

## CHAPTER 8

# Fixation and aftertreatment processes

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### 8.1 INTRODUCTION

If a typical textile print is washed soon after printing and drying, a substantial part of the colour is removed. An appropriate fixation step is therefore necessary. Complete fixation can rarely be achieved, however, and the removal of unfixated dye, thickening and auxiliary chemicals in a subsequent washing process is usually required.

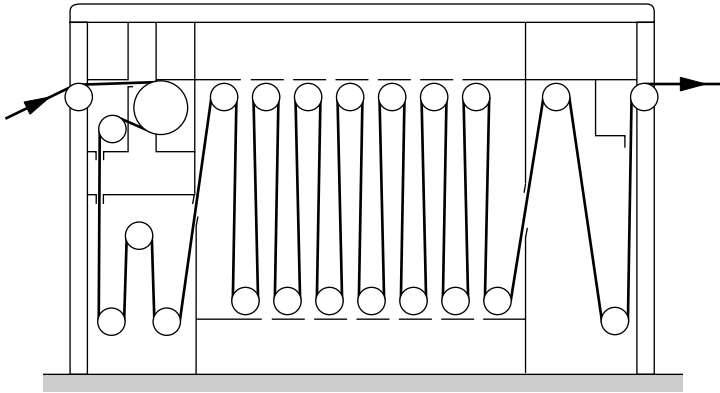
The efficiency with which these processes of fixation and washing are carried out is vitally important, to both the quality and the cost of the prints. The proportion of faults in the final product that are introduced at this stage can be disastrously high. The objective of this chapter is to direct attention to the details of the processes and the understanding of their mechanisms.

### 8.2 PIGMENT PRINTS

When water-soluble dyes are used the necessity for fixation is obvious enough, but even the ubiquitous, simple pigment print shows poor fastness to washing if the fixation process is skimmed or omitted.

Since the pigments used contain significant amounts of dispersing agent, and since the polymeric binder is also a dispersion with its own dispersing agent, the printed deposit is readily redispersed in water after a short drying process (see section 5.2.2). Only when the printed fabric has been raised to an adequate temperature is the binder given enough energy to form a continuous film that incorporates the pigment particles and adheres satisfactorily to the fibre surfaces. At the same time, crosslinking of the binder molecules is completed if appropriate monomers or agents have been incorporated, and the required pH and temperature achieved.

It is possible to use any controllable means of raising the fabric temperature: convection in hot air, conduction on cylinders, radiation or steaming; the first of these is most commonly used. The conventional roller baker or 'curing' oven (Figure 8.1) is



**Figure 8.1** Roller baker unit (Mather and Platt)

an arrangement for carrying woven fabrics through recirculated hot air, with as many fabric transport rollers as are required to provide the exposure time and fabric speed desired. Shorter times are required at high temperatures, but the risks of discoloration or inadequate treatment are greater. Times of 3–5 min at temperatures in the range 140–160 °C have been generally preferred.

The rate of heat transfer in baking is low and times of 20–60 s are required to bring the fabric to a temperature close to that of the air. Treatment times of 2 min or less, therefore, allow little latitude, and any variation in moisture content of the entering fabric can lead to significant differences in the fixation. Thus when drying and fixation are to be carried out in a single unit, control of the conditions is critical. Such a single-stage process appears attractive, but is likely to use more energy than a two-stage process because the large volume of fresh air required for drying and not required for baking will be unnecessarily heated, unless humidity control is practised (limiting fresh air inlet).

Fabrics that cannot be handled on such machines include almost all knitted fabrics. These may be fixed in festoon-type machines or on Fleissner-type perforated drum machines, brattice conveyers or stenters.

### 8.3 STEAMERS

Printed dyes are usually fixed by steaming processes, the steam providing the moisture and rapid heating that brings about the transfer of dye molecules from the thickener film to the fibre within a reasonable time.

Historically, the process of developing printed mordants was known as ‘ageing’ and took a long time, as the term implies. Printed fabric was draped over poles and left in a

room with a warm and humid atmosphere for some days, allowing the processes of diffusion and chemical reaction to occur. The term has been retained in use for steaming treatments, especially for short processes and machines; it has given rise to the descriptive, and euphonious, terms 'rapid ager' and 'flash ageing'. Some authors have attempted to distinguish between steaming and ageing (with steam). This can lead to confusion, so the two terms can be used interchangeably.

The time and conditions for fixation in steam vary with the properties of the dyes and fibres used, ranging from 10 s to 60 min in steam at 200 to 100 °C. Technical and economic factors have encouraged the use of higher temperatures and shorter times, and the change from batchwise to continuous processes. A constant feature in the design of all printing steamers, as distinct from steamers for other textile processes, is the need to prevent the marking-off of printed colour on to pale-coloured areas.

### 8.3.1 Batch steamers

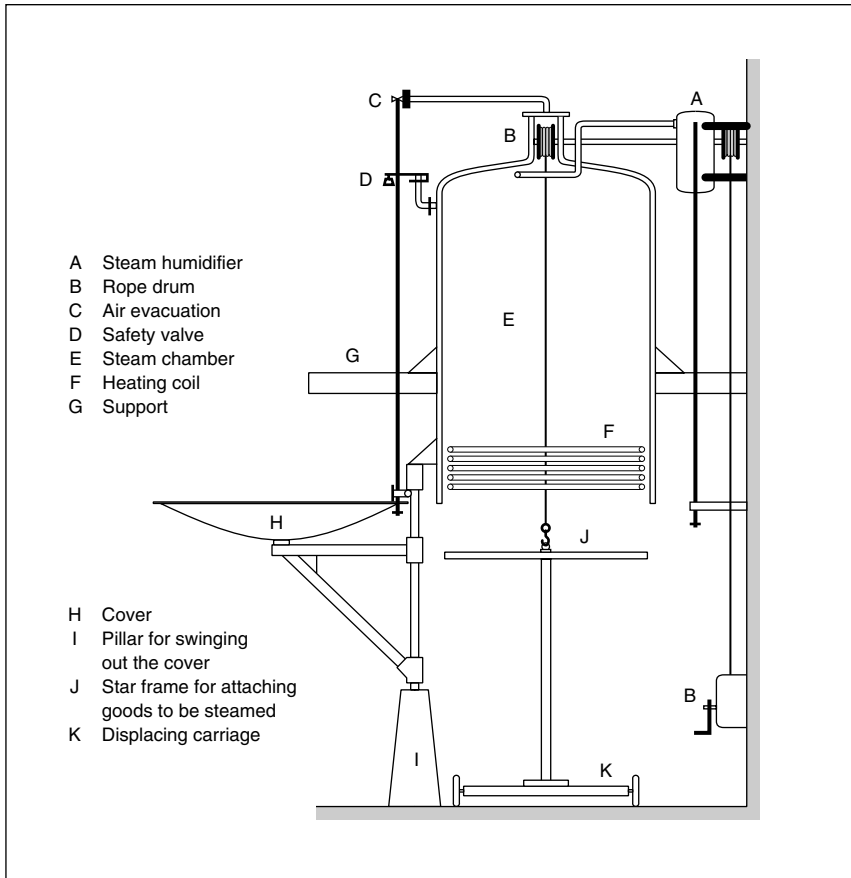
For expensive fabrics and small quantities, there are obvious advantages in using low-capacity steamers that can be quickly raised to their working temperature and that produce no creasing, stretching or other damage to the fabric. Batch steamers also show advantages when colour yields are improved by steaming at above-atmospheric pressure or for extended times, as in the case of deep colours on polyester fabrics.

A successful design for such a steamer is shown in Figure 8.2; it is known as a star or bell steamer. Up to 500 m of fabric is attached by hand, along one selvedge, to the hooks on a star-shaped carrier frame, to form a spirally wound load with a space of about 1 cm between the fabric 'layers'. An interleaved back-grey is used to eliminate all risk of marking-off, as the weight of the fabric and the uniformity of winding are unlikely to be adequate to prevent adjacent layers from touching.

The steam chamber is a cylindrical pressure vessel, mounted vertically and closed at the top (hence likened to a bell) with a door that can be swung into position at its base. It is elevated because steam is lighter than air, so that with this arrangement the bell can remain filled with steam and either the star frame can be raised into the steam, or the bell lowered on to the star frame. Less air is taken in with the fabric, and the air is more easily displaced by steam, than in any other possible arrangement.

The steam supply should be air-free and, ideally, dry but saturated. If there is significant superheat in the steam, a humidifier is used to increase its relative humidity. Wet steam is undesirable because splashes and drops of water inevitably cause local bleeding of dye or auxiliary chemicals.

The older-style cottage steamers were often larger vessels into which the printed fabric on a carrier was wheeled horizontally. Substantial flow of steam is required to displace air from such a steamer.



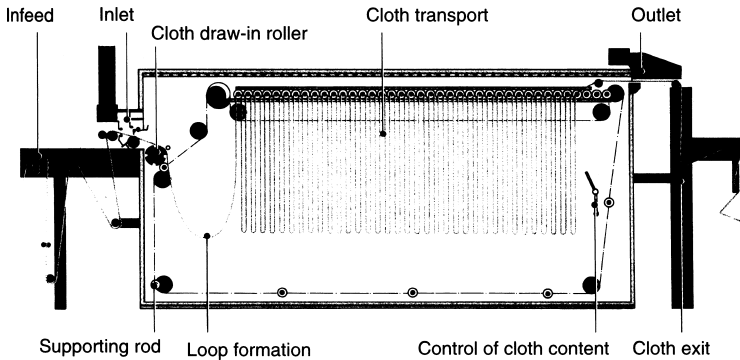
**Figure 8.2** Section through a star steamer (Kerag); the loaded star is raised into the steam chamber

Times of at least 10 min are usually allowed for fixation in batch steamers in order to ensure optimum fixation and therefore keep the staining hazards in washing-off at a minimum. Saturated steam at 1.5–3 atmospheres pressure gives good colour yields on triacetate, acrylic and polyester fibre fabrics.

### 8.3.2 Continuous steamers

A logical development of the ageing of prints while looped on rods led to the continuous transport of printed fabric in festoon steamers (Figure 8.3). Long loops are formed on rods, touching only the unprinted face, which are moved slowly along a

track near the top of a large steam chamber, constructed in brick or steel. The rods may be slowly rotated to avoid bar marks due to non-uniform accessibility to steam. With loops (festoons) of up to 5 m in length, long steaming times or high throughput velocities can be achieved without the tension and mark-off problems associated with top and bottom carrying rollers. Several ingenious mechanisms for the formation of festoons of equal length are available. At the end of the steaming period, the fabric is withdrawn at the same high speed as at the entry point. A fabric content of 800 m allows an overall throughput speed of  $80 \text{ m min}^{-1}$  with a 10 min steaming time. Capacity can be doubled by introducing two layers of fabric, with an intermediate back-grey, if the printed area is not large. The larger the steamer dimensions and the more densely it is packed with fabric, the more difficult it will be to maintain uniform steaming conditions.



**Figure 8.3** Festoon steamer (Stork)

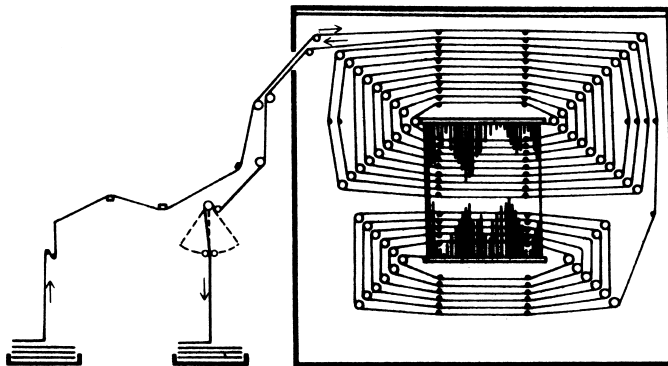
It is now considered essential to have fan-assisted circulation of steam. In older designs a flow of steam through a water tank at the base, which reduces the superheat of injected steam, to exhaust ducts in the heated roof was used to help to maintain uniformity and provided a valuable cooling effect.

In most early festoon steamers, the fabric entry and exit were through slots in the roof, provided with heated roller seals. The seals could never be perfect and escaping steam, absorbed by the print, increased the mark-off from the printed surface to the sealing roller. A doctor blade was therefore required to clean the roller surface, before it again contacted the fabric. In modern equipment the fabric entry and exit ports are usually positioned in or near the base of the steam chamber, which reduces the sealing problem significantly (as steam is lighter than air).

Popular steamers made by Stork or Babcock have steam circulation arrangements whereby steam is extracted by fans from the base of the steamer, passed through heatable radiators, sprayed with water as needed, and forced through ducts to the top of the steamer, whence it passes down the folds to the bottom. In this way festoon steamers are increasingly being produced as universal steamers, so that any temperature between 100 and 200 °C may be employed. Since many knitted fabrics can be satisfactorily handled in festoon steamers, provided the loops are not too long, the term 'universal steamer' can in fact be justified.

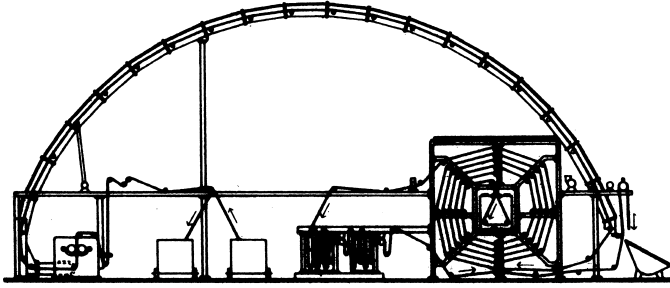
Where the steaming time required is short (up to 2 min), more compact machines with fabric-carrying rollers have been used. The term 'Mather and Platt Roller Ager' was often applied to such steamers, in which the fabric path resembled that in a roller curing oven. With the increasingly important screen prints, which usually have more surface colour than engraved-roller prints, marking-off via the rollers became more probable. The Krostewitz steamer overcame this difficulty by adopting a spiral movement of fabric, using rollers that contacted only the back face of the print (Figure 8.4). At the centre of the spiral it is, of course, necessary to withdraw the fabric by rotating it into a normal plane so that it can be taken through a slot in the side wall. This is achieved by passage around a stationary sword bar (rod) at an angle of 45° to the fabric path. A double rotation of plane and a second, outward-moving, spiral allows fabric exit through the entry slot as in Figure 8.4.

Steamers of this type, with a fabric content of 60 m, are used to give 30 s steaming at speeds of 120 m min<sup>-1</sup>, but are suitable only for stable, woven fabrics. Some of the carrying rollers must be driven, to prevent the build-up of high fabric tensions.



**Figure 8.4** Double-spiral steamer (Krostewitz)

For steaming times of about 30 s, again without touching the print face until fixation is complete, an alternative fabric transport system has been used, where a compact arrangement is not essential. This is the rainbow or arch steamer (Figure 8.5).



**Figure 8.5** Arch steamer of 40 m capacity with prepadding and afterwashing facilities

An important application of either type of such flash agers has been in pad–steam (sometimes called two-phase) processes. Vat prints on cotton, for example, are efficiently fixed by application of alkali and reducing agent solution to the printed and dried fabric immediately before steaming. A thickener that gels on contact with alkali is required, and the time of contact between print and solution must be limited to avoid bleeding. The application of a minimum add-on of solution (about 30% on mass of fibre) using one of the ‘MA techniques’ can give higher visual colour yields than obtained by conventional padding [1]. In the case of prints obtained with reactive dyes, the advantage can be even greater [2].

For short steaming times at low running speeds, the simplest possible arrangement is a chimney or tower steamer, mounted above the pad mangle.

### 8.3.3 Mechanisms of fixation processes

Fox, in a stimulating review of dye-fixation processes, has pointed out that when buying and running process machines we must not forget that the fundamental requirement is the efficiency of the molecular processes [3]. This is a necessary reminder when considering the mechanism of steaming processes, where we find easily overlooked, but significant, molecular phenomena.

It is desirable, in the first place, to understand the properties of steam itself.

### 8.3.4 Steam: terms and properties

Water vapour at 100 °C and standard atmospheric pressure is known as saturated steam, and as dry saturated steam if it contains no droplets of liquid water. Steam at 100 °C is very rarely found in a printworks, however, and the differences are significant.

Boilers are designed to provide steam at pressures substantially above atmospheric pressure. This allows the use of smaller-diameter pipes to convey the substantial weights of water vapour from the boiler to the steamer and other steam-using machines.

Saturated steam at 35 kPa above atmospheric pressure (5 lbf in<sup>-2</sup> gauge pressure) occupies three times the volume of the same mass of steam at 350 kPa (50 lbf in<sup>-2</sup>). At pressures above atmospheric, water boils at a temperature above 100 °C, more heat is required to evaporate a given mass of water and the steam produced has a high temperature. The temperature of saturated steam at 350 kPa above atmospheric pressure is 148 °C. Any cooling would produce condensation, and this is why steam at a certain pressure, and a temperature corresponding to the boiling point of water at that pressure, is known as saturated steam. Table 8.1 shows the temperatures at which water boils, and hence at which steam is produced, for six pressures.

Saturated steam is often deliberately superheated in the boiler house, giving a gas which does not condense until it has given up its superheat. This ensures that steam pipes do not carry a significant volume of troublesome water. Superheat is also introduced when saturated steam is allowed to expand rapidly as it passes through a valve into a chamber at lower pressure. For example, steam at 700 kPa (100 lbf in<sup>-2</sup>) and 170 °C when allowed to expand at 70 kPa (10 lbf in<sup>-2</sup>) falls to 148 °C, but this is

**Table 8.1** Temperatures of saturated steam

Pressure		
Absolute /kPa	Gauge /lbf in <sup>-2</sup>	Temp. /°C
136	5	108
170	10	115
239	20	126
308	30	134
446	50	148
791	100	170



33 degC above the temperature of saturated steam at 70 kPa. The steam therefore has 33 degC of superheat.

If saturated steam is wet, carrying droplets of condensed water along in its flow, a reduction in pressure may provide enough superheat to re-evaporate the water. A water separator, containing baffle plates, will also help by removing the larger droplets.

If the steam in use contains undesirable superheat, its temperature can be reduced by bubbling it through water or injecting water as small droplets. Printers use superheated steam in high-temperature (HT) steamers. These always operate at atmospheric pressure, so that the steam is adequately described by its temperature, which is approximately the superheat plus 100 degC. The concept of relative humidity (RH) has also been applied, and has the advantage that the equilibrium moisture content of fibres can be correlated with the humidity of their surrounding atmosphere over a wide range of water vapour to air ratios and temperatures. The definition of RH is given in Eqn 8.1:

$$\text{relative humidity (\%)} = \frac{\text{vapour pressure}}{\text{saturation vapour pressure}} \times 100 \quad 8.1$$

which applies equally well to 100% vapour and to mixtures with air, because the saturation vapour pressure depends only on temperature.

The vapour pressure in HT steamers is 0.1 MPa (1 atm); at 150 °C, for example, the saturation vapour pressure is 0.5 MPa (5 atm), so that the RH is 20%. The RH must never be quoted without specifying the temperature.

### 8.3.5 Dye fixation in steam

Steam can be a convenient source of both water and heat as both are transferred rapidly and uniformly over the surface areas of printed fabric entering a steam chamber. As we have seen, however, steam may be wet or dry, saturated or superheated, and the conditions of use must be chosen and maintained.

The essential requirements in all print fixation processes using steam are:

- the pick-up of enough water to swell the thickener film, but not so much as to cause the print to spread
- dispersion and solution of the dye, and production of a liquid medium through which the dye can diffuse to the fibre surface
- absorption of water by fibres such as cotton, nylon and wool, which must be swollen to allow penetration of dye
- raising the temperature to a level that accelerates the processes of diffusion, especially into the fibre.

In some cases steam can satisfy all the requirements but, as in all coloration processes, auxiliary chemicals may be introduced to assist dye solution and diffusion, or to make the process less critically dependent on the maintenance of ideal conditions. In order to illustrate the phenomena that can occur during the steam fixation of prints, one of the most critical and best-studied processes is considered here in detail.

*Vat dye prints (all-in process) on cotton*

The insoluble vat dyes must be reduced to their soluble leuco forms, to allow diffusion into the fibre. A stabilised reducing agent, sodium formaldehyde sulphoxylate (CI Reducing Agent 2), is activated when the print temperature approaches 100 °C and reduction therefore occurs inside the steamer, the highly soluble potassium carbonate providing the required alkalinity. It has been shown that the vat dyes must be selected from those with aqueous leuco potentials smaller than -920 mV. A typical paste formulation is shown in Recipe 8.1; the print would be dried rapidly, cooled and then steamed for 8–20 min in air-free steam, before rinsing, oxidising, soaping and drying.

**Recipe 8.1**

Vat dye paste	7 g
Potassium carbonate	15 g
CI Reducing Agent 2	8 g
Glycerol	5 g
Thickener	24 g
Water	41 g
	100 g

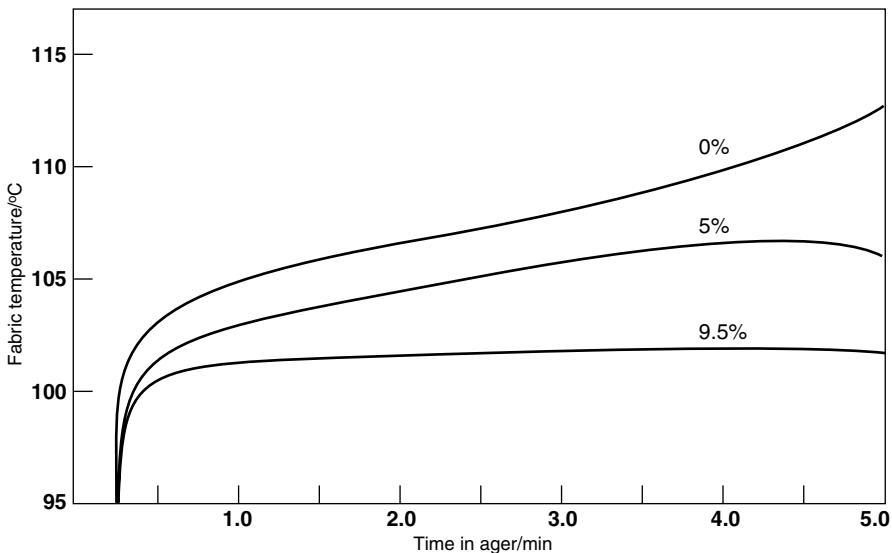
The steaming stage was known to be critical [4], especially where the cover of the design was high. Difficulty was experienced in keeping the temperature of the steam below 103 °C, and dye fixation was reduced when the temperature rose above this level. The incorporation of glycerol in the print paste, to act as a humectant, improved the fixation. Thorough and rapid drying of the print was, however, found to be essential because the stability of the reducing agent in air under damp conditions was not satisfactory [4–6]. In practice, after thorough drying a cooling procedure was necessary.

In this discussion the steam conditions can be assumed to be ideal, that is, no droplets of liquid water are present, and that it has a temperature of 100 °C, with no superheat. When the dry print enters the steam, three exothermic reactions occur.

Firstly, steam will immediately condense on the cold fabric, giving up its latent heat of  $2260 \text{ kJ kg}^{-1}$  ( $539 \text{ cal g}^{-1}$ ), and raising the fabric temperature very quickly to  $100^\circ\text{C}$ . Cotton has a specific heat of  $1.4 \text{ kJ kg}^{-1} \text{ K}^{-1}$  ( $0.32 \text{ cal g}^{-1} \text{ per degC}$ ) and, starting at  $20^\circ\text{C}$  and 7% regain, 5.5 g of steam will condense as liquid water on 100 g of fibre.

As this water condenses more heat will be liberated, partly because of the heat of wetting of cellulose and partly because of the heat of solution of potassium carbonate. For mercerised cotton at 7.5% regain, the heat evolved (when fully wetted) is  $25 \text{ kJ kg}^{-1}$  ( $6 \text{ cal g}^{-1}$ ). Starting at 2.5% regain, the heat is  $50 \text{ kJ kg}^{-1}$  ( $12 \text{ cal g}^{-1}$ ), but at 13% regain it is only  $8.5 \text{ kJ kg}^{-1}$  ( $2 \text{ cal g}^{-1}$ ). As the absorption of condensed water and the consequent generation of heat occur less rapidly than the condensation of steam, the fibre temperature rises above  $100^\circ\text{C}$  by an amount that depends on the initial regain and on the cooling effect of the steam. Fell and Postle have recorded temperatures of  $110$  and  $120^\circ\text{C}$  on cotton and wool respectively after absorption of steam at  $100^\circ\text{C}$  [7].

Fahnoe measured cotton fabric temperatures in a laboratory steamer for three initial moisture contents (Figure 8.6) [5]. The temperature rise that occurs has been turned to advantage by running dry back-greys through steamers to shorten the warming-up period. The initially cold steamer produces a lot of condensed water, which can be partly absorbed and partly evaporated by the heat generated in the cotton back-grey. The damp back-greys are then suitable for running later, with prints, when the steam temperature has to be kept down.

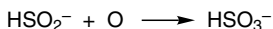


**Figure 8.6** Measured temperatures of cotton fabric of 0, 5 and 9.5% initial moisture content within an ager (steam temperature  $100^\circ\text{C}$ )

Similarly, anhydrous potassium carbonate has a heat of solution of  $27.6 \text{ kJ mol}^{-1}$  ( $6600 \text{ cal mol}^{-1}$ ), and the amount used in the print paste could provide up to  $25 \text{ kJ kg}^{-1}$  ( $6 \text{ cal g}^{-1}$ ) fibre.

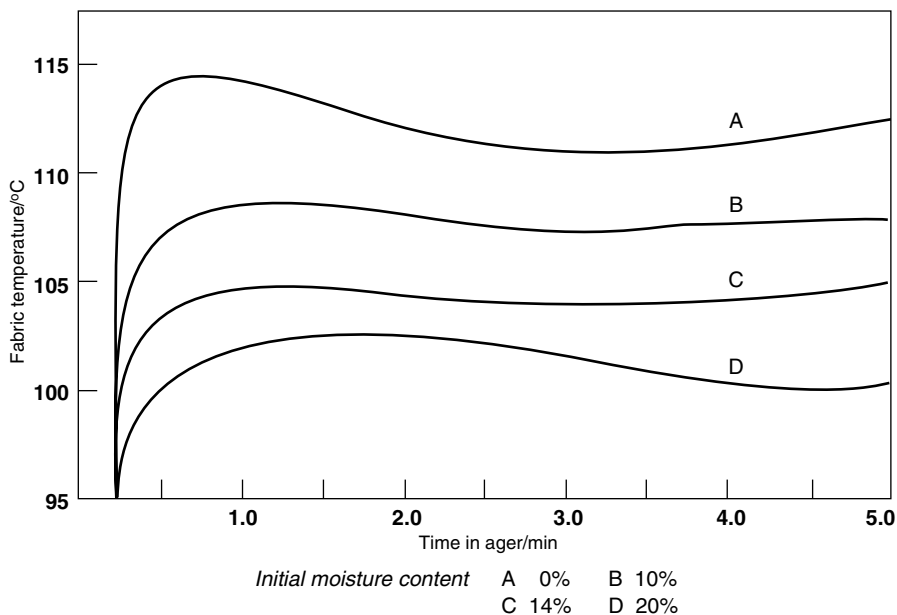
The third reaction is the oxidation of active reducing agent (sulphoxylate ion) (Scheme 8.1), which is strongly exothermic ( $+560 \text{ kJ mol}^{-1}$ ).

**Scheme 8.1**



The air content of the steam should be kept low (less than 0.3%), but the required reduction of vat dye means the equivalent oxidation of sulphoxylate will occur and the production of heat is inevitable [8]. If only 20% of the total sulphoxylate were oxidised in the early stages of the steaming process, about  $50 \text{ kJ kg}^{-1}$  ( $12 \text{ cal g}^{-1}$ ) of dry fibre would be liberated.

It is clear, therefore, that a total heat input of about  $85 \text{ kJ kg}^{-1}$  ( $20 \text{ cal g}^{-1}$ ), over and above the heat of condensation, is likely for a fabric of low moisture content and for 100% print cover. This could lead to a fabric temperature of  $140 \text{ }^\circ\text{C}$ , but actual temperatures will not be so high because the exothermic reactions occur slowly and evaporation from the print and cooling by the surrounding steam also occur. Fabric temperatures of  $115 \text{ }^\circ\text{C}$  have been recorded (Figure 8.7).

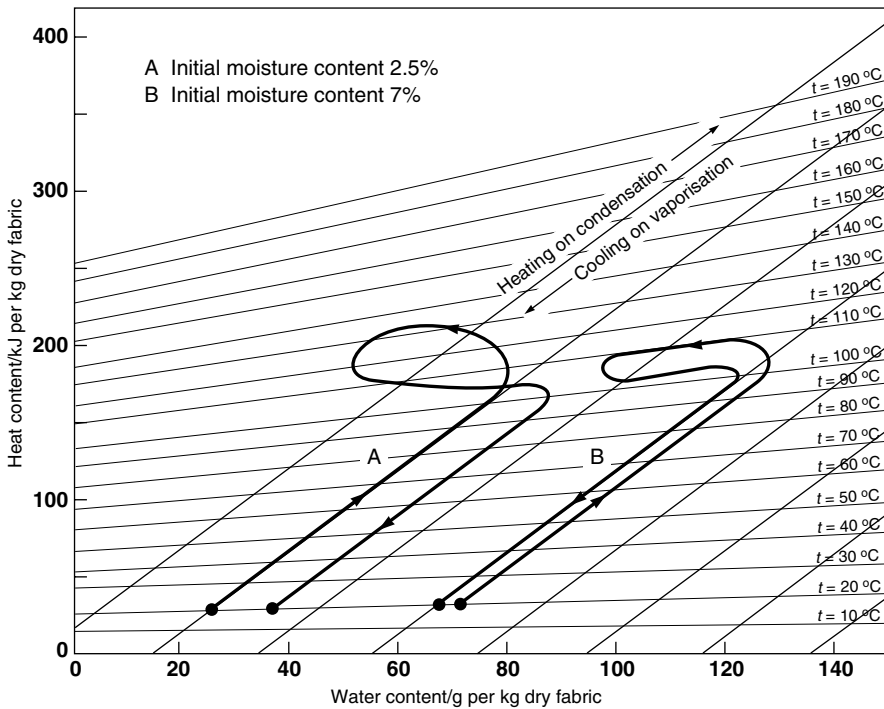


**Figure 8.7** Variation of vat print temperature within an ager

Meggy has shown that the boiling point of the print paste (a concentrated solution) is about 130 °C, so that a substantial rise above 100 °C is possible before the cooling due to evaporation balances the heat input [9].

The changes occurring in steaming can be illustrated by a heat content/moisture content diagram (Figure 8.8). This reveals the importance of the initial regain of the fabric. At only 2.5% moisture content, the maximum heat is generated and the fabric loses water by evaporation, the moisture content falling to a level that is inadequate for complete reduction and diffusion of the dye. At 7% initial moisture content, less heat is generated by wetting and the cooling due to evaporation limits the temperature rise in extent and time. Moreover, the lower temperature of fabric and surrounding steam allow the absorption of more water vapour. During the time allowed for steaming, therefore, the dye fixation is higher in the latter case.

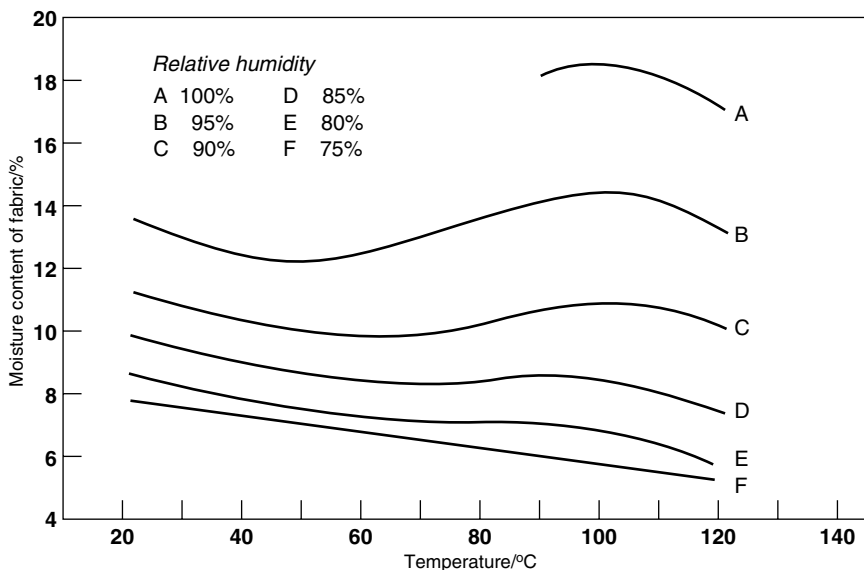
It may now be recognised that the printed and dried fabric, with a regain of perhaps 2.5%, is cooled in order to allow a rise in moisture content (from the atmosphere). One printer found that when printed fabric was taken through a slot in the floor and run over rollers close to the river below, colour yields were consistently good. Adding



**Figure 8.8** Heat content/moisture content for the steaming of vat dye prints on cotton (fabric temperatures shown on the right)

water by spraying is a possible approach, but one that is difficult to control. The rate of flow of steam through the steamer is the other important parameter. Fahnoe found that a flow rate of three steamer volumes per minute was sufficient to prevent the fabric temperature rise to 115 °C that occurred at 0.5 volumes per minute. Such a high-rate flow of steam is of course expensive and the provision of a cooling and recirculation arrangement, possibly with injection of water, reduces operating costs.

Finally, the effects of superheat must be taken into account. Steam at 104 °C and at atmospheric pressure has a relative humidity of 85%, and the equilibrium sorption of water vapour by cotton is substantially reduced at humidities below 100% (Figure 8.9). As the operating steam temperature in vat print steamers often approaches 104 °C, and therefore the moisture content of pure cotton cannot exceed 9–10%, it is not surprising that difficulty is experienced in obtaining reproducible results.



**Figure 8.9** Equilibrium sorption of water by cotton [10]

The practical answer to the problem was the addition of glycerol and the use of the deliquescent potassium carbonate, rather than the cheaper sodium carbonate. Water absorption by the print paste is therefore substantially higher than by the cotton fibre, especially under adverse steam conditions. Some of the glycerol and carbonate will have entered the fibre, thereby increasing fibre swelling. Measurements of water content during steaming showed that a typical vat print paste film absorbed about 20% of water after 2 min and 30% after 10 min, under ideal steam conditions.

The steaming of any other class of printed fabric is less complex, but may involve one or more of the interactions of physical and chemical factors discussed above. For example, nylon is very sensitive to superheat in the steam (which can arise from the heat of wetting of the fibre), lower colour yields being the consequence.

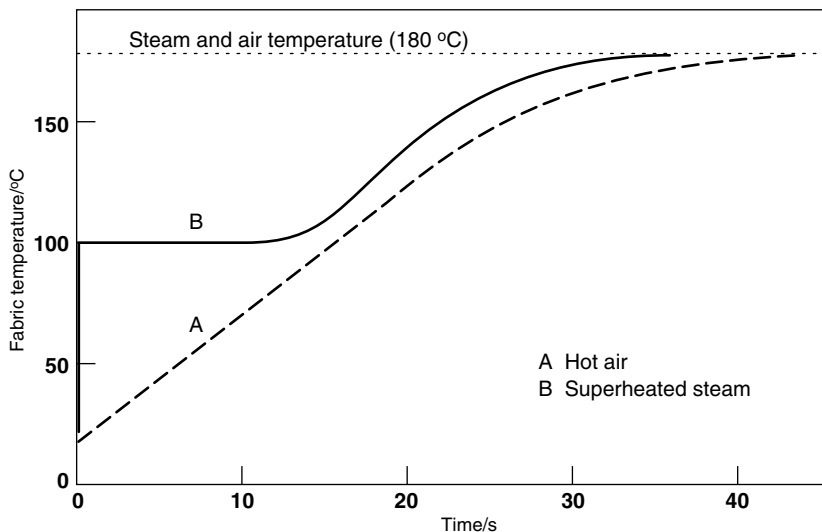
### 8.3.6 High-temperature steaming

In some circumstances the use of superheated steam shows advantages of faster heating, shorter fixation time and less colour spread; this is the case if the print has not been dried and also in the pad–steam situation, where there is usually more than sufficient water in the fabric. The term high-temperature (HT) steaming, however, is normally restricted to the treatment of dry prints in superheated steam at temperatures substantially above 100 °C and at atmospheric pressure.

Lockett, the first to advocate this approach, showed that reactive dyes on cellulosic fibres were efficiently fixed in 1 min in steam at 150 °C, provided that a suitable concentration of urea was included in the print paste [11]. The same dyes might require 5 min in steam at 100 °C or in dry air at 150 °C. Reactive dyes can be of small molecular size and low substantivity, so that diffusion occurs more readily than in other dye–fibre interactions, but a liquid medium is required for transport and for chemical reaction. For fixation in dry air, it was known that urea was required to act as the liquid medium, providing good dye solubility both in the later stages of drying and at temperatures above its melting point (132 °C).

When a printed cotton fabric at 20 °C and 7% regain enters HT steam, the steam will rapidly give up its superheat and then condense on to the fibres. The amount of condensed steam will be similar to that for saturated steam (5.5% o.w.f.), the reduction due to the temperature rise before condensation being outweighed by the strong heat absorption (240 kJ kg<sup>-1</sup>, equivalent to 58 cal g<sup>-1</sup>) occurring as the urea goes into solution. If the print has provided 20% o.w.f. urea and 12.5% water is also present, the total liquid phase is substantial. A fraction will be retained by the thickener, but the major part will enter the cotton fibres, which can absorb 30% by mass of water at 20 °C.

The moisture content will then fall, as steam at 150 °C has only 20% RH and the equilibrium moisture content of pure cotton in this atmosphere is only 1%. Lockett pointed out that urea forms a eutectic mixture with water, however, and holds some water very tenaciously. The temperature of the dye–fibre system therefore rises rapidly to 100 °C, stays at that level as long as the loss of heat by evaporation is high, and then rises towards the temperature of the steam (Figure 8.10). Reaction between dye and fibre, therefore, proceeds efficiently because the fibre is swollen and the diffusion of dye to ionised sites in the fibre can occur. Diffusion of the larger reactive dye molecules



**Figure 8.10** Rate of heating of fabric in high-temperature steam and air

into viscose rayon under these conditions is slow, however, and colour yields are often unsatisfactory. As reaction approaches completion the water content has dropped and the amount of dye–fibre bond hydrolysis may therefore be smaller than in saturated steam.

The large amount of urea required adds to the cost of the process and some decomposition occurs, with the production of ammonia and biuret-type products. Some reactive dyes give low colour yields under these conditions, perhaps as a result of reaction with ammonia and of loss of alkali. There is also a need to reduce the nitrogen level in effluents, and alternatives to urea have been sought [12]. The controlled application of water, as a foam, before steaming may provide the ideal alternative [13].

The use of HT steaming for prints on polyester and polyester blend fabrics has become extremely important because the only satisfactory alternative is the batchwise pressure-steaming method. Although continuous pressure steamers have been used (for continuous bleaching, for example), the difficulty of avoiding mark-off at the entry seal is so great that they have never successfully been employed for prints. Steaming at atmospheric pressure and 100 °C is possible if carriers are incorporated in the print paste, but colour yields are limited and only a few disperse dyes are suitable (section 5.4.3).

At a temperature of 180 °C it is possible to achieve satisfactory fixation of many disperse dyes in 1 min, as compared with 30 min pressure steaming at 120 °C or 1 min in dry air at 200 °C. With the increased availability of festoon steamers, longer times



(5–20 min) at temperatures in the range 160–180 °C have been preferred. The presence of urea improves colour yields, but also increases the fixation of thickener and causes undesirable build-up of deposits in the steaming equipment. Urea can be substantially replaced by liquid ‘fixation accelerators’, typically nonionic surface-active agents of high boiling point and low water solubility, in which disperse dyes are soluble at high temperatures.

To understand the mechanism of fixation, it is important to recognise that, for polyester/cellulosic blends, there are three steps:

- diffusion of dye through thickener film
- diffusion across a vapour gap
- diffusion into polyester fibre.

Comparison with the transfer print mechanism is clearly valid. The presence of steam probably has little effect on the passage across the gaps between fibres. It is in the diffusion through thickener films that the combined effect of condensed steam and liquid urea or other fixation accelerator will be important, both from within the thickener film to a surface where sublimation can occur and through the films surrounding polyester fibres. At a high temperature, such as 180 °C, this would be the slow step because the moisture content and thickener swelling would both be low. Lower temperatures and longer times allow the retention of more moisture and a better balance of diffusion rates in the three steps. Diffusion into the polyester fibre is faster in high-temperature steam than in dry air because of the increased molecular mobility [14].

## 8.4 MISCELLANEOUS TECHNIQUES

In some circumstances, no input of thermal energy is necessary for print fixation. A well-known instance is the printing of diazo salts on naphtholated cotton, where the chemical reaction occurs rapidly at room temperature. Reactive prints on wool and on cotton can also be fixed at room temperature, using a pad–batch process and an interlayer winding of polyethylene film to avoid colour marking-off [15]. Cold fixation is possible only where the dye molecule is small and not aggregated and the fibre in a swollen and thus accessible state.

Reactive dyes of high reactivity, especially those of the vinyl sulphone type, can be treated by a rapid fixation process immediately before entry to the washing-off range. Passage of cellulosic fabric, printed with reactive dyes but no alkali, through a bath containing suitable alkali and a high electrolyte concentration at a temperature of 100 °C can bring about fixation in 10–20 s. Bleeding and marking-off are controlled by the gelling of alginate thickener at the high pH and by the electrolyte. The chemical

costs are high and colour yields lower than in other methods, but this approach is attractive when the capital and labour costs of using a steamer are eliminated. The application of minimum quantities of alkali solution can give savings [2].

Fixation during the drying step is used with selected reactive dyes in the pad-dry process. Such an approach has rarely been attempted for printed dyes because the speed of printing is a variable determined by pattern fitting and similar considerations, which complicate the control of drying conditions. The use of microwave drying would have advantages of high wet-fibre temperature with no overheating of unprinted areas, especially if a low-solids synthetic thickener were used and the amount of dye held outside the fibre therefore minimal.

## 8.5 WASHING-OFF PROCESSES

Pigment-printing systems have been widely adopted because textile printers have been seeking simple, standard and trouble-free methods requiring minimum capital investment. For many end-uses and for discerning customers, however, the use of dyes will be essential, in which case a washing-off process (and consequently an extra drying operation) is usually required.

If the printed colours are all pale, it is possible that the dye fixation will approach the 100% level. Most print designs include at least one medium or heavy colour, however, and dye fixation levels are always lower at the higher concentrations. Even when little unfixed dye is present the removal of thickener and auxiliary chemicals is usually desirable, and sometimes essential: subsequent finishing processes, the crosslinking of cellulosic fibres or the introduction of water-repellency properties, for example, will give unsatisfactory results on printed fabrics that have not been washed.

It is useful to identify the location and the nature of the substances to be removed:

- in or on the fibre (unfixed dye and some auxiliaries)
- in the thickener phase (dye, auxiliaries, thickening agent and decomposition products).

Substances in the second category can often be swollen and removed quite quickly by vigorous washing at low temperature, but diffusion of dye from within the fibre will be much slower unless high temperatures are used.

Staining of unprinted areas by adsorption of dyes from the wash liquor is a major hazard where the concentration of unfixed dye is allowed to build up in the washing-off process. By careful selection of dyes, thickening agents and conditions of fixation, the amount of loose dye to be removed can be minimised. Regular consideration of possible improvements in dye fixation, and hence cost savings and lower effluent discharge, is recommended.

The optimum conditions for washing-off must be selected for each dye–fibre combination. For rapid removal of unfixed dye from the fibre it will be necessary to use high-temperature wash liquors; however, any dye adsorbed on to white areas will then diffuse into the fibres more rapidly than at lower temperatures. The use in the wash liquor of additives that shift the equilibrium away from adsorption may therefore be justified. Four specific situations are considered in detail below.

### 8.5.1 Disperse dyes on polyester fabrics

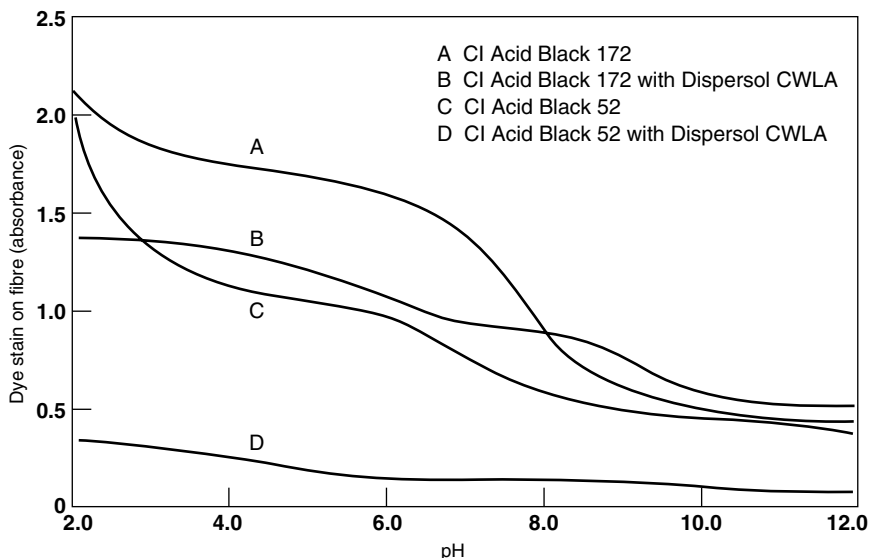
Disperse dyes have a high affinity for polyester, and therefore there is little risk of removing dye that has entered the fibres. Because of the affinity, however, any dye in the wash liquor will stain unprinted areas when the temperature approaches the glass transition value. As much unfixed dye as possible is therefore removed at low wash-liquor temperatures, with correspondingly low dye solubility. The dye is removed in the dispersed, undissolved form, which does not have significant affinity for the fibre.

It is also usual practice to apply a chemical clearing process after the low-temperature wash. A reduction clear, with sodium hydroxide, sodium dithionite and nonionic or cationic surface-active agent, at 60–65 °C will solubilise or destroy loose dye. Dye inside the fibre is not affected, because the reagents do not penetrate the fibre. Clean whites and much improved rubbing fastness of printed areas are therefore obtained, without loss of colour value. Extraction with propanone (acetone) has been used as a test of efficiency of the washing process.

### 8.5.2 Acid dyes on nylon fabrics

Nylon fibres, especially nylon 6, have very low glass transition temperatures in the wet state, and staining occurs at even moderate temperatures if the conditions are not correctly controlled. Dyes of high affinity are preferred, because high fixation levels can be achieved. Levelling acid dyes are not recommended for medium to strong hues. Complete fixation cannot be attained, however, and unfixed dye should be prevented from staining back during washing-off by:

- using slightly alkaline conditions, so that no protonation of the amino end-groups in the fibre occurs and dye affinity is reduced (Figure 8.11)
- adding a cationic agent, such as Dispersol CWLA (Zeneca), which forms a complex with the dye anion and, because of a solubilising ethylene oxide chain, also reduces the dye affinity (Figure 8.11)
- avoiding the build-up of dye in the wash liquors and restricting their temperature to 60 °C or below.



**Figure 8.11** Staining of bulked nylon after washing 1000 m at 60 °C

A typical washing sequence, on a winch, for a print on bulked nylon fabric would be:

1. Rinse in cold 1 g l<sup>-1</sup> sodium carbonate solution for 10 min
2. Treat in 1 g l<sup>-1</sup> sodium carbonate, 1.5 g l<sup>-1</sup> Dispersol CWLA, for 10 min at 35 °C
3. Treat in a fresh bath, identical to that for stage 2, but for 10 min at 60 °C
4. Rinse in cold water, until neutral.

### 8.5.3 Reactive dyes on cellulosic fabric

If suitable fixation conditions are used for reactive dye prints, all the originally reactive colorant will be either covalently bonded to the fibre or hydrolysed. Therefore there should be no danger of loose dye reacting with the fibres in the unprinted areas. If the dye has been selected for printing, it will be of low affinity and, given enough time and water, all the hydrolysed dye can be removed to leave clean white grounds. The amount of hydrolysed dye may be substantial, however, and the rate of removal depends on the diffusion rate from the fibre (as all cellulosic fibres absorb significant amounts of solution and of dye).

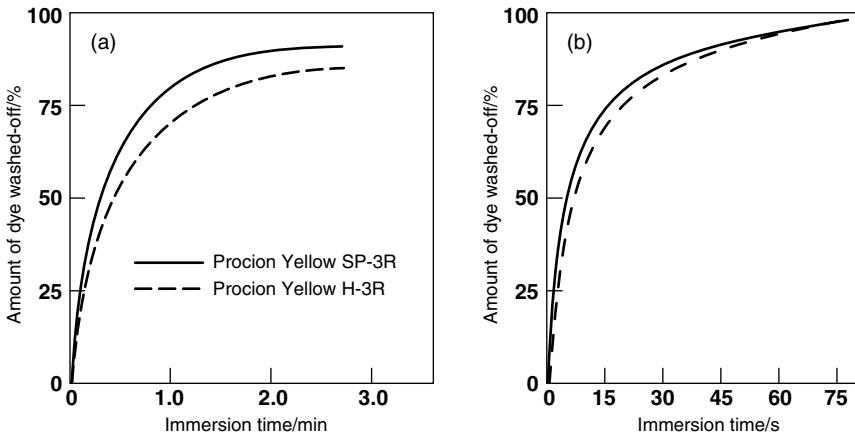
Within the ranges of reactive dyes recommended for printing there are dyes giving high fixation (90%), moderate fixation (75%) and low fixation (60%). The range of affinity also stretches from very low to only reasonably low. The amount of hydrolysed dye to be removed may therefore vary by a factor of 4, and the ease of removal can also

vary widely. The danger is that hydrolysed dye will be left in the fabric and cause marking-off complaints at the first domestic wash.

When the wash-off behaviour is studied, it is found that the factor of principal importance is the temperature of the wash liquor. At 60 °C, even the best dyes require washing for more than 4 min, but at 90 °C the same dyes can be completely cleared in 90 s and the difference due to variations in affinity is very much reduced (Figure 8.12).

As open-width washing machines are unlikely to provide 90 s hot washing (Table 8.2 [16]), when such machines are used it is necessary to maintain a close control of all operating conditions and of the results.

The use of dye concentrations above the maximum recommended level in the print paste will overload the wash liquors.



**Figure 8.12** Removal of reactive dyes (CI Reactive Orange 66 and 12) at different temperatures, (a) at 60 °C, (b) at 90 °C

**Table 8.2** Washing times in an eight-box range (10 m fabric per box)

Speed /m min <sup>-1</sup>	Time/s		
	Boxes 1 and 8	Boxes 2–7 (hot)	Total
30	40	120	160
60	20	60	80
100	12	36	48

General recommendations for washing-off are:

1. Start with a cold-water rinse that swells and removes thickener and dye in the thickener film; a high flow rate, with overflow, is advantageous
2. Maintain the wash liquor temperature at as high a level as possible
3. Use as long an immersion time as is practicable
4. Avoid the build-up of hydrolysed dye in the later units, preferably by using the counterflow principle
5. Avoid the use of water with significant hardness or electrolyte content.

The presence of residual hydrolysed dye after the washing process is readily detected by sandwiching a sample of the print between wet and dry white cotton fabric and drying with a hot iron applied to the dry side. The wicking of water through the print brings all the loose dye to the heated surface.

#### **8.5.4 Mixtures of disperse and reactive dyes on polyester/cellulose blends**

The washing-off of disperse and reactive dye mixtures printed on these blend fabrics presents the printer with a two-fold problem. In the first place, the efficiency of fixation is inevitably lower than when single-fibre fabrics are printed and therefore the amount of unfixed dye to be removed is larger. Secondly, the ideal conditions for the reactive dye–cellulose system (high washing temperature) are the worst possible for the disperse dye–polyester system. Further, reduction clearing cannot be used to remove unfixed disperse dye because the reactive dyes within the cellulosic fibres would be attacked.

A lengthy procedure must be adopted, with the use of selected surfactant mixtures. After thorough cold rinsing, at least one wash in 5 g l<sup>-1</sup> Synperonic BD (or similar nonionic–anionic mixture) at 50–60 °C is followed by use of the same agent at a higher temperature, until no further dye is removed. Because the use of conventional disperse and reactive dyes is so difficult, the advantages of using those disperse dyes that can be cleared by treatment in hot alkaline conditions are very obvious (section 5.9.2).

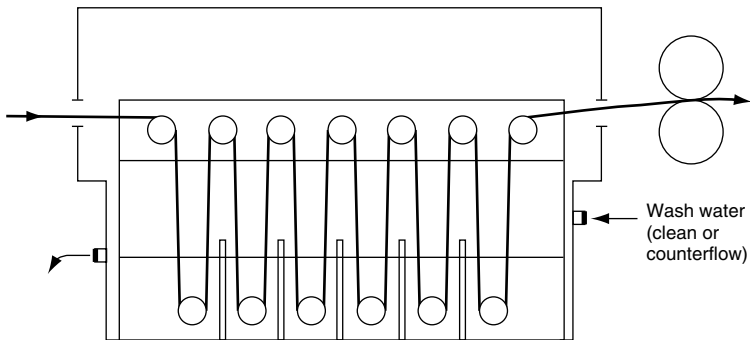
### **8.6 WASHING-OFF EQUIPMENT**

The objectives at this stage of print production are:

- wetting and swelling the thickener film
- removing thickening agent, unfixed dye and auxiliary chemicals
- provision of time at a suitable temperature for the conversion of some insoluble colorants (vat, azoic) to their true colour and fastness.

Most machinery designed for these purposes is continuous in operation, because of the economy in water, energy and labour costs, compared with batchwise operation [17]. When small fabric quantities or fabric-handling problems make continuous treatment impracticable, however, the use of a winch beck is common. The maximum use is made of the counterflow principle of wash-liquor movement, in order to keep the water consumption as low as possible.

Treatment of the fabric in the open-width form has many advantages and the traditional washing range (Figure 8.13), with 8–10 boxes, is compact and productive. The fabric is pulled through each unit (box) by its driven-roller mangle, which squeezes out contaminated liquor held in the fabric interstices. Fresh wash liquor is then picked up in the following unit, and dilutes the contaminants still in the fabric.



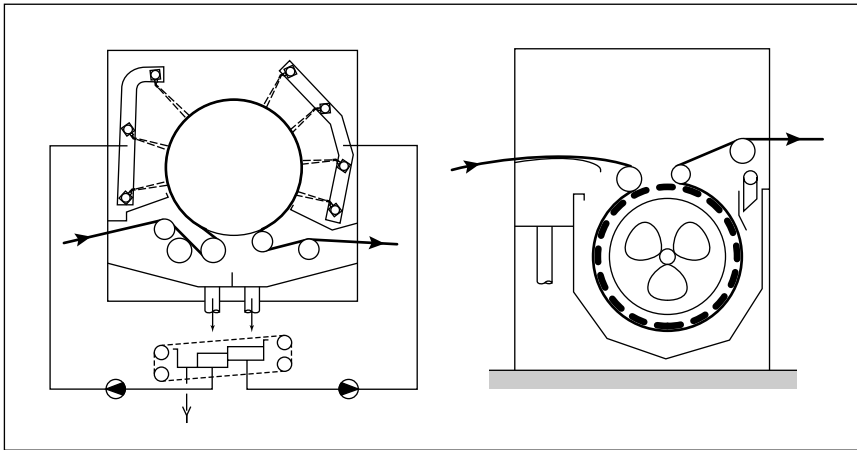
**Figure 8.13** Single unit of an open-width washing range

The removal of soluble materials from the fabric is accomplished by two mechanisms, diffusion and liquid interchange. Diffusion is slow, even when there is little or nothing to be removed from within the fibre, because there will always be water held between the fibres and a stationary boundary layer of water on the fabric surfaces, through which diffusion must occur. The thickness of the boundary layer depends on the velocity at which the wash liquor is moving, relative to the fibres. When the liquor is moved at high velocity through the fabric the boundary layer will be reduced to a minimum mean thickness, but there will still be spaces between fibres where little movement occurs. Raising the temperature accelerates removal by diffusion because the diffusion coefficient is increased and the viscosity of water is reduced, which leads to a thinner boundary layer.

Liquid interchange (the replacement of liquid held inside the fabric structure by washing liquor) can give faster removal of contaminants that have already diffused into the liquor. This happens whenever there is a pressure difference within the washing

liquor causing bulk movement of liquid. For example, when fabric passes around a bottom roller in a washing unit, a small hydraulic pressure builds up between the fabric and the roller surface, and tends to force liquid through the fabric. The larger the roller diameter and the higher its speed, the greater is the pressure (which is exactly comparable to that under a rod squeegee in rotary-screen printing). Some washing machines have been fitted with fluted rollers that produce alternating positive and negative pressures and, therefore, pulsing of water through the fabric as it passes around each roller.

The use of mangles, which reduce the volume of liquor held within the fabric by at least 50%, provides perhaps the most effective means of bringing about liquid interchange. Small pressure rollers acting on the upper carrying rollers of open-width washing units (Figure 8.13) are also used for this purpose. A different approach, used especially for knitted fabrics, draws wash liquor through the fabric as it passes around a perforated cylinder (Figure 8.14). Because the fabric is held in contact with the driven cylinder it is not extended in its passage, and can even be overfed on to the cylinder in order to allow some shrinkage to occur.



**Figure 8.14** Single spray (left) and suction drum (right) washing units for knitted fabrics (Babcock)

Parish has shown that the performance of any washing machine depends on the amount of water used and on the efficiency with which the water is used [18]. For any given set of conditions an efficiency parameter, which is characteristic of the machine and independent of the flow of water, can be determined. The performance of a single



unit  $C_1/C_0$ , i.e. the ratio of impurity concentrations in the fabric after and before the wash, is given by Eqn 8.2:

$$\frac{C_1}{C_0} = \frac{1 - K + KF}{1 - K + F} \tag{8.2}$$

where  $K$  is the efficiency parameter (equal to  $C_1/C_0$  for a wash in clean water) and  $F$  is the flow of wash water per unit mass of solution in the fabric that enters in unit time.

The use of this relationship allows the calculation of water flow required for a machine of known  $K$  value, or of the  $K$  value required when the water available is limited. The value of  $K$  can be varied by changing the temperature of the wash liquor, so that energy may be saved by using a temperature no higher than necessary.

The washing performance of a series of units is given by multiplying together the values of each separate unit. If, for example,  $C_1/C_0$  were 0.3 for each of four units, then the overall performance would be  $0.3^4 = 0.0081$ , i.e. a 99.2% removal of impurity.

The value of  $K$  is determined by time of contact, temperature, amount of interchange and properties of the impurity. The use of counterflow would be obtained, in theory, by applying water at the top of a tower with fabric running upwards from the bottom. Ideal conditions are approached in well-designed horizontal-path washers

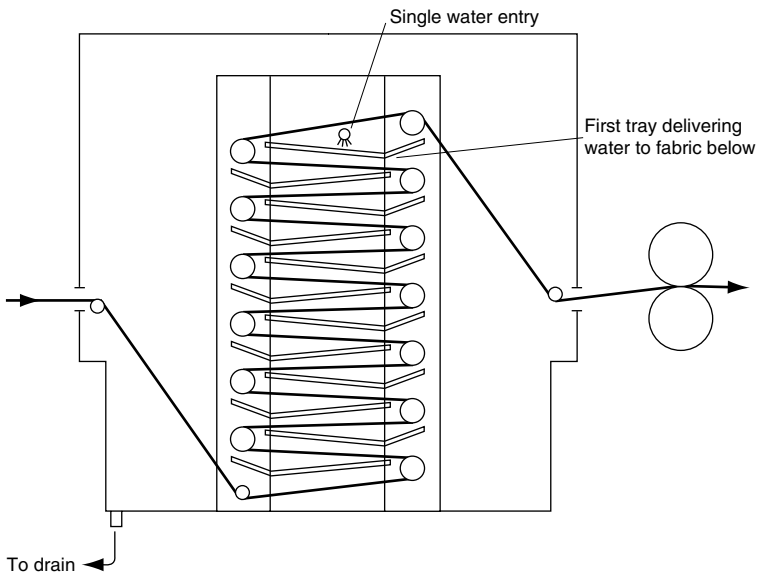


Figure 8.15 Arrangement for a horizontal-path washer

(Figure 8.15), but on wide fabric it is likely to be difficult to maintain uniform treatment across the width. Good counterflow is obtained using the traditional vertical arrangement of units by inserting partitions between bottom rollers and arranging for gravity overflow. Some modification of the open-width washer is required to allow time delays for thickener film swelling and for vat dye soaping. Simple delay scrays, brattice conveyors on to which fabric is rippled and sprayed, J-type units and rotating wash wheel units have all been used. Many printers have continued to use traditional rope-form washers, which provide low tension, mechanical action and extended times. Their efficiency can therefore be excellent, but more space is occupied and scutching is necessary to convert back to open width. Most rope washers consist of a series of units, like winch dyeing machines, with fabric taking a spiral path from entry side to exit side of each unit. An alternative arrangement, introduced by Cilander, uses an efficient counterflow system. The washer is essentially a continuous serpentine tube with water entering only at the fabric exit; it uses water more efficiently than does the conventional rope washer.

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