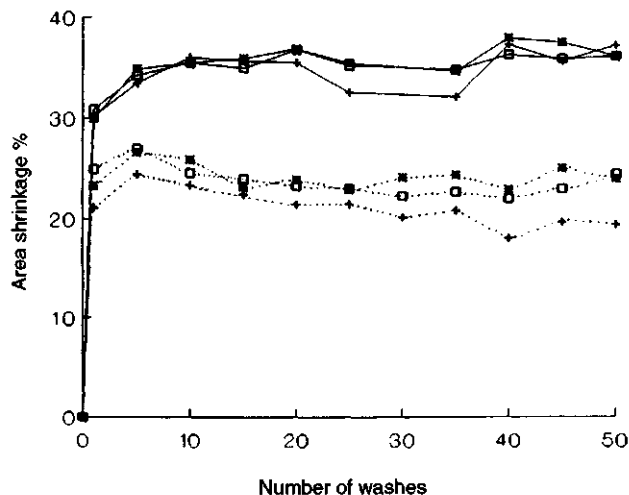
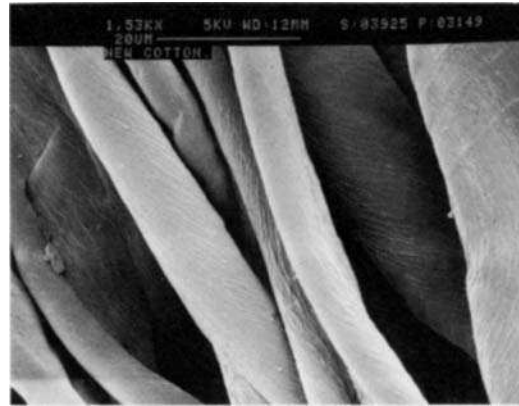


Figure 4.6 Shrinkage behaviour of a cotton interlock fabric; effects of wash temperature and drying method. Solid line, tumble dried; dotted line, line dried; +, 15°C; x, 40°C; □, 60°C.

case the new dimensions resulted from stenter-drying after scouring on a winch. Clearly the stenter-drying conditions set the fabric in a stretched conformation which then led to very high (35%) area shrinkage on washing and tumble drying. This is a typical example of previous processing history determining a fabric's in-wash performance.

(c) *Longer-term changes in cellulosic fabrics.* When water-swollen cellulosic fibres are subjected to vigorous mechanical action—such as beating in papermaking—they disintegrate into their constituent fibrillar structures. The mechanical action used in fabric washing is very gentle by comparison, but nevertheless its repeated application soon begins to have similar effects. From Figures 4.7(i) and (ii) it can be seen that cotton fibres have been found to show clear signs of damage after only six machine wash cycles. After 50 washes (Figure 4.7(iv)) serious fibre fibrillation damage is invariably present at levels which may be expected to change significantly the mechanical and sensory properties of the fabric.

Figure 4.1(iv) suggests schematically how a woven structure may be affected by fibre damage. Certainly surface fibre in fabrics with a raised finish, and fibres in the loop pile of terry weave fabrics, are more prone to damage than those in the underlying fabric structure. It can be expected that the greatly increased number of hydrogen-bonded contacts, which must result on static drying a fibrillated mass, will produce structures with increased shear (and



(i)



(ii)

**Figure 4.7** Cotton fibres in new and washed fabric: (i) new; (ii) after six machine wash cycles; (iii) after eleven machine wash cycles; (iv) after fifty machine wash cycles.

bending) stiffness and hysteresis characteristics. This has been confirmed by experimental results such as those shown in Table 4.2 (Bishop, 1991). These demonstrate the progressive effect of multi-washing followed by static drying, on the shear stiffness ( $G$ ) and shear hysteresis ( $2HG5$ ) of a cotton terry towel fabric.

It is also shown that when the same towelling fabric was tumble dried after every wash, the  $G$  and  $2HG5$  values were, as expected, significantly lower than those of the line-dried fabric, even after a single wash/dry cycle.



(iii)



(iv)

Figure 4.7 (Continued)

The fully relaxed structure, in which adhesions between fibres are largely prevented by tumble drying, would be expected to achieve constant  $G$  and  $2HG5$  values after a few wash cycles (*cf.* the cotton interlock shrinkage shown in Figure 4.6). This seems to be the case from the constant values recorded at ten and 25 wash/dry cycles. After a further 25 cycles, however, the  $G$  and  $2HG5$  values were further reduced. It has been suggested that this was due to the continual shedding of small quantities of fibre during the tumble drying

**Table 4.2** Effects of repeated washing (followed by line drying and tumble drying) on the shear stiffness ( $G$ ) and shear hysteresis ( $2HG5$ ) of cotton terry towelling

No. of washes	Line-dried		Tumble-dried	
	$G$ ( $\text{mN cm}^{-1} \text{ deg}^{-1}$ )	$2HG5$ ( $\text{mN cm}^{-1}$ )	$G$ ( $\text{mN cm}^{-1} \text{ deg}^{-1}$ )	$2HG5$ ( $\text{mN cm}^{-1}$ )
1	1.35	6.7	1.25	6.4
10	1.50	6.9	1.20	5.8
25	2.15	9.7	1.20	5.8
50	2.60	10.4	1.10	5.1
	Re-wetted and tumble-dried		Re-wetted and line-dried	
50	1.25	6.35	2.70	10.4

cycles. Certainly the contents of the lint traps of regularly used tumble driers do suggest that this could be the case.

Since it is the beating, during washing and rinsing operations, that causes cellulosic fibres to fibrillate, it should be expected that the two towelling samples washed 50 times (line-dried and tumble-dried) would exhibit similar overall levels of fibre fibrillation damage. This was in fact confirmed by remeasuring the  $G$  and  $2HG5$  values of both samples after re-wetting them, and then tumble drying the previously line-dried sample and line drying the previously tumble-dried sample. The results are also shown in Table 4.2. It is interesting to note that while the previously tumble-dried sample acquired similar  $G$  and  $2HG5$  values to the 50 times wash/line-dried material, the previously line-dried sample acquired  $G$  and  $2HG5$  values similar to the once wash/tumble-dried sample. This is, of course, exactly in line with expectation, because the 50 times wash/line-dried sample had only undergone the relaxation achievable in one tumble-drying cycle. This result may also be considered to provide indirect evidence that repeated tumble drying causes further reduction in shear stiffness and shear hysteresis via fibre shedding in the drying process.

**4.2.3.2 Resin-finished cellulosic fabrics.** The chemical finishing processes applied to cellulosic fibres that are variously described as resin finishing, crease-resist, easy-care, durable-press or permanent-press finishing encompass reactions with a variety of organic molecules capable of forming covalent crosslinks in cellulosic networks. The application conditions for different products include acid- and alkali-catalysed reactions, and high- and low-temperature reaction conditions on wet or dry fabrics. The performance of different finishes in terms of wet or dry crease recovery, abrasion resistance, whiteness retention, formaldehyde release, and durability to repeated laundering may vary within wide limits, but in principle they all confer important improvements in washing performance.



The introduction of permanent, intra-fibre crosslinks, which are not broken when internal hydrogen bonding is disrupted by imbibed water, restricts fibre swelling, and largely preserves the fibre and fabric conformation that pertained when the crosslinks were formed. From the earlier discussion of swelling, shrinking and wrinkling (section 4.2.3.1) it will be apparent that fibres treated in this way will have greatly enhanced dimensional stability, as well as reduced wet wrinkling and improved wet and dry crease shedding properties.

It may also be anticipated that fibres that are less swollen, and are strengthened by internal cross-links, may be less susceptible to fibrillation damage during washing. For many regenerated cellulose fibres this is certainly the case, and historically this type of fibre has often had unacceptably low wet strength if not resin-finished.

The fibrillation of cotton fibres may also sometimes be retarded by crosslinking, but any benefit is usually confined to the first few washes. Experience had shown (Bishop, 1990) that after about 25 wash cycles, resin-finished cotton fabrics are equally or even more severely damaged in comparison with non-resinated controls. Scanning electron microscope studies have shown that in cross-linked cotton the secondary wall begins to tear away from the fibre in 'sheets', whereas individual fibrillar strands are detached from untreated fibres. At this stage, the crease recovery performance of resin-finished fabrics also begins to deteriorate. While this may be partially attributable to gradual removal of cross-links by alkaline hydrolysis (see section 4.3.2.2), it is suggested that a contributing cause must be the generation of large areas of damaged fibre surface, which can hydrogen-bond together during drying, thus locking-in wrinkles and creases.

**4.2.3.3 Cellulose acetate fabrics.** The importance of cellulose triacetate and diacetate (secondary cellulose acetate) in washable end-uses has declined over the years, as easier-care, bright-polyester filament yarns have replaced them in many 'silk-like' fabric constructions. Nevertheless, it is of some interest to compare the properties of cellulose acetates with those of cellulosic fibres.

It will be seen from Table 4.1 that both triacetate and partially hydrolysed diacetate have a dry  $T_g$  at around 180°C. This probably corresponds to the temperature at which increasing main-chain vibrations overcome the dipole attractions between the ester carbonyl groups in adjacent polymer molecules.

Cellulose acetates swell by 5–10% in water, and hydration of the semipolar carbonyl sites depresses the wet  $T_g$  to about 90°C in triacetate, and about 60°C in diacetate. The lower value for diacetate is attributable to its more hydrophilic character resulting from its hydroxyl group content.

It is essential to wash all cellulose acetate fabrics well below their wet  $T_g$  in order to prevent wrinkling, creasing and shrinking from occurring in the rubbery state. If this does occur, the result is often irretrievable, because any distortions become set in by rinsing in cold water. Many acetate garments

have 'permanent' pleating or shaping which has been set by cooling after steam pressing. This is particularly susceptible to damage by washing in hot water, and such articles are often labelled 'hand wash only', or sometimes 'dry clean only'.

**4.2.3.4 Polyamides.** The polyamide fibres used in washable domestic textiles are mainly of two types which are still widely referred to as nylon 6 and nylon 6.6 types, although other polyamide fibre names are well established. The nylon 6 type is made by ring-opening and self-condensation of caprolactam, and nylon 6.6 is made by condensation of adipic acid with hexamethylene diamine. Thus both are aliphatic polyamides, and the fibres spun from them have sufficiently similar properties, from the point of view of domestic washing, for them to be discussed together.

Nylon 6 and nylon 6.6 have dry  $T_g$  values of 56°C and 62°C respectively, which are thought to be associated with the thermal breakdown of hydrogen bonding between the N—H···O=C groups in adjacent polymer chains. In water, both nylon types swell about 10% by volume, and the hydration effects of imbibed water reduce their wet  $T_g$  values to close to 0°C. Thus polyamide fibres are always washed above  $T_g$  and revert to the glassy state on drying. It might therefore be anticipated that polyamide fabrics would have poor dimensional stability, and creasing problems similar to those described for cellulosic fabrics.

In fact, polyamide fabrics are remarkably stable and smooth drying. This is widely attributed to heat setting at temperatures well above the dry  $T_g$  range, but the moisture sensitivity of the relaxation process should nevertheless be expected to cause loss of set under washing conditions. A possible explanation (Thompson, 1963) for their dimensional stability in washing, and their smooth drying properties, is that the spectrum of their relaxation times and temperatures is sufficiently broad that although the centre of the transition range is depressed to around 0°C by moisture, there remain some relaxation times long enough to retain set even in wet processes.

By comparison with cellulosic fibres, polyamides are mechanically tough. They are not generally susceptible to mechanical damage under domestic wash conditions, except where they are used in fine knitted articles such as stockings and tights in which 'snagging' can easily lead to holes or 'ladders'.

Polyamides have a high affinity for many polar and nonpolar species that may be present in typical wash liquors. Since the fibres are washed at above  $T_g$  these species readily diffuse into the fibres, often causing permanent and unacceptable discolouration of whites and pastel shades. This problem is discussed further in section 4.4 in the context of dye desorption and cross-staining in washing product solutions.

**4.2.3.5 Polyester fabrics and polyester blends.** Polyester fibres used in washable textiles are invariably poly(ethylene terephthalate)s and although

these are marketed in many physical modifications and some minor chemical modifications (to confer differential dyeing properties), they are all sufficiently similar to be discussed together. Polyester fibres are highly crystalline, mechanically tough and hydrophobic. They do not swell significantly in water, and the thermal transition that occurs at around 100°C in the dry state is therefore relatively moisture-insensitive, and occurs at around 85°C in water. Since polyester fabrics are normally washed at 60°C or below, they can be heat-set to give excellent dimensional stability, permanent pleats, and smooth drying properties which last throughout their wash/use lifetimes.

The inherent toughness and stability of polyester fibres is extremely valuable in blends with other fibres. Fabrics constructed from optimum polyester-cotton, polyester-viscose, and polyester-wool blend yarns have dramatically improved easy-care characteristics, and their resistance to wet and dry abrasion is also increased. These benefits are obtained while maintaining to a large extent the more desirable aesthetic and comfort-in-wear properties of the natural fibres.

A disadvantage of fibre blends can be that differential friction effects between fibre types, and the possible mismatch of fibre diameters and cross-section shapes, may lead to increased fibre mobility, and hence to increased pilling. Although pilling is widely associated with in-use abrasion, especially on knitwear, there is undoubtedly a problem of in-wash pilling which appears all over certain types of fabrics after about ten wash cycles. The most affected articles tend to be knitted from blended yarns, although some 100% cotton articles such as T-shirts and sweatshirts are also affected. Where one of the fibres in a blend is polyester there is little or no tendency for the pills to wear off after further washing or use, because the strength of polyester fibres anchors the pill to the fabric structure. The introduction of deliberately weakened 'low-pill' polyester has not eliminated this problem.

The hydrophobic nature of polyester fibres makes them particularly prone to oily soiling, and to the redeposition of oily or fatty soils during washing. Such soiling is often difficult to remove, but since polyester is washed below its wet  $T_g$  there is little penetration of fatty soils into the fibre. As a consequence they can be stripped by washing in strongly alkaline solutions (section 4.3.2). Furthermore, the fibre surface can be rendered somewhat more hydrophilic (and less prone to oily soiling problems) by minor chemical modification of the fibre surface. This is discussed further in sections 4.3.2 and 4.3.6.1(c).

**4.2.3.6 Acrylic fabrics.** The acrylic fibres used in washable end-uses are mainly copolymers containing at least 85% acrylonitrile and up to 15% of other vinyl monomers, which are used to introduce anionic (carboxyl, sulphate or sulphonate) sites into the polymer in order to confer dyeability with basic (cationic) dyes. Dry  $T_g$  values for these fibres are in the region of 70–90°C; the transition is made relatively moisture-sensitive by the presence of the hydrophilic anionic groups and occurs at about 50–70°C in water.

Unlike polyamides, acrylics do not retain heat-set dimensions when  $T_g$  is exceeded. This property is utilised to produce soft, highly bulked yarns which compare favourably with woollen knitting yarns. Bulking is achieved by blending a small percentage of fibres that have been hot-stretched and cooled (to give temporary set) with normally oriented fibres produced by wet spinning and drawing. When the blended yarn is subsequently heated, without tension, to above  $T_g$ , the hot-stretched fibres return to their original dimensions, causing yarn shrinkage of 20–40% and thus buckling the normal fibres to produce a highly bulked yarn.

Provided that acrylic articles knitted from these yarns are washed below their wet  $T_g$  they retain their shape and bulk. Care labelling on acrylics always recommends washing at 40°C or below, and usually indicates a gentle or 'wool wash' cycle, and drying 'flat' or 'supported'. Unfortunately acrylics are often washed too hot because some washing machines either do not have adequate temperature control or do not clearly indicate the temperature associated with particular wash cycles or programmes. There is a tendency for stress applied during washing (or drying) above the wet  $T_g$  to restretch the bulking fibres (which remain under tension) and subsequently to re-set them on cooling. Consequently consumers often complain that acrylic knitwear "stretches when you wash it" and that it "goes flat and lifeless" after a few washes.

Apart from their dimensional instability, acrylic fibres are not susceptible to mechanical damage during washing. They also have good chemical resistance, but the polymer is prone to yellowing by light and heat and there is some evidence that this is exacerbated by washing in strongly alkaline products.

**4.2.3.7 Wool.** Wool fibres have no  $T_g$  in dry air below their thermal decomposition temperature, but they swell (about 40% by volume) and become rubbery in water at all temperatures. The fibres have good recovery properties under both wet and dry conditions which are at least partly attributable to covalent cystine crosslinkages in the keratin structure. 'Dried-in' creases are, however, set by temporary salt linkages and hydrogen bonding.

The fibre is protected from abrasion damage by a tough cuticle, but the scale-like structure of this layer gives rise to the differential friction between the fibres which is responsible for the felting of wool fibre assemblies. Felting is promoted by mechanical agitation; it is greatly increased in water, and is further exacerbated by the presence of surfactants.

Although shrink-resist treatments, which can render woollen knitwear fully machine-washable, are now being widely used, felting shrinkage still remains an area of concern in domestic washing. Furthermore, wool keratin is particularly sensitive to chemical damage by several ingredients that have become commonplace in modern fabric washing products (see sections 4.3.2.2, 4.3.3.1, 4.3.4.2, and 4.3.5.1). Fortunately, this is now leading to the marketing

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of specialist wool wash products which should allow the domestic consumer to wash, and machine-wash, wool with more confidence.

4.2.3.8 *Silk.* Traditionally, silk has been treated with extreme care, many articles being labelled 'dry clean only' and relatively few 'hand wash with care'. In recent years there has been an increase in silk imports, particularly from China, which has led to relatively inexpensive ranges of underwear, blouses and shirts, and even outerwear such as anoraks, being sold in high street stores. Many of these articles are labelled as machine-washable at 30°C or 40°C or 'wash as wool'.

While some experts are confident that silk can be washed without difficulty, others recommend only dry cleaning, and suggest that silk cannot be regarded as a washable fibre (Payot, 1991). Certainly, fabric washing products and processes do have the capacity to cause rapid deterioration in the desirable aesthetic qualities for which silk fabrics are so highly prized.

Like cotton and wool, silk swells in water and is above its wet  $T_g$  at all wash temperatures. In this state, the fibre is particularly prone to fibrillation, and even low levels of damage can give rise to a floury appearance (chafing or 'farinage') on the surface of lustrous satin and taffeta fabrics. This is less of a problem on the 'sand-washed' or 'peach-skin' finished silks that are currently popular, but washing and drying these causes a marked increase in fabric stiffness which impairs their soft, luxurious handle.

Creases in the wet fabric are set by intermolecular hydrogen bonding as it dries, and some skill is needed to achieve a satisfactory crease-free finish after washing.

Silk fibroin is sensitive to chemical degradation by several ingredients commonly used in modern fabric washing products (see sections 4.3.2.2, 4.3.4.2, and 4.3.5.1). The fineness of silk filaments and the lightweight construction of many silk fabrics makes them less able than other fibres to sustain even low levels of chemical attack without impairing their most desirable qualities. In particular, the lustre and lively handle of many silk fabrics is easily destroyed by washing in anything but the mildest products. Specialist wool wash liquids and hair shampoos are however suitable for handwashing 'washable' silk articles.

### 4.3 Chemical effects of fabric washing product ingredients on textile fibres

#### 4.3.1 *Water softeners or 'builders'*

It has long been recognised that calcium and magnesium hardness ions, present in supply waters, are deleterious to textile washing processes. Not only are soaps and anionic detergents wasted by the precipitation of their insoluble calcium and magnesium salts, but these salts are often also deposited

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on and bound by textile fibres, where they build up to cause greying or yellowing, and the development of rancid, fatty odours on the fabric.

Hardness ions are invariably bound to fibres containing carboxylic acid groups, or other anionic sites provided by dyes and fluorescers, because rinsing at the end of the wash is carried out in hard water. All fibres also carry dried-on (rather than ion-exchanged) hardness ions from the last rinse into the next use, wear and subsequent wash cycle. The hardness ions present in washed textiles provide potential sites for the attachment of anionic soils during use. The fatty acid components of sebum are often tenaciously held, especially where they are able to diffuse into the interior of fibres such as cotton, during warm, moist use conditions.

Clearly it is important to effect the removal of hardness ions both from the water and from textile fibres, if efficient washing is to be achieved. Although the term 'water softening' is widely used to describe the various means of removing hardness ions from water, the manufacturers of fabric washing products generally use the term 'building' to describe the process, and hence describe water softeners as 'builders'. The reason for this is that when water softeners such as sodium carbonate or sodium triphosphate (STP) are used in excess of the stoichiometric amounts needed for removing hardness ions, they provide alkalinity, and in the case of STP, soil dispersing and suspending properties, essential to effective fabric washing. That is, they 'build' on the wetting and detergent functions of surfactants.

In order to prevent precipitation of the anionic surfactants used in fabric washing products, and of the soaps generated from fatty soils on the wash load, it is necessary to reduce free hardness ion concentrations to less than  $10^{-4}$  M (1° French hardness) and preferably to about  $10^{-5}$  M (0.1° French hardness). This may be achieved by sequestration (i.e. forming stable complexes) by precipitation, or by ion exchange (e.g. for sodium ions in zeolites).

Whenever precipitant builders such as sodium carbonate or soap are used, or if sequestrant builders are used in 'underbuilt' or precipitating conditions, there is a risk that insoluble calcium and magnesium salts will precipitate, and build up inside or on the surfaces of textile fibres. Such deposits, depending on their level, location, and chemical constitution can cause several undesirable effects such as:

- apparent colour fading
- increased rate of wear
- loss of flame retardancy
- adverse changes in fabric mechanical properties and fabric handle.

*Calcium phosphate deposits.* STP ( $\text{Na}_5\text{P}_3\text{O}_{10}$ ) forms a soluble 1:1 calcium complex ( $\text{CaNa}_3\text{P}_3\text{O}_{10}$ ) which is responsible for its excellent sequestrant building performance. When incorporated into spray-dried powders, however, STP invariably suffers some breakdown into other phosphate species which have insoluble calcium salts. Where there is a molar excess of STP over

hardness ions, no insoluble phosphates are precipitated, but in marginally built conditions insoluble calcium ortho- and pyro-phosphates occur. In underbuilt washes the 2:1 calcium STP complex is also precipitated.

When cotton fabrics are washed repeatedly in underbuilt conditions, significant quantities of calcium phosphates build up on the fabric. Examples have been found in which up to 25% of the fabric weight is accounted for by phosphate 'ash'. (Inorganic deposits in textiles are often referred to as 'ash' because their levels are readily determined by burning off the fibre and weighing the residual ash.)

Surprisingly, when cotton fabrics having high phosphate ash contents are examined microscopically, there is little or no evidence of inorganic deposits on fibre surfaces. Examination of the ash, however, reveals a complete inorganic skeleton of the fibre structure, and it may be concluded that insoluble phosphates are precipitated inside the fibre, rather than being precipitated from solution and deposited, or 'seeded' and grown at the fibre surface.

The process of repeatedly rinsing in hard water, and re-wetting in the next wash with a solution containing phosphate ions, is not unlike that used for weighting silk, and it is perhaps not surprising that such high levels of insoluble phosphates can accumulate in cotton fibres. Even at high levels, these deposits have surprisingly small adverse effects on fabric handle, although some stiffening is detectable, especially in knitted fabrics (Mackay, 1992).

Increased light-scattering by inorganic deposits can cause apparent fading of dyed fibres, but this is small compared with other effects of repeated washing, such as dye desorption, and dye damage by bleaching.

*Calcium carbonate.* Unlike calcium phosphates, calcium carbonate deposits tend to grow on fibre surfaces. Even relatively low levels (<5%) can be readily seen under the microscope as crystalline encrustations of calcite, which give the fabric a harsh and sticky handle, and cause 'frosting' of coloured fabrics. Furthermore, since calcite is mildly abrasive, the wear rate of textiles regularly washed in carbonate-built products is significantly increased compared with that of similar articles washed in phosphate-built detergents (Mohamed, 1982).

The growth of calcite at fibre surfaces, rather than inside the fibre, may be explained by the fact that calcite crystal growth is relatively slow and is easily 'poisoned' by other ionic species present in the wash liquor. As a consequence, the initially high concentration of calcium ions in the dry fibre is greatly reduced by dilution, and by ion-exchange with sodium ions, before calcite precipitation occurs.

The slow growth of calcite, and hence the slow rate of lowering of free calcium ion concentrations in the wash liquor, makes sodium carbonate a poor builder for fabric washing products. Soaps and other anionic surfactants are irreversibly precipitated before the builder does its job.



In the days before 'self-acting' detergent products, washing soda (sodium carbonate decahydrate) was used effectively by adding the soda to the water and boiling the wash load before adding grated soap, or rubbing individual articles with bar soap. This reflected the normal practice in commercial laundries (and in textile processing) of softening the process-water before use.

*Calcium soaps.* The deposition of calcium and magnesium soaps in poorly-built washing conditions has already been mentioned. The problems can be much more severe if fabrics are washed regularly in soap-based products, which rely on soap as both (precipitant) builder and surfactant. Although cellulosic fabrics in particular acquire a pleasantly soft handle, they also become increasingly hydrophobic, and prone to yellowing and the development of rancid odours. More seriously, the substantial soap deposits increase the flammability of the fabrics, and this has been shown to impair the effectiveness of flame-retardant finishes (Carfagno and Pacheco, 1973). A full discussion of the effects of washing on flame-retardant finishes is beyond the scope of this chapter, but the subject has recently been reviewed (Horrocks *et al.*, 1993); see also chapter 3.

#### 4.3.2 Alkalinity

4.3.2.1 *The need for alkalinity in fabric washing products.* Alkali is essential in fabric washing operations that call for the saponification of fatty soils. A substantial part of the soil on domestic laundry is sebum secreted by the sebaceous glands in the skin. Since it is found at levels of 0.5–1.0% on bed linen and clothing worn next to the skin, it can be estimated that around 20 g of sebum is present in a typical 3 kg wash load.

Although it contains some hydrocarbons such as squalene, sebum consists largely of triglycerides and fatty acids which can be rendered effectively self-dispersing by appropriate quantities of alkali. In principle, fats can be dispersed by surfactants alone, but enormously increased levels would be required to achieve this from neutral fabric washing products.

In STP-built detergents, additional alkalinity is required, over and above that provided by the phosphate itself. This is because calcium ion binding by STP is pH-dependent, and deteriorates markedly below about pH 9.5. Sodium silicate is normally used to provide this additional alkalinity because it confers improved structure to spray-dried powders, as well as providing increased alkaline buffer capacity. In zeolite-built products, however, the addition of silicates promotes unacceptable powder 'caking', and sodium carbonate is used instead.

Alkalinity is also required for the efficient functioning of the hydrogen peroxide-based bleaching systems that are used in many fabric washing products. Since sodium perborate or sodium percarbonate are the sources of hydrogen peroxide in these systems, they bring their own additional alkalinity to the wash solution.

#### 4.3.2.2 *Effects of detergent alkalis on fibres.*

*Cellulosic fibres.* These are very slowly degraded by hot alkaline solutions, hydrolysis proceeding stepwise from the aldehydic end group of the cellulose chain (Golova and Nosova, 1973). Oxidative treatments that produce increased numbers of aldehydic or ketonic groups in cellulose greatly increase its sensitivity to alkaline hydrolysis. This is discussed further in the context of detergent bleaching systems in section 4.3.4.2. In general, however, cellulosic fibres are resistant to damage by alkaline detergents, and indeed to the strongly alkaline processes used in scouring and mercerising.

The covalent cross-links introduced into cellulosic fibres to impart crease-resistance and crease-recovery properties are susceptible to slow hydrolysis by repeated washing in alkaline detergents. As a consequence the performance of crease-resist finished fabrics soon deteriorates if they are washed frequently.

*Cellulose acetate fibres.* These are susceptible to deacetylation by alkaline hydrolysis, but since acetate fabrics require very careful wash treatment to avoid creasing (see section 4.2.2.3) they are not normally subjected to potentially damaging wash conditions.

*Wool.* Wool absorbs alkali initially by 'tritiation' of carboxyl groups, but before an end-point is reached, alkali begins to be consumed by reaction with cystine cross-links. These are converted to lanthionine, with the partial elimination of sulphur as sodium sulphide. Ultimately, alkaline hydrolysis of peptide bonds leads to gradual dissolution of the fibre. Clearly, wool is subject to progressive deterioration by repeated washing in conventional alkaline detergents. In the past this was not a serious problem because wool articles were, in the main, washed carefully by hand in mild 'hand wash' products to avoid felting shrinkage. Nowadays many wool articles are fully machine-washable. As a result, they are washed more frequently in conventional machine-wash products. Such products are not only highly alkaline, but they often contain both proteolytic and lipolytic enzymes and bleaching systems, which are also particularly damaging to wool (see sections 4.3.4.2, 4.3.5.1 and 4.3.5.2). A marked deterioration in the handle of wool, often described as 'impoverishment', becomes clearly noticeable after a few washes in these products.

As a result of the serious effects that conventional domestic detergent products can have on wool, the International Wool Secretariat has introduced a new product endorsement scheme for products that meet appropriately low wool-damage criteria. In response, there has been an increase in the availability and advertising of specialist products which are suitable for washing wool in the machine, as well as by hand.

*Silk.* Silk fibroin, like wool keratin, is damaged by alkaline hydrolysis on washing in conventional detergent solutions, particularly when they also

contain proteolytic enzymes. The recent increase in the number of washable silk articles in European markets has, however, led major fabric washing product manufacturers to identify products suitable for washing silk, and even to draw particular attention to their performance on silk in television advertising.

*Polyester, polyamide and acrylic fibres.* When washed at recommended wash temperatures, the relatively hydrophobic synthetic fibres are not noticeably affected by alkaline detergent solutions. Polyesters are, however, subject to slow surface hydrolysis which renders the fibre surface more hydrophilic and less prone to the retention and redeposition of oily and fatty soils. In bright polyesters, this may eventually lead to dulling of the fabric lustre, as the fibre surfaces become roughened and pitted. This is not, however, regarded to be a problem within the normal lifetimes of bright polyester garments.

The polyester-based soil-release polymers that are often applied to polyester fabrics are gradually stripped from the fibre by repeated alkaline wash treatments. It is, however, possible to replenish soil-release performance by incorporating soil-release polymers in fabric washing products (see section 4.3.6.1(c)).

The discolouration of white and pastel shades is the most characteristic form of deterioration in polyamide fibres. Whilst alkalinity may play a role in the long-term yellowing and degradation of polyamides, the principal cause of discolouration, within the lifetime of washable textiles, is undoubtedly the adsorption of fugitive dyes, and other coloured species, from the wash liquor. This is discussed more fully in section 4.4.3.

The deterioration of elasticity, which is a feature of many polyamide garments, is often due to the hydrolytic degradation of elastomeric polyurethane yarns. In other cases, however, oxidative attack on hydrocarbon elastomers is the cause of failure. In either case, washing in low-pH, bleach-free detergents should be recommended for garments of this type.

It is unlikely that washing acrylic fibres in conventional alkaline detergents at recommended temperatures ( $\leq 40^{\circ}\text{C}$ ) contributes to their long-term yellowing. The problems that consumers identify with acrylics are confined to their lack of dimensional stability when washed too hot or tumble-dried (see section 4.2.3.6) and to the harsh handle which develops, as softeners are removed by repeated washing (see section 4.3.3).

### 4.3.3 Anionic, nonionic and cationic surfactants

4.3.3.1 *Adsorption of anionic and nonionic surfactants.* All surfactants, by definition, adsorb at interfaces — they are 'surface-active agents'. Although the anionic and nonionic surfactants used in fabric washing products adsorb on and diffuse into textile fibres to promote wetting and detergency, they

are largely desorbed and washed away during the rinsing process. Thus they do not generally cause modification of fibre and fabric properties. Wool is, however, an exception. Anionic surfactants are bound at protonated amino sites, the concentration of which clearly depends on wash pH. Unfortunately, at near neutral pH, which is necessary to protect the wool from hydrolytic attack, all amino end-groups are protonated, and the potential to bind large amounts of anionic surfactants is at a maximum. Apart from displacing acid dyes (see section 4.4.3), the adsorption of anionic surfactants has also been shown to have deleterious effects on fabric handle, and on the fibre modulus and tensile strength (Nolte, 1994).

Much lower concentrations of nonionic surfactants are adsorbed by wool, and the mechanical properties of the fibre are relatively unaffected (Nolte, 1994). Washing with nonionics does, however, leave the fibre with a particularly harsh handle, and there is clearly a need for effective wool softening agents to be incorporated in specialist wool wash products. Many of the marketed products do contain softeners, and some make specific softening claims, but their performance still leaves room for improvement.

The continual improvement in fatty soil detergency (which is being achieved by careful selection of nonionic surfactant species) also increases the efficiency with which detergents remove finishing agents from textiles. In particular, semi-permanent lubricants, which give the luxurious handle currently demanded by customers, are more efficiently removed. This gives rise to frequent complaints that cotton and acrylic knitwear becomes harsh, even after only one or two washes.

**4.3.3.2 Adsorption of cationic surfactants—rinse conditioners.** The use of rinse conditioners (fabric softeners) goes some way towards alleviating the harsh handle caused by (a) the removal of softeners applied during textile finishing and (b) the fibrillation damage caused by the repeated washing of cotton textiles.

For many years the cationic softeners used in rinse conditioners were either di-tallowyl dimethyl ammonium salts or di-tallowyl imidazolium salts. They adsorb readily on negatively charged fibre surfaces, where they form close-packed monolayers or multilayers which act as excellent boundary lubricants between yarns and fibres (Chugg, 1990). In recent years these actives have come under environmental pressure as 'unnecessary non-biodegradable chemicals'. Although, increasingly, they are being replaced by biodegradable alternatives, they continue to come under pressure, and the market for them, at least in Europe, seems to be in decline.

Other criticisms levelled at rinse conditioners are that (i) they cause hydrophilic fibres to become hydrophobic and (ii) they increase 'snagging', thread-pulling and pilling in some fabric constructions. While all of these phenomena can certainly be demonstrated in controlled experiments, none

of them appears to be a problem perceived by consumers. One reason for this is that the strike rate of cationics is so fast that patchy delivery to the fabric is almost inevitable, especially in automatic dosing washing machines. As a consequence, although localised regions of large articles may be rendered hydrophobic, their overall absorbancy is not impaired. Similar arguments may apply to the overall snagging and pilling propensities of rinse-conditioned wash loads.

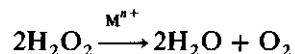
For many consumers, the other benefits obtainable from rinse conditioners far outweigh these possible negatives. For some, the delivery of perfume to the fabrics is an important attribute, while for others (especially those who use tumble driers) the reduction of electrostatic charging and 'fabric cling' may be even more important than improved softness. Other less well advertised conditioner benefits include improved wrinkle shedding and crease recovery, and greater comfort in wear of resin-finished shirts. The elasticity of knitted cottons is also improved, and although this is closely related to the perception of softness, it can manifest itself as better 'fit' and shape retention during wear. Thus, on balance, the adsorption of cationic surfactants from rinse conditioners provides more positive than negative fabric attributes, and their continued use should not be discouraged.

#### 4.3.4 Bleaching systems

4.3.4.1 *The development of bleaching systems for fabric washing products.* For many years, bleaching from fabric washing products was achieved by using sodium perborate as a source of hydrogen peroxide. At about 70°C and above, hydrogen peroxide is effective on a broad spectrum of common stains, but its performance in fabric washing products is extremely variable unless some care is taken to control its decomposition. There are two main causes of hydrogen peroxide decomposition in fabric washing systems: the enzyme catalase; and transition-metal ions such as copper and iron.

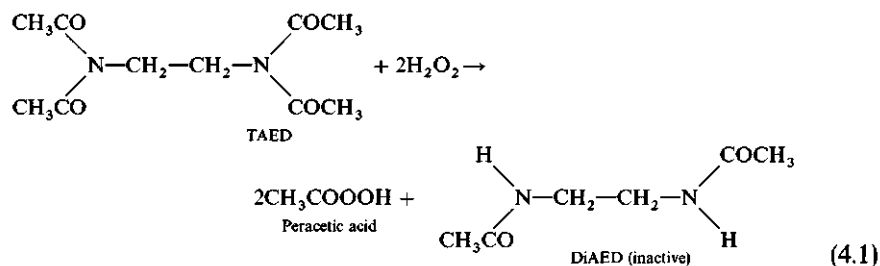
Catalase is a haemoprotein, containing four  $\text{Fe}^{3+}$  ions per molecule, which is produced by many organisms as a defence against the hydrogen peroxide generated by various oxidases. It therefore occurs very widely, and is present on naturally soiled wash loads at concentrations which depend on the level of soiling, the composition of the load, and the storage time of the soiled clothes before washing. No safe method of effectively controlling catalase activity in domestic washing systems has yet been found, but some alternative bleaching agents (discussed below) are less sensitive than hydrogen peroxide to decomposition by catalase.

Catalytic quantities of transition metals, especially copper and iron, are brought into washing systems by domestic supply waters, soils on textiles, the textiles themselves, and as impurities in detergent products. These metals not only catalyse the wasteful decomposition of hydrogen peroxide:



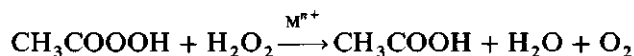
but they also catalyse oxidative attack at alcoholic functions, converting them to aldehydes, ketones or carboxylic acids. Such reactions can be particularly damaging to cellulosic fibres (see section 4.3.4.2) and for this reason, peroxide-based bleaching systems have usually contained powerful metal ion sequestrants, such as ethylene diamine tetra-acetic acid (EDTA) and magnesium silicate, to complex free copper and iron.

Throughout the 1970s average wash temperatures in Europe were falling. This was partly because of the increasing incidence of brightly coloured textiles, which require washing at 60°C or below, and partly also because of the concern over the increasing cost of energy. In order to maintain bleaching performance at these lower wash temperatures, products based on peracid precursors such as tetra-acetyl ethylene diamine (TAED) were introduced. The principle of this system is to use hydrogen peroxide (from sodium perborate) to perhydrolyse TAED in the wash liquor, thus generating peracetic acid, a species which is known to give significant bleaching effects at 50°C to 60°C (equation 4.1).

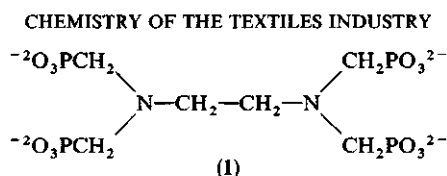


At first, the TAED level was kept down by high initial cost and low availability. The early products therefore used a high stoichiometric excess of hydrogen peroxide (as sodium perborate) over TAED. While this excess was partly to allow for the uncertain losses of  $\text{H}_2\text{O}_2$  through catalase activity, it was also essential to boost high-temperature bleaching performance so that the new products showed no deficiency in 90°C washes when compared with the traditional perborated products.

Unfortunately, excess hydrogen peroxide drives a mutual decomposition reaction with peracetic acid, which is strongly catalysed by transition metals:



This led to a need for more powerful transition metal ion sequestrants, which was met by the introduction of low levels of the sodium or calcium salts of ethylene diamine tetramethylphosphonate (EDTMP) (1) and other similar molecules.



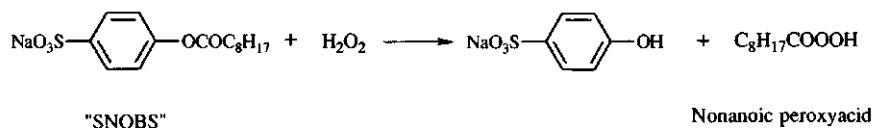
As TAED became more readily available and relatively less costly, the need to maintain boil wash performance was also declining because average wash temperatures continued to fall. Higher levels of TAED with lower levels of perborate were therefore gradually introduced. Since these higher TAED/perborate ratios suffered less from mutual decomposition, it became possible to reduce the level of, and eventually to omit, the expensive sequestrants such as EDTMP.

Apart from providing stain bleaching at lower wash temperatures, TAED/perborate, and other peracid bleaching systems, such as sodium nonanoyloxybenzene sulphonate (SNOBS)/perborate (see Figure 4.8) have three further advantages over hydrogen peroxide:

- (i) they are less likely to cause oxidative damage to cellulosic fibres
- (ii) once generated, the peracids are not decomposed by catalase, and
- (iii) they kill bacteria that are resistant to hydrogen peroxide, thus giving a more hygienic wash, even at low temperatures.

On the other hand, the greater specificity of peracids in oxidising disulphide bonds leads to increased damage to wool, and to sulphur dyes. These aspects of bleaching are discussed more fully in sections 4.3.4.2. and 4.4.2.

By the early 1990s the most widely used domestic wash programmes, in the majority of European countries, were being carried out at 40°C. This fact, together with the ever-present need to improve stain removal, especially under the ambient-temperature wash conditions that pertain in most other parts of the world, has led one of the major detergent manufacturers to develop a manganese-catalysed perborate bleach system. This system has not however proved to be completely free of fibre and colour safety problems. Understandably this has led to adverse comment by representatives of the coloration industry (Smith, 1994).



**Figure 4.8** The generation of nonanionic peroxyacid from SNOBS/perborate, a more hydrophobic alternative to peracetic acid.

4.3.4.2 *Effects of bleaching systems on fibres*

(a) *Cellulosic fibres.* It was noted in section 4.3.4.1 that transition metals catalyse the oxidation of alcohols by hydrogen peroxide. In cellulosic polymers this may result in oxidation of the primary alcohol function at the C6 position of the anhydroglucose ring to an aldehyde and thence to a carboxylic acid group. Similarly, oxidation of the secondary alcohol functions at the C2 and C3 positions leads to the formation of ketone or aldehyde and thence carboxylic groups (Figure 4.9).

When aldehyde groups occur at the C2 and C3 positions, the polymer is particularly sensitive to alkaline hydrolysis (Figure 4.10). Consequently, under alkaline washing conditions, any metal-catalysed oxidation is likely to lead to cellulose degradation, and hence to a loss in the tensile and tear strengths of cotton and viscose fabrics.

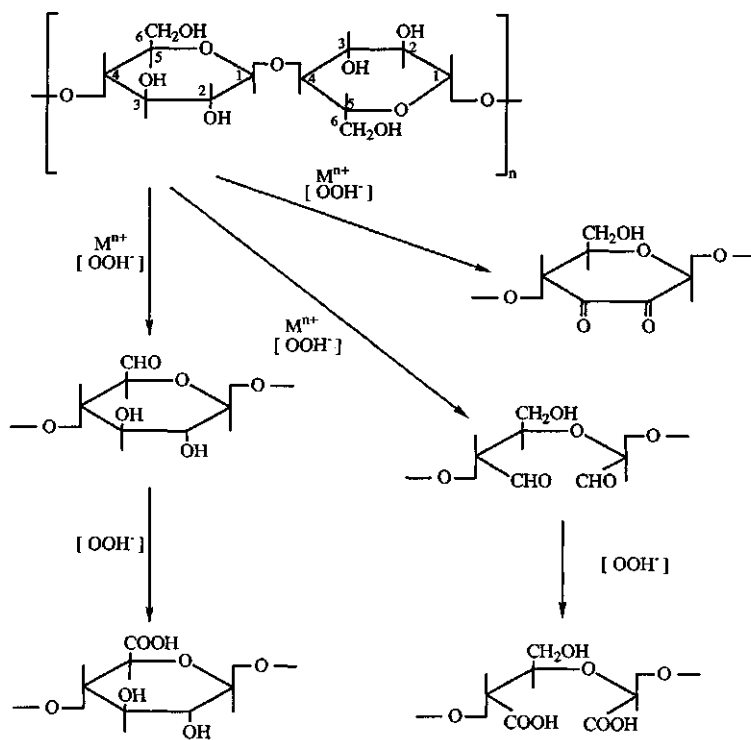


Figure 4.9 Possible mechanisms for the metal catalysed oxidation of cellulose.



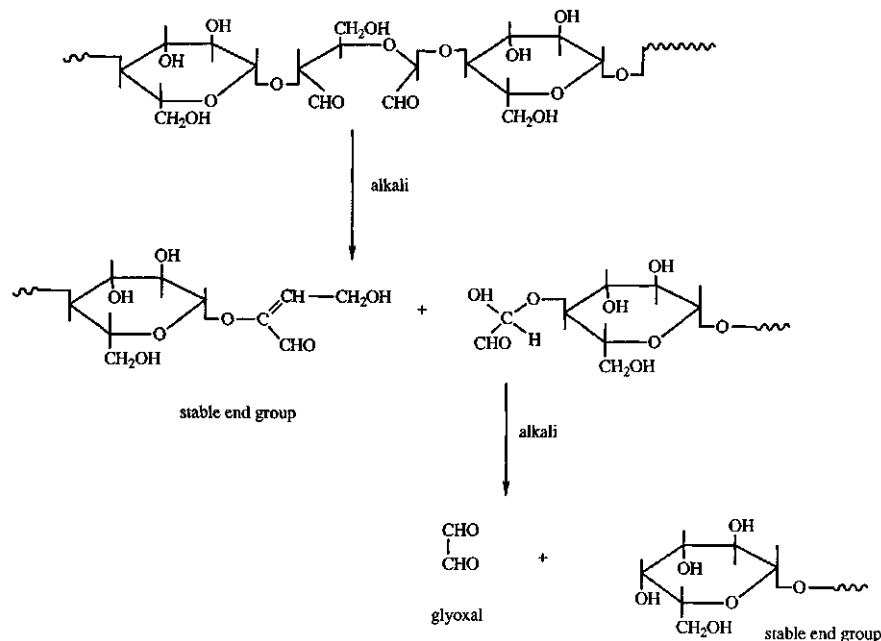


Figure 4.10 Alkaline hydrolysis of oxycellulose.

(b) *Wool and silk.* The damaging effects that alkaline fabric washing products have on wool and silk were discussed in section 4.3.2.2. The combination of alkalinity with conventional hydrogen peroxide-based bleaching systems has the potential to cause serious oxidative damage at the peptide bonds in wool and silk (and cystine links in wool), especially if free transition-metal ions are present. In practice, however, provided that the recommended short, low-temperature (30–40°C) wash programmes are used, no significant oxidative damage occurs.

Although organic peracids are more reactive than hydrogen peroxide at lower wash temperatures, they do not cause general oxidation at peptide bonds. They are, however, highly specific in their attack on disulphide bonds. Consequently, the cystine cross links in wool keratin, which are so important to the physical properties of wool fibres and fabrics, are particularly vulnerable.

Under mildly acidic conditions, peracetic acid quantitatively oxidises cystine to cysteic acid (Figure 4.11(i)). Under alkaline conditions, however, the expected increase in the concentration of sulphonate groups is not detected. Nevertheless, there is marked deterioration in the mechanical properties of fibres, and in the handle of woollen garments, washed under these conditions. It is believed that this results from a different, but nonetheless damaging, mechanism of cystine oxidation and hydrolysis (Figure 4.11(ii)).

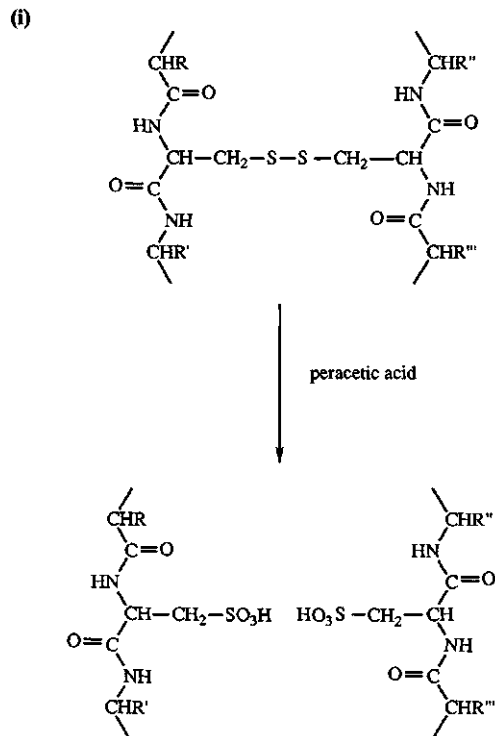


Figure 4.11(i) Oxidation of cystine to cysteic acid under acidic conditions.

#### 4.3.5 Enzymes and their effects on textile fibres

4.3.5.1 *Proteases.* Proteolytic enzymes (proteases) have been included in many fabric washing products since the late 1960s. Such products are often described as 'biological' because of the natural origin and function of the enzymes, and the emphasis that this has been given in certain advertising campaigns. The function of these enzymes is to assist the removal of tenaciously bound proteinaceous soils, by breaking them down into smaller fragments, which are then more easily washed off by detergent action. Their optimum pH and temperature ranges are, of course, selected to fall within those of normal washing conditions.

Since a wide variety of protein types may constitute soils on textiles, non-specific proteases are used. These hydrolyse peptide bonds, irrespective of the structure of the adjacent side chains. As a consequence, protein fibres such as wool and silk are also subject to proteolytic attack. Although

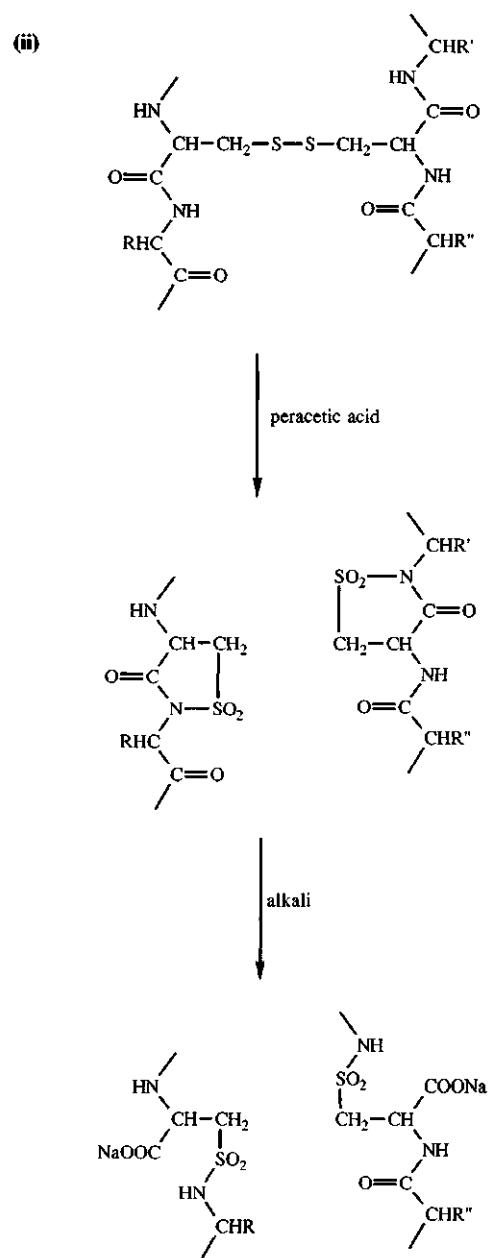


Figure 4.11(ii) Oxidation of cystine by peracetic acid under alkaline conditions.

detergents manufacturers normally warn consumers not to soak wool or silk in these products, they do not label products as 'unsuitable for wool and silk', probably because under recommended use conditions, little or no damage is apparent until articles have been washed many times.

Products which both generate peracid and contain proteolytic enzymes are particularly damaging to wool because of the synergy between peracid attack at the cystine cross links (section 4.3.4.2) and proteolytic attack at the peptide bonds. This can lead to the removal of substantial amounts of protein from the fibre even under recommended wash conditions. It has been reported, for example (Smith, 1994, personal communication), that a machine-washable wool sweater lost in excess of 1% by weight per wash in such a product, and that holes appeared in white areas of the garment after only about ten washes. The white areas were knitted from bleached wool, which is known to be extremely vulnerable to subsequent attack by proteases and peracids.

Since the shrink-resistance of machine-washable wools is usually achieved by oxidation followed by application of a polymer, their susceptibility to further oxidative and enzymatic attack, compared with that of untreated wools, is also of some interest. Recent work (Nolte, 1994) has shown that although the applied polymer layer appears to provide a temporary barrier against enzymatic attack, once this has been breached, proteolytic attack then follows much more rapidly in the shrink-resist treated fibre.

**4.3.5.2 Lipases.** During the past few years, detergent products containing lipases, as well as proteases, have been introduced. Lipases are enzymes which specifically hydrolyse the ester linkage in fats, such as triglycerides and other fatty esters, but do not have general esterase activity. Clearly, their function in washing products is to facilitate the hydrolysis and so improve the detergency of fatty soils. In practice, however, it is difficult to show convincingly that lipases are effective under washing conditions, because their activities are greatly reduced by the absorption of surfactants at their active centres (Benzonana and Desnuelle, 1968; Nolte, 1994). Suppliers of lipases optimised for use in detergents have suggested, however, that lipases absorbed on to fatty soil in one wash are not easily rinsed away, and that they continue to degrade the fatty stains 'between washes' and so give more complete removal in the next wash (Novo, 1994).

There is no evidence to suggest that lipases have adverse effects on fibre properties when they are used in detergent products. They do, however, have the potential to modify lipoproteins on the cuticle and in the cell membrane complex of wool (Nolte, 1994).

**4.3.5.3 Cellulases.** Cellulases of bacterial and fungal origin are responsible for breaking down the cellulosic components of fallen leaves and dead plants. They are complex mixtures of enzymes which exhibit three types of cellulolytic

activity, each of which is nevertheless specific to 1,4- $\beta$ -D-glycosidic bonds. Thus total, crude cellulases always contain:

- (a) Endoglucanases (EGs) which cause random chain scission at accessible points of the polymer chain, producing one new reducing end-group and one new non-reducing end-group at each cleavage point.
- (b) Cellobiohydrolases (CBHs) which exhibit so called 'exoglucanase' activity — stepwise cleavage of cellobiose units from the ends of cellulose chains.
- (c) Cellobiase or  $\beta$ -D-glucosidase, which hydrolyses cellobiose to glucose.

Natural cellulases are always found to contain several (possibly as many as six) different EG components. Their individual roles and the interactions between them are not yet fully understood (Emari and Niku-Paavola, 1987), but clearly there is synergy between the EGs which continually produce new end groups and the CBHs which attack them. At least two CBH components (CBH I and CBH II) always occur in natural cellulases. These components have differing affinities for cotton cellulose and cause differing rates of hydrolysis. There is recent evidence that CBH I preferentially attacks reducing end-groups while CBH II attacks non-reducing end-groups (Biely *et al.*, 1993). Only one cellobiase component is known; its role is essential to the complete degradation of cellulose, since hydrolysis is retarded by increasing concentrations of cellobiose.

Advances in biotechnology have made it possible to manipulate the composition of crude cellulases so that mixtures can be produced in which the activities of particular components have been deleted. Furthermore, pure, single cellulase components can also be produced, so that in principle it is now possible to tailor cellulase mixtures for specific textile finishing applications.

The use of cellulases in domestic detergents was first proposed over 20 years ago, as a means of alleviating the harshness that develops in cotton textiles as a result of fibrillation damage (section 4.2.3.1(c)). At the time, however, there were few commercially available cellulases, and none that was sufficiently effective, at alkaline wash pH, for successful exploitation in detergents. More recently, as a wider variety of cellulases has become commercially available, there has been renewed interest in their exploitation in detergents, not only to give a softening benefit, but also to remove pills from cotton articles, and to improve colour brightness and stitch definition by removing fuzz fibres.

Since cellulases degrade cotton cellulose, a compromise between delivering the required benefit within a reasonable number of washes and causing excessive cotton damage has to be achieved. By using a cellulase mixture with the EGs deleted, considerable weight loss can be tolerated without causing serious loss in tensile strength. On the other hand, mixtures with CBHs deleted, or pure EGs, can be used to cause drastic modification in fibre mechanical properties with very little weight loss. The few cellulase-

containing detergent products, that are currently being marketed, do very little damage to cellulosic fibres, even over 10–20 wash cycles. It is questionable, however, whether they contain sufficient cellulase activity to deliver any perceptible benefit.

4.3.5.4 *Amylases.* A few domestic detergent products contain amylase to break down starch-based soils and so aid their removal. Since amylases are specific to the hydrolysis of 1,4- $\alpha$ -D-glucosidic bonds, they cause no damage to textile fibres.

#### 4.3.6 *Other ingredients*

4.3.6.1 *Antiredeposition agents.* When soils have been removed from textiles in washing processes, it is important to keep them dispersed in the aqueous phase, and to prevent their redeposition on to the textiles. This is not a problem when a sufficiently high product dosage is used to deal with the total water hardness and the soil level present in the system. In domestic washing, however, the variability of wash load size, soil level, water hardness, and dosage selected by the consumer can often lead to marginally under-dosed conditions. In these conditions, a variety of polymers can help to reduce soil redeposition by mechanisms which are specific to particular types of soils and fabrics.

(a) *Sodium carboxymethylcellulose (SCMC).* Sodium carboxymethylcelluloses (SCMC) with a degree of substitution of about 0.6 are water-soluble, but are strongly adsorbed on to cellulosic fibres under washing conditions. A monolayer of SCMC adsorbed on cellulosic fibres significantly increases their negative surface potential by virtue of the increased density of  $-\text{COO}^-$  sites. This has the beneficial effect of increasing the repulsion of negatively charged soil particles, especially clay soils, and precipitating calcium phosphates.

SCMC is therefore incorporated in most fabric washing products, at levels which will maintain monolayer coverage of all the cellulosic fibres in typical wash loads, and assuming typical levels of product dosage by the consumer. This provides protection against the redeposition of clay soils on to cellulosic fibres in marginally 'built' conditions (see section 4.3.1), but once significant levels of calcium phosphates, calcium soaps, or calcium salts of anionic surfactants begin to precipitate, the  $-\text{COO}^-$  sites provided by the SCMC become occupied by free calcium ions and the benefits of electrostatic repulsion are lost. Under these circumstances the binding of the redeposited soils on fibre surfaces (via calcium salt 'bridges') becomes a problem.

(b) *Polyacrylates.* A variety of polyacrylates, and other polycarboxylic acids such as ethylene/maleic acid co-polymers, has been used in fabric washing products to help delay the onset of precipitation and deposition of

insoluble calcium salts. Unlike SCMC, these polymers do not function by adsorption on the fibre, and although they provide some additional calcium 'building' capacity, their main role is to become incorporated into growing precipitates thereby poisoning crystal growth, and inhibiting flocculation and deposition.

(c) *Soil release polymers and cellulose ethers.* Since polyester fibres are relatively hydrophobic, they strongly adsorb hydrophobic, fatty and oily soils during use or wear, and tend to retain them even under ideal wash conditions. Under poor wash conditions polyester fabrics readily re-adsorb any precipitating or non-solubilised fatty soils. Then they become grey, and develop fatty odours after only a few washes. This problem can be alleviated by making the fibre surface more hydrophilic. Textile finishers can achieve this by the application of soil-release polymers, which are often block copolymers of polyethylene glycols and polyesters.

The polyester blocks can be adsorbed on, and, under heat-setting conditions, co-crystallised with the fibre surface. The polyethylene glycol blocks provide some hydrophilic character, and on washing they become heavily hydrated and so aid the release of oily soils, and prevent their redeposition. Such polymers can also be applied during fabric washing or rinsing processes to provide similar benefits, albeit at lower efficacy. The major manufacturers of detergents have, however, been slow to adopt them, and they are perhaps not yet convinced of their cost-effectiveness.

An alternative route to providing similar benefits in the wash was applied in a few detergent brands during the 1970s. Cellulose ethers, such as methyl cellulose, and certain ethylhydroxyethyl celluloses are water-soluble, but have the correct hydrophobic-hydrophilic balance to adsorb on to polyester under washing conditions, thereby rendering it somewhat more hydrophilic. The use of cellulose ethers, as oily soil anti-redeposition polymers for polyester, appears to have been discontinued. Again, the detergents manufacturers are, perhaps, unconvinced of their cost-effectiveness.

(d) *Polyvinylpyrrolidone (PVP).* It has been known for many years that PVP interacts strongly with some dyes (Scholtan, 1954), especially those with large planar chromophores such as dis- and tris-azo direct dyes. From time to time this property has been utilised in fabric washing products in order to reduce cross-staining by fugitive dyes. Unfortunately, powerful dye scavengers not only reduce the activity of dyes in solution (thereby reducing dye staining) but also encourage the desorption of more dye from the source fabrics. Indeed, PVP solutions have been used in the dyeing industry as an aid to stripping dyed fabrics which require shade correction.

There are certainly combinations of dye, fabric, and wash process conditions, under which PVP reduces cross-staining with a barely measurable increase in the amount of dye desorbed from the source fabric. Such combinations

are not, however, so widespread that PVP could be claimed to have generally beneficial effects in fabric washing. Furthermore, the interaction of dyes with PVP is strongly influenced by surfactant type and level.

In general, the interaction between anionic dyes and PVP is reduced in the presence of other anionic surface-active species. Thus, potentially beneficial effects of PVP are reduced, or eliminated, not only by the presence of anionic surfactants in the detergent product, but by the fatty acids which are invariably present in natural soiling on domestic wash loads.

**4.3.6.2 Fluorescers (optical brightening agents).** Fluorescers, fluorescent whitening agents (FWAs) and optical brightening agents (OBAs) are all terms frequently used to describe essentially colourless dyes which have strong absorption maxima in the near UV between 300 and 400 nm (normally around 350 nm) and which re-emit the absorbed energy as violet to blue visible light at about 400–440 nm. Such dyes have been widely used in fabric washing products since the 1950s (as well as in the textiles and paper industries) to improve the perceived whiteness of bleached textiles. They were, and still are, the basis of the many detergents' advertising claims for washing 'whiter than white' and 'adds brightness to whiteness' and so on.

Although some 'nylon fluorescers' were used in the past (when white nylon was more widely used in washable end-uses), the majority of fluorescers are direct cotton dyes. Many of these are based on diaminostilbene, with the dianilino, dimorpholino, cyanuric chloride derivatives (Figure 4.12) probably being the most popular, for their good all-round performance in terms of solubility in a variety of product types, and reasonable stability to light when adsorbed on cotton. As for direct dyes in general, the substantivity of cotton fluorescers is inversely correlated with their water solubility. Similarly, their rates of adsorption and their equilibrium concentrations in the fibre are strongly influenced by temperature and electrolyte concentration. In countries where washing is carried out in cold water, alternative fluorescers, with

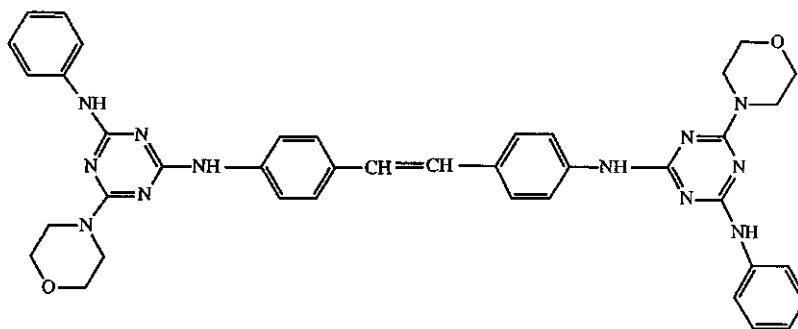


Figure 4.12 A typical cotton fluorescer derived from diaminostilbene.



increased cold-water solubility, may be required. Usually, however, these are variants of the same diaminostilbene derivatives, which have been micronised, or produced in modified, more readily soluble crystalline forms.

In tropical climates, where the lightfastness of conventional fluorescers is inadequate, 'superbrighteners' with greatly improved light (and chlorine) stability may be preferred. They are, however, expensive, and while they have good cold-water solubility, they have relatively low substantivity to cotton.

Fluorescers give white cotton a bluer and brighter whiteness, which is almost universally preferred by consumers, but this has the disadvantage of making pale yellow and beige shades look 'washed-out', and of making pink and red shades look noticeably bluer. For this reason they are omitted from 'coloureds wash' detergent brands. This is only a partial solution to the problem, however, since fluorescers, like other direct dyes, have poor wash-fastness and tend to desorb and transfer from one fabric to another during the wash process.

**4.3.6.3 Antifoams.** It has been mentioned (section 4.2.2.4) that front-loading automatic, or other forms of horizontal-axis, rotating-drum machines can generate excessive amounts of foam. Consequently, products intended for use in these machines contain antifoam systems. Historically, these were based on finely divided hydrophobic particles formed by the precipitation of the calcium salts of long-chain  $C_{18-22}$  fatty acids. During the 1980s these were replaced by more efficient and cost-effective systems, based on the combination of much lower levels of hydrophobic particles (such as calcium stearyl phosphate) with hydrocarbon or silicone oils.

The danger with any antifoam system based on hydrophobic oils and/or particles is that in poor wash conditions these will be deposited on hydrophobic fibres such as polyester (see section 4.3.6.1(c)). It is certainly the case that the early calcium soap-based antifoams could be found deposited on polyester fabrics. The much lower levels that are required for particle-in-oil antifoams have reduced this problem, and this may be the reason why the use of cellulose ethers to control fatty soil redeposition on polyesters (section 4.3.6.1) has been discontinued.

**4.3.6.4 Perfume.** For many years the role of perfume in fabric washing products was to mask unpleasant odours of product ingredients, both in the pack, and when the product was dissolved in water. Since the introduction of rinse conditioners, the consumer has also come to expect the washing product to leave a pleasant odour on the clean washing—not only while it remains wet, but even after drying and in subsequent use.

This has necessitated the development of fragrances containing components which partition between textile fibres and surfactant solutions, so that perfume is slowly released from fibres at their normal regain moisture contents.

Attempts have also been made to utilise so-called 'deodorant-perfumes' (which are used successfully in toilet soaps and other personal products) to reduce the perception of body odour while wearing clothes that have been freshly washed.

An alternative approach to providing long-lasting fragrance on textiles is to deposit micro-encapsulated perfumes on the fabric, which are slowly released during use or wear as capsules are continually being ruptured. This route has been used by some fashion houses and stores to give their goods a distinctive 'house fragrance' which is intended to influence the future buying habits of their customers!

#### **4.4 Effects of wash process and product formulation variables on dyed fabrics**

##### *4.4.1 Introduction*

It will be apparent from the preceding sections that there are several factors in the domestic washing process which can contribute to colour changes in dyed textiles. Some of these factors, such as the effects of cotton fibrillation damage (section 4.2.3.1(c)), the encrustation of fibres with insoluble calcium salts (section 4.3.1), and the adsorption of fluorescers (section 4.3.6.2), have already been described. These will not be discussed further here, except to note that they are of relatively minor importance by comparison with the colour changes that may result from the effects of bleaching agents or the desorption of fugitive dyes.

##### *4.4.2 Effects of bleaching systems*

The tendency for any detergent bleaching system to damage dyes is strongly dependent on the wash temperature and product concentration selected by the consumer. At the recommended wash temperature for a particular dyed textile, and recommended detergent product dosages, the potential for bleaching systems to cause damage increases with their increasing reactivity: hydrogen peroxide < organic peracids < catalysed hydrogen peroxide. The sensitivity of dyes to oxidative damage depends on the structure of their individual chromophores, rather than on dye application class. The characteristics of dyes in some application classes do, however, make them more or less sensitive, as a class, to oxidative damage. This is particularly true for vat dyes and sulphur dyes. The anthraquinonoid, indigoid and other polynuclear aromatic ketonic chromophores that are characteristic of vat dyes are developed in the fibre by mild oxidation, and are not sensitive to damage by further oxidation. Sulphur dyes are also applied in their soluble, reduced form and are developed by oxidation. In this case, however, the polysulphide structures, which constitute many of their insoluble chromophores, are particularly sensitive to further oxidation by organic peracids. This results

in cleavage of —S—S— bonds by analogous mechanisms to the oxidation of cystine in wool (section 4.3.4.2(b)). Thus, the chromophore is broken down into smaller, more soluble fragments, which can be washed off by detergent action. Consequently, sulphur dyes which have good wash-fastness, and adequate fastness to perborated products, are likely to have very poor fastness to products containing TAED/perborate or other peracid bleach systems.

The sensitivity to peroxide oxidation of dyes based on azo chromophores can be increased by chelation of transition metal ions, and the associated damage to cellulosic fibres dyed with such metallised chromophores may also be increased (Anon, 1985). For this reason some metal complex dyes have poor fastness to washing in perborated detergent products. Similarly azo chromophores with the potential to complex metal ions may also have poor fastness in perborated detergent products which do not contain stabilisers to sequester transition metal ions.

#### 4.4.3 *Dye desorption and cross-staining*

4.4.3.1 *Effects of washing process variables: time, temperature, liquor/cloth ratio and agitation.* Dyes that are applied by exhaustion from solution, and which are not subsequently either covalently bonded to the fibre or rendered insoluble, will tend to re-equilibrate with washing solutions. This applies in principle to direct, acid, disperse and basic dyes, and to any hydrolysed reactive dyes that have not been thoroughly washed off after dyeing.

In practice, however, basic dyes do not cause cross-staining problems in washing because they are used almost exclusively on acrylic fabrics that must be washed below  $T_g$  (section 4.2.2.2). The diffusion of dyes in fibres below  $T_g$  is so slow that significant desorption does not occur within the duration of typical washing cycles. This also applies to disperse dyes on polyester and on cellulose acetate fabrics, but since disperse dyes diffuse readily in nylon (which is above  $T_g$  at all wash temperatures) they can give rise to significant cross-staining problems. Disperse dyes on polyester microfibre fabrics may also be expected increasingly to contribute to dye staining problems in domestic washing. The problem here is that the high surface area of the fibres, and the increased dye-in-fibre concentrations required to achieve a given depth of shade, combine greatly to increase the amount of dye that desorbs from the fibre surface, especially in the first few washes.

Acid dyes on nylon and wool, and direct dyes on cellulosic fibres (especially if not after-treated) re-equilibrate readily with washing solutions. Hydrolysed reactive dyes behave like direct or acid dyes having low affinity for the fibre.

The desorption and cross-staining behaviour of dyes under washing conditions clearly has much in common with their dyeing characteristics. Consequently, the effects of the main wash process variables are predictable, at least in general terms, from the relationships used to predict dyeing

equilibria and dyeing kinetics. For example, the quantity  $\Delta\mu_{sf}^0$  in the equation:

$$-\Delta\mu_{sf}^0 = RT \ln \frac{[D]_f}{[D]_s}$$

represents the partial molar free energy change associated with the transfer of one mol of dye from its standard state in solution to its standard state in the fibre. This is the 'standard affinity' of the dye for the fibre, and once determined (from a series of equilibrium dyeings) it can be used to predict the equilibrium concentrations of an undissociated dye (such as a disperse dye) in the fibre  $[D]_f$  and in solution  $[D]_s$  at any temperature  $T$ , or for any liquor/cloth ratio. Since this applies equally to dyeing and dye desorption, it is predictable that washing at long liquor/cloth ratios drives dye desorption in order to achieve the equilibrium dye activity in the large volume of water. Similarly, the presence of a large amount of undyed fibre must drive desorption and cross-staining in order to achieve the equilibrium dye activity in both the originally dyed and undyed fibres.

The effect of temperature on dye desorption is also predictable; high wash temperatures cause greater equilibrium dye desorption. In any given wash, however, the effect of temperature on the rate of dye desorption is more important than its effect on equilibrium dye distribution.

The rate of dyeing — or dye desorption — is determined by (a) the driving force for dye transport and (b) the resistance to dye transport:

$$\text{Rate} = \frac{\text{Driving force}}{\text{Resistance}}$$

Clearly the driving force at any instant in time is determined by how far the system is from equilibrium. In dyeing this can be represented by the 'instantaneous' chemical potential gradient between the fibre and solution phases. At short times this approximates to the dye concentration gradient (grad  $C$ ).

Resistance to dye transport is provided primarily by the slow diffusion of relatively large molecules through the fibre bulk and is therefore inversely proportional to the diffusion coefficient of dye in the fibre ( $D$ ). Thus the mass ( $M$ ) of dye diffusing through the fibre surface at any instant can be represented by the general equation:

$$M = -D (\text{grad } C)$$

It has been mentioned (section 4.2.2.2) that diffusion coefficients increase exponentially with increasing absolute temperature according to the Arrhenius equation. Consequently, the rate of dye transport is approximately doubled for every 10°C rise in wash temperature. Clearly the choice that the consumer makes between a 40°C and a 60°C wash for a coloured fabric can influence the amount of dye transported by a factor of four.

In practice, washing machines go through heat-up cycles and the real effect of programme choice is determined by the combination of heat-up time and the length of time for which maximum temperature is maintained. The longer the total cycle time, however, the greater the dye transport, and in general higher temperature wash programmes have longer total cycle times.

In poorly stirred systems, dye transport to the fibre surface from the bulk solution (or vice versa in dye desorption) may also become a rate-determining factor. This has not been found to be the case in washing machines, since they provide relatively high agitation levels to assist the detergency process.

#### 4.4.3.2 Effects of product ingredients

##### (a) Alkalinity and electrolyte concentration

*Direct dyes.* Increasing alkalinity increases the negative potential of cellulosic fibres by increasing the ionisation of carboxyl groups and any other anionic groups that may be present as a result of processing and finishing operations. This would be expected to reduce the equilibrium concentration of direct dyes in the fibre according to well-established relationships (Peters, 1975a). In fact, the effects in washing processes are very small because anionic groups in the fibre are almost completely ionised under (neutral) dyeing conditions. The increase to pH 9–10 in washing therefore has very little additional effect on fibre potential.

By contrast, the effect of electrolyte concentration on the equilibrium distribution of direct dyes is extremely large. The salt concentration used in direct dyeing may be of the order of 20–30 g/l. The purpose of this is to increase the activity of dye in solution (by increasing the sodium ion concentration), thereby forcing the equilibrium in favour of the fibre:

$$-\Delta\mu_{sf}^0 = RT \ln \frac{[\text{Na}]_f^z [\text{D}]_f}{[\text{Na}]_s^z [\text{D}]_s}$$

where  $z$  = the number of sulphonate groups in the dye molecule. Washing at sodium ion concentrations that are equivalent to only about 2 g/l of sodium chloride leads to equilibrium desorption of about 80% for typical tetrasulphonate direct dyes (Marshall and Peters, 1947). Clearly, this does not happen in the course of a single wash, because at moderate wash temperatures the dye diffusion coefficient is greatly reduced. The driving force for desorption, however, remains essentially the same for successive washes.

Although washing products which provide relatively high ionic strengths help to reduce direct dye desorption, they also drive the re-adsorption (cross-staining) of desorbed dye on to other undyed (or pale shade) cellulosic fibres in the wash. Since cross-staining is perceived to be a more serious problem than the colour fading that may result from dye desorption, it may

be considered preferable to formulate 'coloureds wash' products to a very low ionic strength, in order to minimise the cross-staining problem.

*Acid dyes.* Acid dyes are adsorbed at protonated amino end-groups and side-chains during the dyeing of nylon and wool. The concentration of such sites is maximised during dyeing by setting the dye bath at about pH 4.0 or lower. The concentration of protonated sites is progressively reduced by increasing pH, as the  $pK_a$  values of the various amino groups in the fibre are exceeded. It can be shown for a monobasic acid HA (such as monosulphonated acid dye) that:

$$\frac{-\Delta\mu_{HA}^0}{2.303} = 2RT \left\{ \log \left( \frac{\theta}{1-\theta} \right) + \text{pH} \right\}$$

where  $\theta$  is the fractional occupation of positive and negative sites by  $A^-$  and  $H^+$  ions respectively, and it is assumed that the concentrations of positive and negative sites are always equal.

From this equation the equilibrium acid dye distribution can be predicted for washing product solutions of varying pH. Clearly it is essential to minimise the wash pH in order to minimise dye desorption. On the other hand, cross-staining by desorbed dye increases with decreasing pH. In practice, however, neutral or very weakly alkaline products are most appropriate for wool washing because of the damaging effect of alkali on the fibre (section 4.3.2.2).

It will be apparent from the preceding discussion that increasing the concentration of anions other than  $A^-$  dye anions must increase the competition for protonated dye sites. Thus, high electrolyte concentrations promote the desorption of acid dyes, but retard their cross-staining—the opposite dilemma to that posed by direct dyes. It is, however, usual to formulate specialist wool wash products as low ionic strength liquids. Relatively low concentrations of anionic surfactants (see below) have similar effects to high concentrations of inorganic anions and act as effective retarding agents against cross-staining by any small amount of acid dyes desorbed under neutral washing conditions.

*Reactive dyes.* The covalent bonds formed between the triazinyl and pyrimidyl reactive dyes and cellulose have more 'ester-like' than 'ether-like' character. They are therefore prone to slow hydrolysis under strongly alkaline washing conditions, and full shades tend to 'wash down' over many wash cycles. Hydrolysed dye washed from the fibre behaves towards cellulosic fibres in the same way as direct dyes of low affinity, and towards wool and nylon in the same way as acid dyes.

(b) *Surfactant effects.* Water-soluble dyes have some features in common with surfactants. They are relatively large organic molecules with one or more solubilising groups, and indeed many dyes show marked surface

activity. Like surfactants, dyes aggregate in solution above 'critical' concentrations. Typical aggregation numbers are in the range 2–20 and some dyes (with alkyl side chains) form true micellar solutions (Peters, 1975b). Mixtures of dyes and surfactants interact strongly in solution in a variety of ways depending on the charge of the individual dyes and surfactants. Consequently, surfactant solutions have a marked influence on both the desorption of dyes from dyed fabrics, and the uptake of dyes from solution.

*Disperse dyes.* Since disperse dyes have no charge, or other solubilising groups, they are only sparingly soluble in water. Typical solubilities are in the range 0.2–50 mg/l, but their solubility increases dramatically at the critical micelle concentration of surfactant solutions. The dye may be considered to be solubilised in the hydrocarbon-rich interior of the surfactant micelles, and since disperse dyes are nonionic, the effect is independent of surfactant charge.

When fabrics dyed with disperse dyes are washed in surfactant solutions, dye is desorbed until the equilibrium partitioning of dye between the fibre and micellar surfactant phases is achieved. Clearly, the higher the concentration of micellar surfactant, the greater the equilibrium dye desorption. Thus, high product or surfactant concentrations tend to increase dye desorption, but also tend to retard cross-staining, at least until the micellar phase is saturated with dye.

*Direct and acid dyes.* Interactions between surfactants and anionic dyes, such as direct and acid dyes, are dominated by the ionic character of the surfactant:

Cationic	>	Zwitterionic	>	Amphoteric	>>	Nonionic	>	Anionic
Insoluble complexes formed		Dyes taken into soluble complexes in the micelle				Many dyes strongly solubilised		Some dyes weakly solubilised

The formation of insoluble complexes between cationic surfactants and direct dyes may be used to insolubilise dyes on cellulosic fibres in order to improve their wet-fastness. These complexes can, however, be dispersed and solubilised in excess nonionic surfactant. Such systems have been used to control the strike rate and levelling of anionic dyes (Hughes *et al.*, 1971) and to reduce cross-staining by anionic dyes in fabric washing products (Bishop and Nelson, 1978).

The anionic dye restraining effects achievable with zwitterionic and amphoteric surfactants are generally more powerful than those obtained with optimised nonionic–cationic mixtures (Bishop, 1978). Their exploitation in domestic detergents has until now been limited by the high cost and low availability of the appropriate surfactants.

Interactions of anionic dyes with nonionic surfactants have been widely studied (Peters, 1975b) and there is good evidence from spectral shifts, the raising of the cloud points of the nonionics, and lowering of the critical micellar concentration, that mixed dye/surfactant micelles are formed. In general, the effect of nonionics is to increase dye solubility and to retard

dyeing by lowering the dye monomer concentration in solution. In washing processes, however, where dye cross-staining results from the combination of the dye desorbing and restraining properties of the surfactant system, the net effect is not always beneficial compared with that obtained with predominantly anionic active systems.

Anionic surfactants do not interact strongly with anionic dyes in solution, but they are used to retard dyeing with acid dyes on wool and nylon where they compete with the dye for cationic sites in the fibre. In washing systems, this has the beneficial effect of reducing cross-staining by acid dyes on these fibres, but high concentrations of anionic surfactants also increase the driving force for the displacement of dyes from the dyed fabrics.

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