

CHAPTER 5

Direct print coloration

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5.1 INTRODUCTION

Printing can be considered as a controlled form of localised dyeing and, in principle, any dyes used to produce plain-coloured fabric could be used to print that fabric. The same mechanisms of dye fixation apply in both dyeing and printing. Careful selection of appropriate dyes for a particular dyeing process is desirable, however, and selection for printing is essential. The primary reason is that in printing dye solubility is more critical, even more so than for continuous dyeing processes, which admittedly compare closely with printing. Not only is the amount of water in the print paste severely limited but, at the fixation stage, the dye must be redissolved in a small volume of condensed steam. (Fixation and other aftertreatment processes are fully discussed in Chapter 8.)

There are further reasons for careful selection. The dye must diffuse through the film of thickener before adsorption on, and diffusion into, the fibre. Unless the dye diffuses rapidly, therefore, the fixation time must be extended. Consequently the lower-m.w. dyes will often be preferred, provided that their fastness levels are adequate. It is also necessary to choose dyes that can be washed off satisfactorily, without staining the ground or other printed areas in the fabric.

Not only must the dye manufacturer select the dyes that show satisfactory printing properties, but when one dye is recommended for both dyeing and printing the standardisation will be different. For example, lower electrolyte content is desirable for printing, especially where electrolyte-sensitive thickening agents are used.

In this chapter, therefore, the factors that determine the selection of colorants for particular fabrics and fixation methods are considered. The term 'colorant' is used here because it covers both dyes and pigments.

Pigments, of course, are used for the production of plain-coloured fabrics, but are of much greater importance in printing. The principal reason is that the stiffening effect of the pigment binder is less noticeable where significant areas of fabric are left

uncoloured and flexible. For this reason, a far higher proportion of low-cover designs are printed with pigments than of high-cover prints. Secondly, and perhaps equally importantly, the elimination of the washing-off stage has extra value to the printer because this is a more critical operation for prints than for plain-dyed fabric. Thirdly, rub marking, to which pigment prints are susceptible, is more objectionable on dyed fabrics than on prints, where the pattern conveniently distracts the eye.

Because pigments can be applied to all textile fibres, including glass fibre for which there is no alternative, and because pigments are used more than any other colorant type, pigment printing is here considered first.

5.2 PIGMENT PRINTING

In pigment printing, insoluble pigments, which have no affinity for the fibre, are fixed on to the textile with binding agents in the pattern required. This description is perhaps oversimplified, but it does obviously set pigments apart from dyes that are absorbed into the fibre and fixed there as a result of reactions specific to the dye.

The economic importance of pigments in printing is substantial: since around 1960 these have become the largest colorant group for textile prints. More than 50% of all textile prints are printed by this method, mainly because it is the cheapest and simplest printing method. After drying and fixation, these prints meet the requirements of the market. The washing process, carried out on classical prints to remove unfixed dye, thickening agents and auxiliaries, is not normally necessary when using the pigment printing technique.

For more than 3000 years, mineral pigments have been ground with natural binding agents (drying and boiled oils, or viscous, aqueous solutions of albumen products and vegetable gums) and 'applied' to the textile to form a pattern. Even though pigment printing is the oldest printing method, it was unimportant until the Second World War because of the poor results of the technique: dull colours, loss of textile character as a result of hardening, and poor fastness to wear and washing.

The basic products for modern pigment printing were available quite early, but the techniques required development. In the 1920s dispersions of useful organic pigments like those found in pigment printing today were available on the market; Hansa Yellow pigment pastes were an example. In the 1930s emulsion copolymerisation of olefinic substances (such as butadiene, vinyl esters, acrylonitrile and acrylic acid esters) was discovered at the former IG Farben in Leverkusen and Ludwigshafen. These were integral steps in the development of modern pigment printing. Another important step was the introduction of emulsions as printing paste thickeners. In 1937 the first pigment printing pastes based on water-in-oil (w/o) emulsions were developed in the

USA by Interchemical Corporation. In the following years these emulsions were often used on the American continent – even as late as the 1960s – for cheap staple goods with modest fastness requirements.

These water-in-oil emulsion pigment pastes were not accepted by the European market, where fastness properties were of more importance. In Europe aqueous pigment systems, for use in oil-in-water emulsions, were developed. The o/w emulsions ultimately drove out the w/o emulsion-based systems, even in the USA [1,2]. Eventually, synthetic thickeners became available.

A good-quality pigment print is characterised by:

- brilliance and high colour value relative to the pigment concentration in the paste
- minimum stiffening in the handle of the textile
- generally acceptable fastness properties.

The currently available ISO-approved methods for fastness testing and evaluation of prints do not take into account the mechanical effect on pigmented binder films during washing, and do not adequately reproduce the mechanical action of washing in a household machine. In practice, additional tests have proved successful in judging fastness properties, tests of resistance to scrubbing under defined conditions being particularly important.

Successful pigment printing systems are based upon three equally important components:

- pigment dispersions
- binders and crosslinking agents
- thickeners and auxiliary agents giving the required rheology.

5.2.1 Pigment dispersions

Most of the pigments used in textile printing are synthetic organic materials, except for carbon black, titanium dioxide of the rutile and anatase types (for white pigments), copper and aluminium alloys (for metallic bronze pigments), and sometimes iron oxide (for browns) and titanium dioxide coated glimmer (for pearl lustre pigments). When choosing synthetic pigments, the price, the fastness properties, the brilliance and the colouring power of the many products available are all taken into consideration.

Among the organic pigments in use, the following are important:

- azo pigments (yellows, oranges, reds)
- naphthalene, perylenetetracarboxylic acid, anthraquinone, dioxazine and quinacridone pigments (very fast and brilliant oranges, reds and violets)
- halogenated copper phthalocyanine derivatives (blues and greens).

Examples include:

- CI Pigment Yellow 81 (disazo, arylamide), bright greenish yellow
- CI Pigment Yellow 83 (disazo, arylamide), reddish yellow
- CI Pigment Orange 13 (disazo, pyrazolone), orange
- CI Pigment Red 7 (monoazo), neutral red
- CI Pigment Red 122 (quinacridone), bright bluish red
- CI Pigment Green 7 (perchlorinated copper phthalocyanine), bright green
- CI Pigment Blue 60 (anthraquinone), navy blue
- CI Pigment Violet 23 (dioxazine), bluish violet.

The chosen pigments are treated in a disintegrator or grinding mill in the presence of suitable surfactants until they have been reduced to the optimum particle size – in the region of 0.03–0.5 μm . If the pigment is not fine enough, the prints are dull and grey: a particle size of less than the wavelength of visible light, however, results in a loss of covering power and colour intensity.

With aqueous pigment pastes, the dispersion medium is of course water. The surfactants used must have an HLB value (see section 7.4) >10 ; nonionic dispersing agents based on ethylene oxide condensates with C_{12} to C_{20} alcohols are commonly used. When producing a pigment paste starting from a wet press-cake that contains about 25% pigment mixed with water, it is only possible to make about 20% pigment dispersions. Highly concentrated pigment pastes (with 35–45% pigment content) are obtained from dried press-cake; the drying conditions for this must be as mild as possible, in order to avoid formation of hard pigment agglomerates.

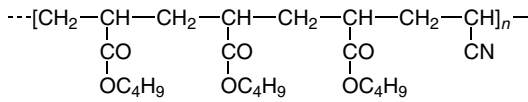
Water-free pigment pastes (for w/o emulsion pastes) were produced from aqueous pigment press-cakes by using the ‘flushing’ process, which is usually employed in paint production. The press-cake is worked with a solution of selected polyester resins in suitable hydrocarbons in a container known as a ‘flusher’, equipped with efficient kneading and stirring apparatus, until the pigment is finely dispersed and has completely passed over into the hydrophobic phase. The water in the press-cake is almost completely separated and can be removed. Binding agents, based on the condensation of maleic anhydride, saturated and unsaturated fatty acids and polyols, are added; they also act as dispersing agents.

5.2.2 Binder systems

The binder film in a pigment print is a three-dimensional structure, the third dimension of which is of rather less importance than the other two. The binder is a film-forming substance made up of long-chain macromolecules which, when applied to the textile together with the pigment, produce a three-dimensionally linked network.

The links are formed during some suitable ‘fixing’ process, which usually consists of dry heat and a change in pH value, bringing about either self-crosslinking or reaction with suitable crosslinking agents.

The degree of crosslinking should be limited, to prevent the macromolecules becoming too rigidly bonded, thus preserving some extensibility. The important criteria, which ensure that the pigment within the crosslinked binder film is fast to wear and cleaning, are elasticity, cohesion and adhesion to the substrate, resistance to hydrolysis, as little thermoplasticity as possible and absence of swelling in the presence of dry-cleaning solvents. The binders used are all addition polymers, preferably copolymers such as structure 5.1.



5.1

The technique used is that of emulsion copolymerisation, which leads to a product containing 40–45% binder dispersed in water. These ‘dispersion binders’ look like milk, are comparatively readily produced, and can be easily transported for use. Moreover, they have the advantage of high concentrations of active binding substances, together with low flammability because they contain no organic solvents. Depending upon the properties required in the binding film (softness, elasticity, plasticity, solvent stability, light and weather fastness), binders can be ‘tailor-made’ by choosing suitable base products [3,4]. Typically, unsaturated monomers are used, such as vinyl chloride, dichloroethene, acrylic acid, methacrylic acid, acrylamide, acrylonitrile, acrylic acid esters, vinyl ethers and vinyl esters, styrene and diolefins like butadiene.

The monomers are dispersed by using sufficient amounts of suitable surfactants, and polymerisation is initiated by means of free radicals originating from redox reactions such as that between potassium persulphate and sodium bisulphite. These add to the monomers, producing more radicals that also have the capacity to accumulate monomers. As a result of this reaction, macromolecules in chain form are produced. Their growth is limited either by the combination or disproportionation of two radicals, or by chain transfer to a monomer or to another macromolecule to give branching. The addition of ‘regulating’ substances can influence, if necessary, the length of the polymer chain, in order to give the required properties to the end-product or to prevent premature crosslinking. The size of dispersed polymer particles is determined for the most part by the type and amount of surfactant present during

polymerisation, and in the case of mechanically stable dispersion binders is in the region of 120–300 nm.

While the prints are being dried, a film is formed from the dispersed binder. Its formation takes place in two stages: flocculation (or coagulation) and coalescence.

During the first stage of film formation, water and surfactants are removed from the binder by absorption and evaporation. The dispersed solids coagulate to form a gel-like layer of very tightly packed 'balls', which have only poor solidity and adhesive properties. If the mechanically more stable, more redispersible, dispersion binders are used, these coagulated particles can be brought back to their original form by rubbing them with water.

During the second phase, the gel particles flow together to form a continuous film. The lowest temperature at which a film can be formed depends upon chemical constitution, but for pigment printing it is usually around 5 °C. The speed at which the film is formed depends upon the range of particle size. Poly(butyl acrylate), for instance, can form a film at 0 °C, whereas the more polar polyacrylonitrile is a very poor film-former even at high temperatures. For pigment printing, such a film would require to be softened by copolymerisation with, for example, butyl acrylate, in a ratio of butyl acrylate:acrylonitrile in the range 3:1–5:1. The higher the ratio the softer the film becomes, but at the same time it becomes more thermoplastic and develops poorer fastness to dry cleaning.

Binder systems for w/o pigment printing have been based on the reaction products of polyols with saturated and unsaturated mono- and di-carboxylic acids, combined with the hydrophobic butyl ethers of urea- or melamine-formaldehyde condensates. More recently, emulsion copolymers based on butadiene have been added to improve the dry-rubbing fastness of the prints.

Binders can also be made from high-r.m.m. polyols (mainly based on polyethers) and di- or tri-isocyanates. The polyurethanes thus obtained produce a soft, elastic binder film with excellent binding powers and fastness properties, but the printing pastes have to be water-free. These have a very short pot-life and are of interest to the textile printer only for special articles, since in general there is a preference for printing pastes that present no problems when applied and which can be stored for a long period of time. Although it has been possible to produce polyurethanes in the form of aqueous dispersion binders, by incorporating hydrophilic groups, these have not been able to compete with the dispersed binders obtained from emulsion copolymerisation because of their relatively high cost.

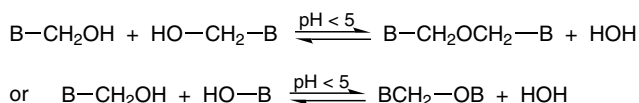
Crosslinking

Elasticity and improved adhesion of the film to the substrate is achieved by

crosslinking. The crosslinking reaction must produce covalent bonds which are insensitive to hydrolysing agents (washing liquors, body sweat, industrial atmospheres). The reaction should be activated only during fixation and not while the binder and the printing pastes are in storage.

The simplest crosslinking reaction would be the condensation of carboxyl groups with hydroxyl groups of film-forming macromolecules. The disadvantages of this process are that it needs very high temperatures and an acid medium, and thus entails the risk of the textile yellowing, and that an ester bond is formed which is relatively sensitive to hydrolysis.

Crosslinking through *N*-methylolamide groups takes place under milder conditions, also in acid media (Scheme 5.1, where B is the principal part of the binder molecule). The compounds formed are relatively fast to hydrolysis as the consequence either of a reaction of methylol groups with each other, or of a reaction of methylol groups with hydroxyl groups which are also present in the binder copolymer. The reaction equilibrium requires that water is removed from the reaction system. Hot air above 120 °C is therefore suitable for this type of reaction. Steam can have adverse effects on crosslinking and consequently on the fastness of the print. High-temperature steam is of course able to remove water, but it is nevertheless itself water vapour and the reaction cannot go completely to the right. The effect of dry hot air is better.



Scheme 5.1

This poly-*N*-methylol crosslinking of aqueous pigment print binders was first introduced in 1955. Today, it is common for monomers (such as methylolacrylamide, methylolmethacrylamide or the more stable methyl ethers of these compounds) to be polymerised with the main monomers (such as acrylic acid esters, acrylonitrile or butadiene) in such a way that the macromolecules contain about 2% *N*-methylol groups, evenly distributed along the chains. A considerably larger percentage of methylol groups would result in the chains being fixed too rigidly together after the crosslinking reaction: the extensibility, and with it the resistance of the binder film to rubbing and washing, would be impaired as a result of ‘overcrosslinking’, and the handle of the printed article would be stiffened.

Other crosslinking mechanisms have been based on epoxy and chloromethyl groups, which react with hydroxyl and amino groups under warm alkaline conditions,

or on polyethyleneimines, which react with carboxyl and hydroxyl groups. These, however, have not become important. Binders with such crosslinking groups are not sufficiently stable during storage; they react prematurely. Moreover, polyethyleneimines are toxic. All ingredients in pigment printing must be physiologically harmless at every processing stage, and since there is no final washing process this is especially vital for the consumer.

External crosslinking agents

Binders containing copolymers with *N*-methylol groups for 'internal' crosslinking may be combined with poly-*N*-methylol compounds as 'external' crosslinking agents. These are especially useful for prints on hydrophobic materials. The water-soluble methyl ethers of tetra- to hexa-methylolmelamines are preferred. They act mainly as adhesive agents between the textile and binder, but also contribute to the crosslinking at the surface of the binder film. Their reaction with the hydroxyl groups of aqueous thickeners and with nonionic dispersing agents based on polyglycol ethers also reduces the swelling of the film and improves the wet fastness of the prints. Because of their large content of very polar groups, the external crosslinking agents themselves form inextensible, rigid networks after the crosslinking reaction, and harden the handle of the printed goods a great deal more than does the binder film. For this reason only relatively small amounts, up to about 10% based on binder quantities, are used.

Since 1953 one of the oldest aqueous binder systems has used external crosslinking agents which, because of their epoxy and chloromethyl groups, react under alkaline conditions. The stability of the printing paste during storage is achieved in the products and pastes by including an excess of volatile organic acid. The crosslinking reaction begins when the acid is vaporised or neutralised with aqueous alkali [5,6].

5.2.3 Thickening systems

The colloidal polysaccharide thickening agents, such as starch, cellulose ether, alginates or locust bean gum, have been used successfully throughout the history of textile printing in printing pastes for various groups of dyes. They are not suitable for pigment printing, however, because their flow properties are unsuitable and because the films they form are brittle. The prints produced with such thickeners are dull and flat, with poor fastness and a harsh handle.

It is necessary for pigment printing pastes to have pseudoplastic (shear-thinning) flow (see section 7.7.3); they can then be transferred on to the textile material easily, but their penetration is limited. Pseudoplastic flow is usually found in heterogeneous and, physically speaking, coarsely dispersed systems. Flow occurs under shear, but when the shear is removed the pastes return to the consistency of a solid on the surface of the

textile. Unlike pastes with no yield value, they cannot penetrate deep down into the textile because of their rheology. Since they therefore remain on the fabric surface, they produce much better colour value, a sharp mark and brilliance of colour. In addition, because of the superficial coating of the fabric with printing paste, the textile yarns are not bonded to each other by the binders and crosslinking agents, and this results in a better handle to the printed goods. The hardening of the handle of the textiles after printing is mainly caused by the sticking together of the yarns and fibres, and this harshness can be broken down by using a suitable breaking machine. It is important for the fastness to wear and to washing that the same flow characteristics also hold the binder, crosslinking agent and pigments very close to one another.

Typical systems, and the ones most suitable for pigment printing, are the emulsion thickeners, of which the white spirit/water emulsions (o/w type) were of greatest practical interest. They consist of about 70% by mass of hydrocarbons in the disperse phase, 0.5–1% of nonionic emulsifiers with HLB in the region 12–15, and 29% of water in the continuous phase. The droplet size of the emulsified white spirit depends on the emulsifying agent and the efficiency of the high-speed mixer necessary to produce the emulsion. Efforts must be made to achieve a uniform droplet size (homogeneous emulsions), as this gives maximum stability and yield value. For physiological reasons the white spirit should have as little toxicity and aroma as possible, and a flash point of at least 30 °C, a boiling range of between 160 and 200 °C and a density of 0.76–0.80 g cm⁻³ are desirable.

Emulsion thickeners of the white spirit type are particularly suitable for pigment printing because all the components, except the emulsifying agents, will evaporate completely, leaving no residues. The thickener does not therefore cause any hardening of the handle of the textile and, because the evaporation enthalpy for white spirit is about 25% of that for water, drying of the printed textile is quicker; this improves the printing speed and consequently the production output. This is particularly important in drying chambers with a limited drying capacity.

On the other hand, mineral oil products are too valuable to be used just as print paste thickening agents and, for environmental reasons, the emission of organic substances into the atmosphere has met with opposition in many countries and has been prohibited by law in some. Recovering the white spirit from the exhaust gases of drying chambers, by means of cooling apparatus and batteries of charcoal filters, is too complicated and too expensive to provide a solution to this problem. The burning or catalytic combustion of evaporated white spirit, to comply with emission protection laws, also requires substantial capital expenditure. It is vitally important that the gases in the dryer should contain no more than 0.4% by volume of white spirit, to avoid explosions in the plant. White spirit emulsions for pigment printing are therefore being phased out all over the world; perhaps this may be regarded as a sign of our times.

In the 1960s, in anticipation, synthetic-polymer thickening agents were developed for pigment printing, with rheology similar to that of emulsion thickeners and extremely low solids content [7,8]. They are polyanionic compounds derived from monomers such as acrylic acid and maleic anhydride. A small degree of transverse crosslinking of the polymer molecules is built in, so that packets or bundles of chain molecules are held together. These products have very high swelling power, which is at a maximum at pH 9–10 when ionisation increases the degree of solvation in water. The original polymer with undissociated carboxylic acid groups will be in the coiled-chain form. Neutralisation leads to a straightening and separation of the polymer chains because the carboxylate ions are fully dissociated and strongly repel one another. This brings about a hundredfold expansion in size and the solvated particles then have dimensions similar to those of the white spirit droplets in emulsion thickeners. When the water-swollen particles are tightly packed they give a paste with pseudoplastic flow properties.

As coarse colloids they are subject to salting-out effects, and small additions of electrolyte reduce the viscosity, which is not the case with white spirit emulsions. Another disadvantage is that, on drying, this type of thickener leaves a residue; depending upon the requirements, 0.5–1% of solid substance remains on the textile. This residue, because of its extremely polar character, produces a hard, inflexible film which can (depending upon its chemical constitution and particularly in the case of carbonamide groups) react with crosslinking agents. This rigid film has an adverse effect on the handle of the printed goods, although it is considerably less than that of polysaccharide thickeners. The effect on the handle can be satisfactorily balanced by adding suitable softening agents, such as polydimethylsiloxane, mineral oils or synthetic wax. The neutralising agent, usually ammonia, in the synthetic thickener is removed under drying and fixing conditions; the free carboxyl groups in the polyanion then produce the acid medium which the binder and external crosslinking agents require for the crosslinking reaction. Printing pastes based on emulsion thickeners need about 0.5% potential acid, such as diammonium phosphate, in order to obtain the necessary acid medium during fixation.

Some manufacturers have combined softeners, synthetic thickeners neutralised with ammonia and dispersing agents to make application simpler and have marketed these products in paste form ('printing concentrate').

Emulsion and synthetic thickeners can be grouped under the heading 'disperse thickeners'. They are to a large extent interchangeable. If, for example, it is not possible to print economically with spirit-free pastes on the grounds of inadequate drying capacity, an emulsion thickener and a synthetic thickener can be used together to give pastes containing perhaps 25% white spirit.

The printer knows from experience that ‘short’ flow pastes (see section 7.7.3) are more sensitive to crushing effects (section 1.3.2) than are ‘long’ pastes. The less mobile the pastes are on the textile, the more easily are they picked up on the following printing rollers, in the case of multicoloured prints. This phenomenon makes itself unpleasantly noticeable, particularly in roller printing, with disperse thickeners having yield values and very steeply decreasing shear resistance; the original colour depth may be reduced by up to 70% after three or four times crushing.

In screen printing the decrease in colour depth as a result of crushing is not nearly so pronounced, but for this reason there is the risk that uneven prints will be obtained on smooth, hydrophobic textiles. In flat-bed screen printing there may, in addition, be screen frame marks. Combinations of disperse thickeners with colloidal thickeners (for example, cellulose ethers of average viscosity) reduce the crushing effect considerably. The pastes are, in the printer’s terms, softer or longer. The larger the proportion of colloidal thickener in the printing paste, the harder is the handle of the printed goods. Auxiliary substances with dilatant flow properties are more suitable and are effective as ‘flow moderators’ in comparatively low concentrations [9–12].

5.2.4 Pigment printing pastes

Although the products needed for the production of pigment printing pastes are marketed under the trade names of various manufacturers, very few differences in their basic composition are worthy of mention. The results obtained from the various systems may differ, however, especially from the viewpoint of problem-free printing properties, fastness properties, evenness, brilliance and handle of the goods.

The ratio of the amount of pigment paste to binder necessary to produce good fastness properties is influenced by the fact that even the smallest amount of pigment (perhaps 1 g pigment paste per kg paste) requires a layer of binding film at least 5 µm thick. Including a safety factor, this means a minimum of about 7% binder (of about 40% solid content) in the paste. Additional pigment needs about 1.5–2 times its own mass of binding substance. The relation shown in Recipe 5.1 results. For prints on hydrophobic materials (including polyester/cotton blends), another 0.5–1% of external crosslinking agent is added to the paste, depending on the colour depth and the desired wash fastness.

Recipe 5.1	
Pigment paste (30–40% pigment content) requires	x g
Binder (approx. 40% solid content)	80 g + 3x/2 g

The reduction thickener contains 8% binder, and other components as listed in Table 5.1. Often several components (emulsifier, printing concentrate, crosslinking agent, softener and flow moderator) are combined in one product by the product manufacturers, which means that the recipe is simpler but also that there is not the same amount of flexibility with respect to optimum printing recipes.

5.2.5 Possibilities and limitations of pigment printing

There are of course limitations to balance against the substantial advantages of pigment printing. The printer should be fully aware of these, since the use of pigments in applications where dyes are required can bring about a negative attitude to pigments, even in suitable applications [9].

Advantages

1. Pigment printing is the most economical printing process and allows maximum output of goods because of the elimination of washing-off, quick sampling and high printing speeds.
2. Properly produced pigment prints, using selected products, have an unsurpassed fastness to light and good general fastness properties.
3. Pigment printing can be applied to all substrates which are of interest to the printer, including glass fibres, PVC and imitation leather, subject to some limitations in colour depth. It is extremely well suited for colour resist effects, for example, under azoic and reactive dyes.
4. Pigment printing presents the fewest problems for the printer of all the coloration processes, with regard to labour costs, equipment, and reliability of production. Mistakes in printing can be recognised quickly.
5. From the ecological point of view, pigment printing, using pastes free from white spirit, is more acceptable than any other system, excepting only transfer printing methods.

Disadvantages

1. The fastness levels of medium- or dark-coloured prints on materials made from polyester and acrylic fibres, as well as on wool, are at best only suitable for articles that will not be subjected to a great deal of wear. Dark-coloured prints on woven and knitted goods made of synthetic fibre blends are especially susceptible to abrasive wear, as well as to reduction in colour strength by frequent use or washing. This applies particularly to men's polyester/cotton shirts.

2. The handle of the printed goods is often unduly hard because of the large amounts of external crosslinking agents, and this necessitates aftertreatment of the prints on breaking machines to produce some improvement.

Table 5.1 Reduction thickener

<i>Emulsion</i>		
Start with	x g	water
Stir in	20–30 g	diammonium phosphate 1:2 in water
	40 g	thickening agent 3–4%
	0–5 g	softener ¹
	10–25 g	urea ²
	10–25 g	emulsifier ³
Stir in and mix well	80 g	acrylic- and/or butadiene-based binder ⁴
	0–10 g	crosslinking agent ⁵
	650–700 g	white spirit ⁶
	1000 g	
<i>All-aqueous</i>		
Start with	x g	water ⁷
Stir in and mix well	0–5 g	flow moderator ⁸
	5–20 g	softener ¹
	2–3 g	defoamer ⁹
	2–5 g	emulsifier ³
Stir in and mix well	25–30 g	synthetic thickeners ¹⁰
	80 g	acrylic- and/or butadiene-based binder ⁴
	0–10 g	crosslinking agent ⁵
	1000 g	

Notes

1. Softeners and lubricating agents are hydrophobic and must be carefully dispersed.
2. Used to prevent the print paste from drying prematurely, particularly in the case of emulsion thickeners.
3. Nonionic product, based on ethylene oxide derivatives; HLB values in the region of 11–15.
4. Because of the danger of yellowing with butadiene binders, acrylate binders are recommended for white pigment prints and for furnishing prints. Binders that have limited mechanical stability should be added only after emulsification of the white spirit.
5. Methylated methylolmelamines, which are marketed in the form of aqueous solutions.
6. When storing and emulsifying white spirit the local safety regulations must be taken into consideration. Efficient mixers, with a variable speed of between 1500 and 3000 rev min⁻¹, are necessary.
7. For the all-aqueous thickener, water with minimum electrolyte content produces a higher viscosity than hard water which contains an abundance of electrolytes. The water should also be neutral.
8. Dilatant synthetic product.
9. A solid substance should not be used. Specially prepared products are necessary. In emulsion pastes antifoaming substances are not normally required. Care should be taken that the defoamer chosen does not lose its effect during storage of the pastes and printing.
10. Quantity of thickener, neutralised with ammonia. Thickeners produced by emulsion copolymerisation are considerably weaker than precipitation polymerisation products. The fastness properties obtained are also somewhat worse.

3. Pigments are sensitive to crushing during roller printing, particularly where bulky materials and deep engravings are concerned. Pigment printing needs shallow engravings, and bulky textiles should be printed on screen-printing machines.
4. When pigments are overprinted, the second paste has little effect: the paste first printed on the fabric determines the colour. 'Fall-ons' must therefore be limited to outlines.
5. The original surface of the textile material is covered by the binder film. This is occasionally aesthetically effective, but usually undesirable.
6. No pigment print is completely fast to dry cleaning. Depending upon the pigment and binder (which must be characterised as 'fast to solvents'), the prints can show rub marks and/or a loss in colour depth.

This summary makes it clear that the best fields for the application of pigment printing are:

- decorative prints on cotton and regenerated cellulose materials (pigment printing has played a dominant role here for many years)
- furnishing prints with selected pigments and binders fast to weathering (pigment-printed areas become hydrophobic)
- women's and children's clothes, nightwear of woven and knitted material (cotton, spun viscose, nylon and blends thereof)
- cotton towelling goods (leisurewear, curtains, bathrobes)
- fabrics of nylon, cotton, polyester/cotton and spun viscose for aprons and bedlinen, in pastel and medium colours only
- women's outdoor wear made of cotton, spun viscose and blends with polyester up to medium colour depths.

For blotch prints on wool, polyester and acrylic fibres, pigment printing is less satisfactory where the blotch prints are darker and the mechanical demands during wear and washing are greater. There are limitations to pigment printing which are connected with local demands, which vary from country to country, and it cannot therefore be considered as generally accepted. Its reputation appears all too often to be threatened less by its use for colouring unsuitable substrates than by the poor fastness to wear and washing which results from the use of insufficient binder or inadequate fixation conditions. In these cases the only advantage of pigment printing, namely that irrespective of its fastness it produces attractive printing effects, becomes an aggravating disadvantage. Only during use or after the first few washes does one discover whether or not the fastness properties are good, or catastrophically bad. Strict control of fastness properties relative to trade demand is therefore absolutely essential.

5.3 CELLULOSIC FIBRES

Cotton, linen, viscose and polynosic fibres all consist of the same natural polymer, but differ in the chain length and orientation of their molecules and in their morphology. Natural and regenerated cellulosic fibres differ from one another not only in their degree of polymerisation, strength and elasticity but also in their impurities, the packing density of the molecules and their regain, their degree of crystallinity, and, above all, their capacity for dye sorption. The fastness properties of a dye differ on different substrates.

Pretreatment of fibres depends on the nature of the fibre concerned. Some foreign substances do not absorb the dye (cotton wax is an example) or are dyed a different colour from the fibre (pectin) or impair the clarity of the colour and the stability of the material (lignin). In fabrics which have poor wetting properties or tend to retain sizing agents, the absorption of the dye is considerably impaired. In the descriptions that follow it has been assumed that the goods to be processed have been pretreated, and are ready for printing.

5.3.1 Direct dyes

Direct dyes are characterised by their affinity for cellulose (arising from their chemical structure) and their solubility in water (the result of the presence of sulpho groups). This means it is possible to dye them easily and with some degree of fastness, even if limited. In printing practice, the direct dye in a thickened solution is printed on to the fabric and then dried.

During subsequent steaming in saturated steam the thickened paste and the fibres swell, and the dye dissolves again and diffuses from the film of paste into the fibres. Here the dye is held fast on the fibril surfaces by van der Waals forces and hydrogen bonds. After an adequate steaming time an equilibrium is established between dye in the fibre and dye in the paste. During the final washing of the print, however, the unfixed dye together with the thickening paste are rinsed off and can stain the undyed parts of the cellulose. At the same time the equilibrium, which has been established at this stage, can be disturbed by the dye migrating from the fibre into the washing liquor. For both these reasons, textile printing using direct dyes gives good results only if a special fixing agent is employed.

A quaternary ammonium (cation-active) compound may be applied after printing and steaming to interact with the dye anions. The larger, less soluble, complexes which are formed in the fibre as a result show considerably lower mobility, and the print is noticeably 'faster'. In many cases, however, the usually very good fastness to light deteriorates noticeably after such treatment. Alternatively, dyes suitable for aftertreatment with copper may be used. These are azo direct dyes which contain one

or two hydroxyl groups and one carboxyl group in positions *ortho* to the azo groups. The result is an increase in the size of the molecule around the central copper(II) ion, and a consequent noticeable improvement in light fastness properties. It is only the need for the relatively complex and lengthy process of aftertreatment with copper in a bath of acetic acid (10–30 min at 60–70 °C) that has prevented this group, which lies somewhere between direct and mordant dyes, from becoming significant in textile printing.

5.3.2 Acid and basic dyes

Acid dyes differ from direct dyes only in that their molecules are smaller, better brilliance can be obtained and they are able to dye protein fibres from an acid solution. Acid dyes show little affinity for cellulose and hence, in the light of what has been said in the previous section, their wet fastness properties are poor. The printing method and the need to improve fastness are common to both acid and direct dyes.

Both classes are of little importance in textile printing; they are used only for the production of cheap goods. Such goods can also be printed with basic (cationic) dyes, which dye by a completely different mechanism and can be dyed on cellulose only with the help of a mordant.

Tannin, a glycoside of gallic acid, and tartar emetic (antimony potassium tartrate) together form a mordant on the cellulose in the form of an insoluble compound, which has not been defined in any detail chemically but which possesses acid groups. The dye cation can form a water-fast complex salt with these acid groups during a lengthy steaming process. Dyeings and prints produced in this way have a high degree of brilliance, but poor fastness to light. Synthetic products, such as those marketed under the names Katanol ON and Thiotan MS, may be used instead of tannin. These products are in some cases applied together with the dyes from the printing pastes, but then a longer steaming process for fixing is required. This process is no longer very important today.

5.3.3 Mordant dyes

Many of the natural dyes are mordant dyes; Alizarine red (CI Mordant Red 8), Persian berry yellow (CI Natural Yellow 13) and Logwood black (CI Natural Black 3), for example, were of enormous importance in early textile printing. Synthetic mordant dyes, sometimes described as chrome colours, have also been used in large quantities for printing cotton.

The dyes themselves have little affinity for the fibre, but can be printed with additions of hydrolysable metal salts (mordants) to give dye–metal complexes during

steaming. With some dyes the use of salts of chromium, aluminium or iron or, less frequently, nickel, cobalt or zinc gives different colours. Good fastness properties and low dye costs are characteristic.

These dyes are no longer of great importance, however, because of the problems they present under modern conditions. Their disadvantages include limited print paste stability (due to premature complexing), steaming times of up to 1 h and deterioration in fabric handle as a result of interaction between thickener and metal salt.

5.3.4 Vat and sulphur dyes

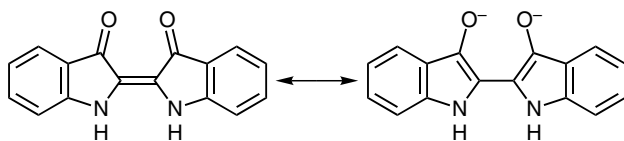
Vat and sulphur dyes are dealt with together here because their method of application is similar. They differ entirely in their chemistry, however, and in their importance in textile printing. Whereas in this field vat dyes are still widely used, the use of sulphur dyes is restricted mainly to the production of black.

The dyeing mechanism in both cases depends upon the insoluble dye being transformed into a water-soluble alkaline leuco compound under the influence of alkalis and reducing agents. The alkaline leuco compounds diffuse from the thickener into the swollen fibres, during the steaming process. Oxidation then precipitates the dye in a finely dispersed insoluble form inside the fibre, to give a print with typically good fastness properties.

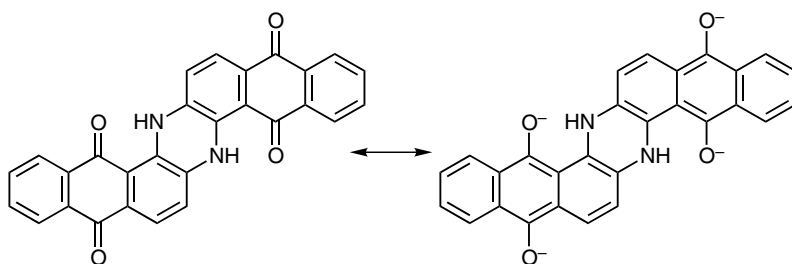
The formulae for indigo (CI Vat Blue 1) and indanthrone (CI Vat Blue 4) (5.2, 5.3) illustrate two typical vat dye structures and their reversible reduction–oxidation behaviour. The presence of at least two conjugated carbonyl groups is common to all vat dyes [13]. Sulphur dyes are, in chemical terms, complex molecules produced by the reaction of alkali sulphides with simple organic compounds, in which thiazine and thiazole rings provide the chromophore groups.

It is not normally possible to print vat dyes in the leuco form, because exposure to air during and after printing results in premature oxidation. For the same reason, the reducing agent itself must either be stable in air or be introduced at a late stage in the process. Both approaches are important, the former in the ‘all-in’ method and the latter in the two-phase or two-stage process.

All-in method: In 1905 it was discovered that sodium formaldehyde sulphonylate, $\text{CH}_2\text{OHSO}_2\text{Na}$, had the required stability at low temperatures and reducing action in steam to be used in vat print pastes. A typical paste, as formulated in Chapter 8, can be stored for long periods, printed and dried with only a small loss of reducing power. When the print is steamed in air-free steam, reduction of most vat dyes is efficiently brought about. The control of conditions for optimum fixation is discussed in Chapter 8.



5.2



5.3

Potassium carbonate has been preferred to the cheaper sodium carbonate because of its higher solubility, and the danger of a hydrated sodium carbonate crystallising out from the paste, which can cause 'doctor streaks'. The higher solubility of potassium salts of vat leuco compounds is also advantageous.

Vat dyes marketed for printing should be of small particle size and of crystal form selected to give maximum rate of reduction. Colourless reduction accelerators, such as aminoanthraquinonesulphonic acids, are often incorporated. It has been observed that the reduction of a vat dye is often catalysed by the presence of another vat dye, and the choice of thickener can also affect the reduction rate. The use of British gum thickenings has been shown to accelerate decomposition of the sulphoxylate.

Two-stage method: Indigo can be printed together with caustic soda on to cotton fabric previously padded with 25% glucose solution. Reduction occurs in steam. In this traditional method premature oxidation was avoided by applying the reducing agent and dye separately, in two stages. A two-stage method that is now employed to print the complete range of vat dyes starts with dye and thickener only. The alkali and reducing agent are subsequently applied by padding. Steaming follows immediately, so that even sodium dithionite (hydrosulphite) can be used because exposure to air is limited to a few seconds. Substantially more water is present than in the steaming of all-in prints, and this leads to higher and more reproducible fixation levels. Delays between printing and steaming also cease to be disadvantageous.

In order to prevent smudging or bleeding of the printed colour, it is necessary either to use a thickener that coagulates in the presence of alkali, or to add borates to the pad liquor. The extent of coagulation should be controlled, however, to make subsequent removal at the washing-off stage easier. Mixtures of coagulation thickeners are therefore often preferred.

The conditions of padding must also be considered. The time of contact between printed fabric and the liquor should be kept short, by nip padding or use of a two-roll horizontal pad or even of an overall engraved printing roll.

Steaming times can be as short as 20 s ('flash ageing') or longer if less severe reduction conditions are preferred. In either case the printed face is not allowed to contact carrying rollers until fixation is complete.

Solubilised vat dyes

Vat dyes provide a wide range of colours of good all-round fastness properties, but great care, or specialised equipment, is required for their successful use. The solubilised vat dyes offer a simpler method of application, at somewhat higher dye cost. The leuco forms of many vat dyes can easily be transformed into sulphuric acid esters, which can be isolated as stable powders. They are water-soluble, have affinity for cellulose and, after printing, can be oxidised under acid conditions to the insoluble parent vat dye. Exposure to light can cause premature oxidation, which must normally be avoided; this can be exploited, however, for the production of photographic effects on fabric.

Very deep colours are impossible to obtain, or of prohibitive cost. These dyes have consequently rarely been used alone, but they have found application to supplement the azoic colours. Two methods of fixation have commonly been used: the nitrite and the chlorate processes.

In the former, sodium nitrite is incorporated either in the print paste or in the naphthol preparation. After printing and drying, followed by a short steaming for optimum yield, development is obtained by a short immersion in dilute sulphuric acid.

When sodium chlorate is used as the oxidising agent, the alkalinity of the colour print paste is maintained with ammonia, and an acid generator, usually ammonium sulphocyanide, is activated by steaming. Ammonium vanadate is also needed, in small quantity, as an oxidation catalyst.

5.3.5 Reactive dyes

The full gamut of colours in the reactive class of dyes, which is one of its significant advantages, is obtained by employing a wide range of chromophores. The introduction of reactive dyes for cellulosic fibres has given the printer the possibility of using only

one type of dye and simple application conditions, in place of the complex permutations necessary at one time.

The formation of a covalent bond between dye and fibre makes it possible to use dyes which, unlike the vat and direct dyes, are of small molecular size and good solubility. These dyes can be brighter, faster-diffusing and, in the hydrolysed form, easily removed in the washing-off process [14,15].

When selecting reactive dyes for printing, the factors of importance for dyeing must be considered but, in addition, attention must be paid to print paste stability and staining of the ground during washing-off [16,17].

As with vat dyes, it is possible to use either an 'all-in' print paste or a two-stage pad-steam approach. The first method has simplicity, but the need for print paste stability limits the selection of dyes to those with a low rate of hydrolysis.

Fabric pretreatment

For optimum results, pretreatment of the cellulosic fibre is especially important when reactive dyes are used. Woven fabrics must be thoroughly desized as reaction with size and azo dye reduction, under hot alkaline conditions in presence of reducing end-groups, both lead to lower colour yield. Mercerisation of cotton, or semi-mercerisation, is recommended because few reactive dyes give full colour value on unmercerised cotton. If this is not possible, however, dyes that diffuse rapidly and show minimum differences in yield may be selected.

With regenerated cellulose also, suitable pretreatment leads to improved prints [18]. Swelling in caustic soda solution of 4–6 °Bé at room temperature, under tensionless conditions, improves the colour yield of the print. The fabric should be well rinsed, but not neutralised, to achieve maximum effect. An alternative would be to pre-pad with 100 g l⁻¹ urea and 10 g l⁻¹ soda ash.

Printing by the all-in method

A typical print paste is prepared by sprinkling the required amount of reactive dye into a stock paste (Recipe 5.2). The solubility of most reactive dyes is sufficient for this sprinkling method, followed by high-speed stirring, to give perfectly smooth prints. The dye can alternatively be predissolved, using the urea to increase the solubility, in a small volume of hot water. Sodium bicarbonate should only be added after the mixture of dye solution and thickener has cooled to room temperature.

Thickeners: Alginates are the only natural thickeners suitable for use in printing with reactive dyes. All other carbohydrates react with the dye and this results in low colour

yields or unsatisfactory fabric handle due to insolubilisation of the thickener. Sodium alginate also contains hydroxyl groups but it reacts very little, presumably because the ionised carboxyl groups on every ring of the polymer chain repel the dye anions.

Recipe 5.2

Alginate thickener (3–12%)	400–500 g
Urea	100–200 g
Sodium bicarbonate	20 g
Sodium <i>m</i> -nitrobenzenesulphonate	10 g
Water	470–270 g
	1000 g

Because of the relatively high cost and limited supply of alginates, attention has recently been paid to finding alternatives. Synthetic thickeners with anionic charges show great potential. Poly(acrylic acid) does not react at all with typical reactive dyes and colour yields are higher than with alginates. Washing-off is difficult, however, and the handle may be impaired.

Emulsions of both *o/w* and *w/o* types are also suitable and ‘half-emulsions’ have been widely used. A stock paste of the half-emulsion type (*o/w*) can be prepared by Recipe 5.3.

Alkali: Alkali is essential to produce ionisation of accessible cellulose hydroxyl groups, which can then react with the reactive dye. Sodium bicarbonate has been the preferred alkali because it is cheap and gives sufficient print paste stability with all but the most reactive dyes. During steaming or baking it loses carbon dioxide, and increased ionisation of cellulose follows. Where the stability of the dye is high enough,

Recipe 5.3

Emulsifier	10–20 g
Water	280–90 g
Urea	80–150 g
Sodium bicarbonate	20 g
Sodium <i>m</i> -nitrobenzenesulphonate	10 g
Alginate thickener (3–12%)	100–200 g
White spirit, added with high-speed stirring	500 g
	1000 g

sodium carbonate and even caustic soda may be preferred because the more stable dyes will give higher colour yields under more alkaline conditions.

For dyes of high reactivity the concentration of bicarbonate may be reduced or sodium trichloroacetate used. The latter decomposes during steaming to form sodium carbonate, and allows the use of neutral print pastes or even pastes slightly acidified with acetic acid.

The choice of alkali must therefore be made on the basis of the reactivity of the dyes to be used and the stability of print paste required. Acceptable stability, for 28 days, for example, is normally attainable.

Fixation: In textile printing it is most important that the fixation and hydrolysis proceed to completion, so that no dye in reactive form remains to stain the white ground. The choice of dyes to be used must therefore be determined by the fixation equipment available [19]. Dyes of high reactivity allow the use of rapid fixation processes, but if some of the dyes have lower reactivity it is safer to use normal steaming times and temperatures.

The second factor, which then becomes relevant, is the stability of the dye–fibre bond under hot alkaline conditions. Too long a fixation time will lead to a fall in colour yield. For most reactive dyes the stability of the dye–fibre bond is related to the reactivity of the dye, and it is possible to obtain rapid fixation under mild conditions only at the expense of stability of the print paste and of the dye–fibre bond. Higher reactivity can, however, be obtained by using reactive fluoro compounds, rather than the chloro analogues, without affecting the dye–fibre bond stability. Reactive dyes based on fluorochloropyrimidine exemplify this approach.

The actual level of fixation is important, not only for economic reasons as in dyeing, but also because unfixed hydrolysed dye must be removed very thoroughly. A routine washing-off procedure may be inadequate if the percentage of unfixed dye is higher than normal. One successful approach to obtaining significantly higher fixation levels has been to build two reactive centres into each dye molecule. This increases the probability of reaction with the fibre and leads to fixation levels of about 90%, rather than the usual 70%, and consequently reduces by two-thirds the amount of hydrolysed dye to be removed [20].

The fixation of most reactive dyes is effected by saturated steam at 100–103 °C within 10 min. The most highly reactive dyes may require only 1 min.

Faster fixation is obtained in superheated (high-temperature) steam at temperatures of 130–160 °C, 30 to 60 s only being required. Such short reaction times allow the use of smaller steamers ('flash agers'). Some of the savings in capital expenditure on plant may, however, be offset by the necessity to use higher concentrations of urea in the print paste. When cold printed fabric is entered into superheated steam, almost the

same amount of water condenses on to the fibres as with saturated steam, but loss of this water follows. Urea holds some of the water very strongly, and the eutectic mixture of urea and water provides the solvent required for the dye–fibre reaction to occur. In the absence of urea colour yields are low, unless fixation can take place during drying. For many dyes, colour yield increases up to a maximum when 150–200 g kg⁻¹ of urea are used. An alternative is to use controlled damping at the steamer entrance [21].

Because reactive dyes are typically of small molecular size and low affinity, fixation can be achieved even in hot, dry air. Urea at concentrations of 150–200 g kg⁻¹ is essential, and selection of dyes is more critical than for steaming processes, especially for regenerated cellulose. Dyes of high diffusion rate and reactivity give the best yields [19,22]. The diffusion of dye and alkali into the fibre that occurs before and during drying must materially affect the fixation that is achieved.

When hot-air bakers are used, as they are for crease-resist finishing, times of 1–3 min are required at temperatures of 180–160 °C. The time required is of course dependent on the rate of fabric heating and can vary substantially from one machine to another.

When contact heating is employed, using heated cylinders or a transfer printing drum, the fabric attains the required temperature very rapidly and a time of 1 min at 150 °C is often adequate. Some stiffening of regenerated cellulose fabrics must be expected, and discoloration of the cellulose can limit the brightness of pale colours.

Printing by two-stage methods

Reactive dyes can be printed without alkali, an alkaline solution being subsequently applied to bring about fixation [23,24]. Because the volume of water in the fabric at the fixation stage will be at least 50%, rather than the 20% or less in all-in processes, there is no necessity for high concentrations of urea. Up to 50 g kg⁻¹ may, however, be used to improve solution of dye in the print paste.

Sodium alginate shows the required thickener properties. The composition of a typical stock paste is shown in Recipe 5.4.

Recipe 5.4

Urea	0–50 g
Water	440–590 g
Sodium <i>m</i> -nitrobenzenesulphonate	10 g
Alginate thickener (3–12%)	400–500 g
	1000 g

Fixation: Application of an appropriate solution of alkali will initiate dye fixation, which is usually accelerated by raising the temperature but can be allowed to proceed more slowly, at room temperature.

Because reactive dyes have high solubility and high rates of diffusion, it is important to use alkaline solutions with a high electrolyte concentration to prevent loss of dye from the printed areas and consequent bleeding and staining. Two types of solution have been found to be suitable for padding or wet fixation processes:

- high concentrations (47 °Bé) of sodium silicate ($\text{Na}_2\text{O}:\text{SiO}_2 = 1:2.1$) and
- mixed alkali solutions, with a possible addition of salt (Recipe 5.5).

Recipe 5.5

Soda ash	185 g
Potash	185 g
Water	600 g
Caustic soda (38 °Bé)	30 g
	1000 g

The alkaline solution can be applied on a vertical two-bowl padder at high speed or, if lower speeds are used, on a horizontal two-bowl or nip pad. The steam temperature is preferably at least 130 °C, for a steaming time of 30–50 s. Washing equipment is usually coupled with the steamer for immediate removal of unfixed dye.

With dyes of high reactivity it is not necessary to steam, and an ‘alkali shock’ process can be employed for prints on cotton fabric: 10–20 s passage in open width through the alkaline liquor (as above) at 100–103 °C is followed by immediate washing. The high electrolyte concentration allows the use of temperatures up to 105 °C, without pressurisation, because of the elevation of the boiling point. The process is not suitable for viscose fabrics.

An alternative approach uses a longer fixation time at, or near, room temperature. The fabric is batched after pad application of the development liquor, at 70–80% pick-up. Fixation takes place while the batch is left standing for about 6–12 h. Wrapping the batch in plastic film protects the fabric from acid in the atmosphere and prevents drying at the edges.

Sodium silicate liquor can be padded at 40 °C to reduce its viscosity and assist penetration.

Washing-off of reactive prints

In the early years of printing with reactive dyes, difficulties were experienced at the washing-off stage. Some unsuitable dyes, of high substantivity, were used, and the fixation conditions were not always adequate. By selecting dyes of lower substantivity, and using methods appropriate to their reactivity, washing is significantly simplified but remains important.

The first step must always be a thorough rinsing with cold water. If the print is dry, the thickener film must be allowed time to swell. Alkali, electrolyte and most of the thickener should be removed in this first stage. Surface dye, which should all be hydrolysed, will also be rinsed off.

High-temperature washing, close to the boiling point, is then used to remove hydrolysed dye from inside the fibres. For any dye there will be a minimum combination of time and temperature to complete the removal by diffusion from the fibre. Longer times will be required if inadequate flow of washing liquor slows down the removal of dye from the fibres. Surface-active agents do not, in general, improve the washing effect. If hard water is used thickener removal will be more difficult, and addition of sequestering agents will be advantageous.

A cold rinse completes the washing. It is not wise, and should not be necessary, to use cationic fixing agents. Adsorption of cations on to unprinted areas increases the affinity for traces of hydrolysed dye, and makes any staining more difficult to remove.

Effect of chemical finishing

Most cellulosic fabrics printed with reactive dyes and used for shirts, dresses and similar apparel are given chemical finishes to improve their easy-care properties. The crosslink finishes are achieved with catalysts which are usually left in the fabric, even though they develop acidity. If the fabric, and garments made from such fabric, are stored for any length of time, especially in damp and warm conditions, some hydrolysis of the reactive dye–fibre bond will occur. Mild household washing of such garments is not likely to remove this hydrolysed dye completely and staining may occur.

Clearly, an alkaline wash to remove catalyst residues, as well as free formaldehyde (methanal), is highly desirable. An aftertreatment of finished fabric with cationic agents is often used as an alternative. It is also possible to choose reactive dyes that form covalent bonds with high resistance to acid and alkaline hydrolysis.

Some change in colour and in fastness to light can also occur as a result of finishing. The extent of the changes depends on the dyes, catalysts and crosslinking agents used. Ammonium salts and nitrates used as catalysts have particularly adverse effects.

5.3.6 Insoluble azo colorants (azoics)

The main characteristic of the azoic colorants is that they are formed in the fibre as a result of a chemical reaction. This reaction depends in the first place on the capacity of an aromatic amine to react with nitrous acid to form a diazo compound, and then on the reaction (coupling) of this diazo compound with a suitable organic grouping to form an azo linkage. Both reactions are among the oldest known reactions in organic chemistry, and have been well reviewed [25].

In order to produce insoluble azo colorants in the fibre, diazo compounds of selected amines (the so-called 'fast colour bases') and selected coupling components (generally known as 'naphthols') are used in textile printing. Two possibilities are available:

- the coupling component and diazo component can be applied separately (Method A), or
- the coupling component and a stabilised diazo component can be applied together (Method B).

Initially, Method A was used for applying insoluble azo colours. In 1880 the British firm Read, Holliday and Son found that a red dye was produced on some cotton fibres by impregnating with an aqueous solution of the sodium salt of 2-hydroxynaphthalene (β -naphthol), and then developing it with an aqueous solution of diazotised aromatic amine, such as 4-nitroaniline. The product of 4-nitroaniline coupling with 2-hydroxynaphthalene became known by the name of Para Red (CI Pigment Red 1); over many decades in the past millions of metres of cotton fabric were dyed and printed with Para Red. Since diazotisation must take place at low temperatures in order to avoid premature breakdown of the diazo compound, ice was added to the reaction solution to cool it down, and hence the name 'ice colours' became linked with dyes of this nature.

The first coupling component, and the most widely used, was the above-mentioned 2-hydroxynaphthalene. This was later replaced by the arylamide of 2-hydroxy-3-naphthoic acid, discovered by Laska and Zitscher in 1911. This new coupling component, generally known today as Naphtol (or Naphthol) AS, made it possible to achieve dyeings of a previously unknown brilliance and fastness [26]. The Naphtol AS series has subsequently been greatly expanded and it is now possible to reproduce many colours with almost every desired fastness property. Besides the arylamides of 2-hydroxy-3-naphthoic acid (Naphtol AS, AS-D, AS-OL, AS-E and many others), arylamides of the *o*-hydroxycarboxylic acids of anthracene (Naphtol AS-GR), carbazoles (Naphtol AS-LB) and benzocarbazoles (Naphtol AS-SR and SG), as well as diphenyloxides (Naphtol AS-BT) were used as coupling components. Using these compounds it is possible to produce greens, browns and blacks with, in some cases,

remarkable fastness. Another important group of coupling components is the acylacetylammides, derivatives of the acetoacetic acid derivative (Naphtol AS-G). The individual members of this group can be combined with red bases to form yellows with the necessary fastness properties, and they have therefore become known as Yellow Naphtols. In 1958 another coupling component, based on the phthalocyanine molecule, found its place among the Naphtol AS products (Naphtol AS-FGGR). This Naphtol produces brilliant yellowish greens, which show excellent fastness [27].

Most of the diazo components are derivatives of aniline, 2-methylaniline or 2-methoxyaniline. Other substituents in the benzene nucleus are chloro, nitro, cyano, trifluoromethyl, carbonamide, sulphone, sulphonamide, arylamine and acylamine groups. The rather complicated process of diazotising bases and the poor stability of diazo compounds have made the textile finishing industry look for diazo components with adequate coupling capacity which are nevertheless stable. These compounds should be stable during storage, should not be dangerous, should be easily soluble in water and should couple quickly with the coupling component. The first preparations of this sort were powder mixtures, which contained diazo components in the form of water-soluble salts, but not in a concentrated form for safety and storage reasons. They were produced by concentrating the diazonium salt solutions in a vacuum at low temperatures, and blending the product with simple salts.

Further development led to precipitation of the diazonium salts from aqueous solution as complex salts with halides such as zinc chloride, complex fluorides of boron or salts of aromatic sulphonic acids. These products are still known as 'Fast Colour Salts' in the trade. The salts have the special merit that they are very soluble, stable and easily weighed out.

There is no general rule as regards the properties and fastness of the possible insoluble azo colorants. If the coupling component is of the 2-hydroxy-3-naphthoic acid type, then the colour produced depends greatly on the type of diazo compound (hence the trade name for a Fast Colour Salt). The useful combinations were determined empirically. Conclusions about the relationship between properties and composition could only be drawn afterwards on the basis of a large amount of research.

Base printing: A summary of how to apply coupling and diazo components separately (Method A) is given in Recipe 5.6. Nearly all naphthols can be used for impregnation, but those of low substantivity, Naphtols AS, AS-D, AS-OL and AS-G, have become the most important in practice. Dyes of different classes, including soluble vats, reactive dyes, pigments, Phthalogen dyes and others, may be added along with Fast Colour Salts as complementary dyes in base printing. This method is very popular for Africa prints (section 6.5.1).

Recipe 5.6

1. Impregnate the fabric with an alkaline solution of the naphthol, followed by drying; this first stage is often called 'preparation'
2. Develop (couple) by printing with the thickened solution of diazo component
3. Rinse and soap to remove unfixed components.

Recipe 5.7

Naphthol AS (sprinkled and dissolved)	20 g
Soft water (90 °C)	800 ml
Caustic soda (38 °Bé)	20 ml
Dispersing agent	6 ml
	1000 ml

Recipe 5.7 illustrates preparation of a sodium naphtholate solution. The goods are impregnated on a pad mangle, at a temperature of 90–95 °C. It is advisable to dry them on a hot flue or a cylinder dryer. The naphthol-prepared goods, when stored, must be protected from light, moisture and acid fumes.

Recipe 5.8 summarises the preparation of a printing paste. Cellulose ethers, locust bean or guar products are generally used today as thickening agents.

The following sequence is recommended for washing, in open width or rope form:

1st beck	Water at 80–90 °C: 10–20 ml l ⁻¹ sodium bisulphite 38 °Bé
2nd beck	Water at 80–90 °C; 3–5 g l ⁻¹ soda ash
3rd–6th beck	Boiling water with 0.5 g l ⁻¹ washing agent and 1 g l ⁻¹ polyphosphate
7th beck	Warm water
8th beck	Cold water

If, instead of using Fast Colour Salts, the bases are diazotised by the printer, then the manufacturer's recommendations should be followed.

Naphtholate printing: By printing two or more naphtholates which produce different colours with one Fast Colour Salt, a multicolour effect can be obtained.

The process consists of printing the thickened naphtholate solution, drying, and passing the printed fabric in open width through a developing bath containing a diazo

Recipe 5.8

Fast Colour Salt	30–60 g
Acetic acid (50%)	1–20 g
Sodium acetate	10 g
Cold water	150–200 g
Dispersing agent	1 g
Thickener	400 g
	1000 g

salt. After squeezing, the fabric is allowed an air passage, and then rinsed through a bath of hot sodium bisulphite solution, rinsed and soaped hot.

By reducing the concentration of naphtholate printing colours, both light and dark colours may be printed next to each other. It is possible to expand the existing range of colours by mixing selected naphthols. Naphtholate printing has, however, never acquired the importance or popularity of base printing [28].

Rapid Fast and Rapidogen colours

Method B, the application of coupling component and stabilised diazo component in a single printing paste, has obvious advantages.

The first products of this kind were made in 1914 and they were introduced into the trade under the name of Rapid Fast colours. The practical range of colours is limited, however, and the necessary activation of coupling by acid steaming is not a popular process.

Rapidogen colours are essentially equimolar mixtures of a water-soluble diazamine compound (or triazene) and a coupling component.

Compared with the antidiazoates used in Rapid Fast colours, diazo compounds stabilised as triazenes have the advantage that they produce more brilliant prints. Furthermore, this triazene principle can be applied to nearly all bases, which leads to a considerably larger range of dyes.

When Rapidogen colours were first introduced they had to be fixed in an acid medium, either acid steam or a developing bath of hot dilute acid. These fixing processes have hardly any significance today: fixation is almost exclusively by neutral steaming, which makes it easier to combine them with other dye classes. Stabilising amines such as *o*-carboxyphenylglycine provide the required reactivity. This kind of dye is marketed under the trade names Neutrogene (FMC), Rapidogen N (BAY) and

Sinagene (Rohner). The range includes nearly all colours: yellow, golden yellow, red, bordeaux, brown, green, blue, navy blue and black; only turquoise is missing.

There are limitations to the extent that Rapidogens can be mixed. Careful note should be made of the recommendations made by the manufacturer, otherwise the colours may vary considerably because of the cross-coupling possibilities. A standard recipe for printing paste is shown in Recipe 5.9.

With some dyes it might also be advisable to add neutral chromate solutions or urea. The actual recipes should be taken from the pattern card of the manufacturers. Nowadays a starch ether is used almost exclusively as a thickener.

Recipe 5.9

Rapidogen N dye	60 g
Caustic soda (38 °Bé)	15 g
Ethanol	50 g
Water	100 g
Thickener	500 g
Water or thickener to	1000 g

Fixation is carried out in neutral steam at a temperature of 100–102 °C for 5–10 min. By changing the recipe, fixation in hot air or high-temperature steam can be used. Washing can take place on suitable apparatus at full width or in rope form. Generally no particular problems arise. Prints with excellent fastness to wetting and washing, as well as good to very good fastness to light, can be obtained [29–31].

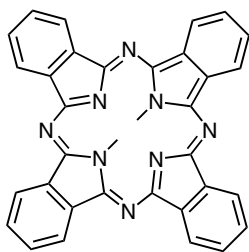
Rapidogen colours can be used in mixtures with solubilised vat dyes and also printed alongside vat, reactive, oxidation and Phthalogen dyes. Rapidogen resists under aniline black, reactive and Phthalogen dyes have also been important.

The increased use of reactive dyes has reduced the importance of these azoic compositions, except for specialist applications, and many commercial products have been withdrawn.

5.3.7 Phthalocyanine colorants

Many pigments and certain fast dyes for cotton have been developed from the important chromophore phthalocyanine (Pc, 5.4). The pigments found wide acclaim in nontextile applications because of their good fastness properties, and are important in the mass coloration and pigment printing of textile fibres. The colours obtainable – bright blue in the metal-free form, turquoise-blue when complexed with copper (5.5)

or nickel (5.6) and green when highly halogenated (5.7–5.9) – exceed in brightness those obtainable from other chromophores. Turquoise direct dyes (5.10, 5.11) are obtained by sulphonation in the benzene rings. Acid dyes (5.12) for complexing with chromium and also cationic dyes (5.13, 5.14) give turquoise-blues. Sulphur dyes (5.15–5.17) and an azoic coupling component (5.18) that gives bright greens have also been marketed. The largest number of these dyes are in the reactive dye ranges, however; 5.19 is an example.



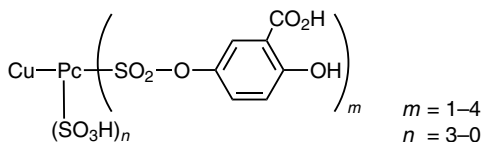
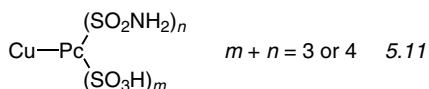
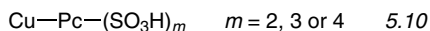
5.4

Metallised Pc
(mainly Cu—Pc and Ni—Pc)

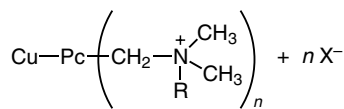
5.5 5.6

Metallised and halogenated Pc
(e.g. Cu—Pc—Cl₁₅, Cu—Pc—Br₆Cl₈, Cu—Pc—Br₁₅)

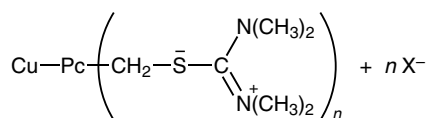
5.7 5.8 5.9



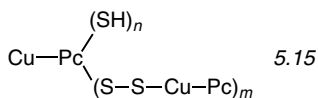
5.12



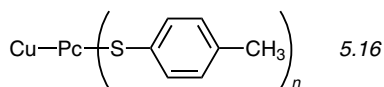
5.13



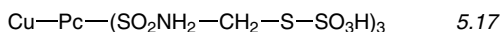
5.14

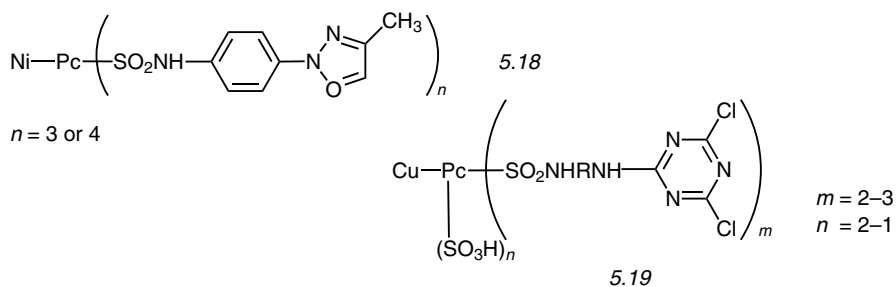


$m + n = \text{max. } 3\text{--}4$

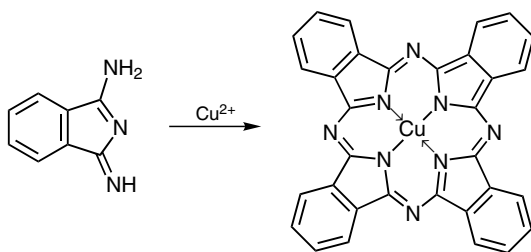


$n = 3 \text{ or } 4$





Scheme 5.2 shows the formation of an ingrain colour, inside the fibre, from a Phthalogen colorant.



Scheme 5.2

Solvents of the glycol or glycol ether type and also emulsifiers are necessary, because the dye precursor has limited solubility in water. Drying, after the application of the print, must be quick and complete, so that hydrolysis of the 1-amino-3-iminoisoindole is suppressed. Dye formation can be fully completed in hot air at temperatures above 100 °C, but it is usually more practical, when other complementary dyes are used, to achieve fixation of the phthalocyanine dye by steaming.

During the washing-off process, it is important to remove all surplus copper or nickel by treatment in an acid solution of sodium nitrite or by using sequestering agents of the ethylenediaminetetraacetic acid type. Anion-active washing agents may be used in the alkaline, boiling wash. Only in this way is the full brilliance and fastness produced.

Variations in the colour, towards green, can be made by replacing the copper completely or partially with nickel, and by making substitutions at the benzene nucleus. In practice aminoiminoisoindolenes substituted by halogens, phenol or methoxy groups have achieved a certain amount of importance because of the brilliant and very fast turquoise and green colours produced. An example of a printing paste is shown in Recipe 5.10.

Recipe 5.10

Aminoiminoisindolene (Phthalogen)	5–60 g
Dissolving medium (polyethylene glycol)	80–140 g
Copper (nickel) complex (Phthalogen K/Ni)	2–15 g
Water	x g
Ammonia (22–25%)	3–8 g
Thickener (e.g. starch ether 10%)	500 g
	1000 g

There are variations depending upon application – for example, when printing on Naphtol AS-prepared fabric, as a resist under aniline black or on polyester/cotton. Recipes are provided by the manufacturers.

In addition to the combinations described above, dye precursors from the tetraazomorphine range can produce very fast browns. From the reaction of aminoiminoisindolene with 2,5-diaminotriazole, or 4,7-dithio-4,5,6,7-tetrahydro-1-amino-3-iminoisindolene, navy blues can be obtained with copper salts and navy blues to black with nickel salts.

Phthalocyanine complex dyes

Solubility can be obtained by forming a heterocyclic macro complex of phthalocyanine, in which quaternary end-groups are linked to a hexavalent copper, nickel or cobalt central atom. Copper and nickel complex dyes (Phthalogen Brilliant Blue IF3GK and Phthalogen Turquoise IFBK) require a given amount of special solvent, mainly polyglycol ether and tertiary amino alcohol. They are fairly stable in the printing pastes and are suitable for resist printing, under or over aniline black, with the addition of zinc oxide. As they can be easily fixed in hot bisulphite baths, they are suitable for resist printing with Variamine Blue. Both are used in yarn dyeing.

The most important Phthalogen complex dye is the cobalt complex Phthalogen Blue IBN. This complex becomes soluble with addition of only 5–10 g l⁻¹ acetic acid 60%. In practice more acid is usually used, for safety reasons and because this product is more popularly used in African printing on naphtholated fabrics, which contain alkali.

The dye can be easily fixed moreover by dry heat, by steam or by reduction. When printing with complex dyes alongside vat dyes, following the two-stage printing method, the dyes are fixed in the reduction treatment. An important characteristic of Phthalogen Blue IBN is that it can be used in mixtures with Fast Colour Salts. Brown to black colours can be produced on Naphtol AS-G preparations, which is important for Africa prints, particularly as they cannot be obtained so easily by any other method [32,33].

5.4 POLYESTER FIBRES

This group of fibres, first marketed by ICI in 1952, has become the most important of all the man-made fibres, because of their desirable properties and relatively low cost.

By far the most important polyester is poly(ethylene terephthalate), but dimethylolcyclohexane esters of terephthalic acid have also been used. So-called basic-dyeable polyester has also been manufactured by incorporation of anionic monomers.

For trouble-free printing, suitable pretreatments must be employed. Water-soluble sizes and spin finishes must be removed from woven and knitted fabrics respectively. Anionic surface-active agents are preferred, as nonionic products cause subsequent difficulties if incompletely removed. The bath should be mildly alkaline and scouring should be carried out between 40 and 80 °C. The removal of paraffin-based lubricants from knitted fabrics is improved by the use of chlorinated hydrocarbon solvents, either as emulsions in the scouring liquor or as nonaqueous solvents in dry-cleaning apparatus.

Heat setting, preferably after scouring, is normally required to ensure fabric stability in subsequent processing and use. By using hot air at 190–210 °C for 20–30 s on a stenter, the fabric dimensions can be chosen for optimum appearance and properties. For fabrics made of bulked yarns a lower temperature must be used, within the region of 150–170 °C.

Bleaching should not normally be necessary, but sodium chlorite can be used where high whiteness levels are desired. Fluorescent brighteners can be applied by exhaustion processes or by the pad–thermofix approach, exactly as in the case of disperse dyes. CI Fluorescent Brighteners 179, 185, 229 and 316 give excellent results at concentrations of 0.25–1% on fibre mass.

5.4.1 Dye selection

On unmodified polyester only disperse dyes are used; cationic dyes can be used on appropriate copolymers, but light fastness is limited.

Azo, anthraquinone, coumarin and quinoline disperse dyes can be used. The commercial products are reduced to optimum particle size by grinding with suitable dispersing agents and finished in powder or granule form (20–40% pure dye) or as liquids (15–30% pure dye). The liquid forms are easier to handle, do not require redispersion and usually give higher colour yields.

Excellent wet fastness properties are obtained, provided that the fixation and aftertreatment processes are correctly carried out. The fibre is hydrophobic and has a high glass transition temperature; thus washing solutions do not penetrate the fibre and dye inside the fibre is removed only with difficulty.

Considerable deterioration of the wet and rub fastness is observed, however, if

significant quantities of nonionic products are left on the fibre surface; products of this type may have been applied as scouring agents, fixation accelerators, softeners or antistatic agents. In this case, any treatment of the goods at temperatures above 140 °C leads to migration of dye (thermal migration) to those areas of fibre surface where the nonionic agents have concentrated. Even if processing at such temperatures is avoided, hot pressing during garment manufacture and consumer use can bring about migration.

Wet fastness tests using nylon 6 as adjacent material are the most critical, and should be employed, since this fibre absorbs disperse dye more readily than does polyester.

Two other important criteria in selecting dyes are the fastness to sublimation and the behaviour during afterwashing. Since dye fixation takes place in high-temperature steam at temperatures up to 180 °C or in dry air up to 210 °C, it is necessary to reject dyes that sublime on to adjacent white fibre under these conditions. Similarly, it is necessary to avoid staining of the ground by unfixed dye during washing at high temperatures by selecting either dyes of low affinity or those that can be destroyed by a reduction clearing treatment.

5.4.2 Print paste formulation

The thickening agent must be selected for adhesion to the fibre, film elasticity and ease of removal, as well as the normal requirements. High-solids-content thickeners, like crystal gum or British gum, give optimum sharpness of outlines, but form brittle films that crack and scatter dye by 'dusting off'. The lower-solids-content thickeners, such as alginates and locust bean ethers, form elastic films and are easily washed out. The latter are most commonly used, often in mixtures with starch ethers. Half-emulsions are also used, but tend to give a less sharp mark and a risk of rubbing off [34,35].

A typical recipe is shown in Recipe 5.11. The acid donor is important because many disperse dyes are affected by hot alkaline fixation conditions. Sodium

Recipe 5.11

Disperse dye	1–200 g
Water	x g
Acid donor	5 g
Fixation accelerator or carrier	0–20 g
Oxidising agent	0–5 g
Thickener	500 g
	1000 g

dihydrogenphosphate is recommended because, unlike some organic acids, it has no corrosive effect on nickel screens and is compatible with alginate thickeners. Destruction of dye by reduction, especially in steaming under pressure, is prevented by adding an oxidising agent, either sodium chlorate or sodium nitrobenzenesulphonate. Depending on the dyes being printed, their concentrations and the fixation conditions, the use of a carrier or fixation accelerator can have a substantial effect on dye sorption.

5.4.3 Fixation

With saturated steam at 100 °C fixation is incomplete unless a carrier is used. Small dye molecules, of low sublimation fastness, diffuse faster and are more efficiently fixed than dyes of higher fastness. By adding 30–60 g kg⁻¹ of a carrier of the *o*- or *p*-phenylphenol type, and steaming for 20–40 min, acceptable fixation is obtained with selected dyes. Suitable dyes include CI Disperse Yellow 54, 93 and 184; Orange 25 and 66; Red 60, 82, 106 and 343; Violet 28; Blue 56, 60, 81 and 287; Brown 4 and 13; Black with mixtures.

Complete removal of the carrier is required if impairment of light fastness is to be avoided, and is only possible by stentering the printed fabric at temperatures above 160 °C.

A wider range of dyes can be used, and deeper colours can be obtained, by steaming under pressure. The absorption capacity (build-up) increases in proportion to the steam pressure, and corresponding temperature, up to 0.35–0.40 MPa (50–60 lbf in⁻²). The colour depth obtained at high pressures cannot be obtained by using longer times at lower pressures.

Steaming for 20–30 min at 0.25–0.30 MPa (36–44 lbf in⁻²) gives very good results, the fixation reaching 90% with selected dyes. The cost of using carriers cannot normally be justified by dye savings when pressure steamers are used.

Recommended dyes include CI Disperse Yellow 93, 126 and 184; Orange 25, 29 and 66; Red 60, 82, 106, 177 and 343; Violet 28 and 40; Blue 56, 60, 81, 154 and 287; Brown 4 and 13; Black with mixtures.

Since the development of high-temperature festoon steamers, high production speeds are compatible with steaming times of 5–20 min and this has become the most important of the fixation methods. Temperatures of 160–185 °C can be used, depending on the dyes and times of treatment chosen. Steam condenses on to the cold fabric, raising its temperature to 100 °C and swelling the thickener film. The condensed water is largely evaporated again during the exposure to superheated steam, but the thickeners are not 'burnt in' to the fabric as in dry fixation and the subsequent handle of the fabric is softer [36–38].

Dye selection must take account of the danger of sublimation on to white or pale colour areas. Dyes of poor sublimation fastness should not be used and the selection requires special tests because the sublimation of unfixed dye must be considered in addition to that from the dyed fibre.

It must also be recognised that the risk of staining the white ground depends on the circulation of the heating medium and the movement of the fabric within the steamer, as well as on the temperature and time of treatment.

High-solids-content thickeners (more than 12%) are not recommended as they are difficult to remove in the afterwashing process. Mixtures of alginates with starch ethers, in a ratio between 4:1 and 3:1, have proved successful. Ready-made mixtures of this type are marketed. Where hard water has to be used the addition of polyphosphate sequestrants improves the ease of removal of alginate-based thickeners, and may also increase their compatibility with acid donors and carriers.

Higher colour yields are obtained with medium and deep prints by adding an effective fixation accelerator, usually an ethylene oxide condensate [39].

The following are among the most suitable dyes for high-temperature steam fixation: CI Disperse Yellow 126, 184 and 198; Orange 66, 71, 73 and 80; Red 82, 106, 159 and 177; Violet 31 and 48; Blue 60, 73, 79, 154, 165 and 287; Brown 4 and 13; Black with mixtures.

The thermofixation process also has some significance, the printed fabric being passed through stenters or specially built equipment. The best results are obtained at 200–220 °C, at which temperatures the sublimation characteristics of the disperse dyes used are particularly critical. The time of treatment required may be 40–50 s, but in the absence of a carrier fixation is only in the range of 50–70%. The use of 20–30 g kg⁻¹ of fixation accelerator in the print paste considerably increases the depth of colour obtained.

Texturised polyester is not suitable for dry-heat fixation, because the high temperatures required cause loss of bulk.

Dyes of high heat fastness are required, as recommended for high-temperature steam fixation.

5.4.4 Aftertreatment

Washing is required to remove thickener and unfixed disperse dye. Thorough rinsing first in cold, then in warm water, should be followed by an alkaline reduction treatment at 40–50 °C (Recipe 5.12). Most of the unfixed dye is quickly solubilised or destroyed and, because of the low temperature, the reduction products are not absorbed on to the white polyester. Staining of the ground could occur if the temperature were suddenly raised to 80 °C. A low-temperature soaping liquor and two

Recipe 5.12

Surface-active agent	1 g l ⁻¹
Sodium hydroxide (38 °Bé)	2 ml l ⁻¹
Sodium dithionite (hydrosulphite)	1–2 g l ⁻¹

baths at 70–80 °C are therefore recommended. Finally the goods are rinsed in warm, then cold, water and dried under minimum tension.

A softener or antistatic agent may be applied in the final rinse or by padding before drying. Drying should not raise the fabric temperature above 120 °C, as higher temperatures increase the thermomigration of dye to the surface and the fastness to rubbing deteriorates.

5.5 CELLULOSE ACETATE FIBRES

5.5.1 Secondary acetate

This fibre, produced by partial hydrolysis of fully acetylated cellulose, has been in use since 1921. During pretreatment of acetate fabric it must be remembered that it is sensitive to alkaline hydrolysis, particularly at temperatures above 85 °C, with adverse effects on lustre and stability.

Water-soluble sizes are almost exclusively used, and scouring at 60 °C with anionic or nonionic detergent is normally adequate. Bleaching is rarely required, but either chlorite or an acid reduction bath with CI Fluorescent Brightener 112 or 226 respectively may be used.

A typical print paste recipe is shown in Recipe 5.13. Dye fixation is accelerated by limited amounts of urea, polyethylene glycol derivative or glycerol acetate, but larger quantities may damage the fibre.

Recipe 5.13

Disperse dye	1–150 g
Thickener (locust bean or guar)	500 g
Urea or alternative	0–50 g
Water	x g
	1000 g

Steaming for 10–40 min is carried out in festoon steamers at 100–103 °C or in a star steamer at not more than 35 kPa (5 lbf in⁻²) pressure (see section 8.3). In the latter, it is important that the steamer backcloths are clean because some dyes sublime very readily. Soaping temperatures should not exceed 40–50 °C as many dyes have limited wet fastness.

The following dyes have been used: CI Disperse Yellow 93 and 184; Orange 25, 33 and 80; Red 1, 4, 11, 50, 54 and 343; Violet 8 and 38; Blue 3, 7, 56, 81 and 154; Brown 4 and 13; Black with mixtures.

Because of the poor wet fastness of disperse dyes on this fibre, methods have been developed to apply acid, basic and vat dyes. Swelling agents such as ethanol, benzyl alcohol, urea, thiodiethylene glycol or dicyanoethylformamide must be used. Basic dyes are significant for the particularly brilliant colours that can be obtained. Recipe 5.14 is suitable for use with such dyes. The prints are steamed for 20–30 min in saturated steam at 100–103 °C, then rinsed and soaped in anionic detergent solution at 40 °C. Staining of the white ground can be prevented by careful addition of hydrosulphite.

Recipe 5.14

Basic dye	1–40 g
Thiodiethylene glycol	20–30 g
Acetic acid (30%)	20–30 g
Water	x g
Thickener	500 g
Urea	50 g
	1000 g

5.5.2 Triacetate

Triacetate shows better resistance to heat and alkali than that of secondary acetate, and can be heat-set.

A controlled surface saponification, or S-finish, may be used to raise the safe ironing temperature, provide a permanent antistatic finish and improve fastness to gas-fume fading. Conditions used may be 3.5 g l⁻¹ sodium hydroxide for 1 h at 90 °C, the extent of the saponification being monitored by dyeing samples of the treated material and of the control material with CI Direct Blue 78.

One disadvantage of this treatment is that print colour yields are lower unless pressure steaming is used for fixation.

The whiteness may be improved if necessary by treatment at 90 °C for 30 min in

1 g l⁻¹ sodium hydrosulphite, 2 ml l⁻¹ 30% ammonia and 1% CI Fluorescent Brightener 121.

The choice of dye depends on the fixation method to be used and on the fastness required. Fabric to be pleated requires dyes of high sublimation fastness. Gas-fume fading inhibitors can be added if the dye used has inadequate fastness. The following dyes have been used: CI Disperse Yellow 5, 7, 42, 50, 60, 66, 83, 85, 93 and 126; Orange 13, 53, 55, 66, 67, 106 and 127; Red 5, 11, 72, 76, 82, 90, 91, 132, 134 and 159; Violet 12, 33, 40 and 50; Blue 56, 72, 73, 82, 87, 128, 139, 154 and 284.

Steam fixation at atmospheric pressure and 100–103 °C requires 30–45 min, and maximum depth of colour is not obtained with all dyes. Addition of 5–10 g kg⁻¹ of carrier or fixation accelerator, as with secondary acetate, is essential.

Saturated steam at 120 °C and 0.25 MPa (35 lbf in⁻²) pressure for 30 min gives optimum yield, without carrier, and on S-finish fabric.

For fabric that has not been S-finished, high-temperature steaming for 5–10 min at 180–165 °C in a festoon steamer gives satisfactory results with selected dyes, provided a fixation accelerator is used.

Similar results are obtained using dry heat for 1 min at 190 °C. Navies, blues, blacks and dark browns of adequate wet fastness are difficult to achieve with disperse dyes. Metal-complex dyes may be used for these colours, provided adequate amounts of swelling agent are used, with 30 min steaming at 100–103 °C.

Washing requires care to prevent staining of the ground. When reduction clearing treatments are employed the temperature should not exceed 50 °C, since at higher temperatures the dye inside the fibre can be attacked.

5.6 ACRYLIC FIBRES

Fibres made from linear polymers consisting of at least 85% acrylonitrile units have been given the generic name 'acrylic fibres'. The commercial fibres vary in their properties because other monomers are incorporated to improve dyeability, and both dry- and wet-spinning systems are employed. Small amounts of vinyl acetate, methyl acrylate or acrylamide copolymer increase the accessibility of the fibres, and anionic sites provide affinity for cationic dyes. The similarities between the different fibres are sufficient, however, for a general treatment of the group.

Modacrylic fibres are defined as containing more than 50% acrylonitrile, but less than 85%. The comonomers principally used have been vinyl chloride and vinylidene chloride; these produce fibres that are very difficult to ignite, but which have low softening temperatures.

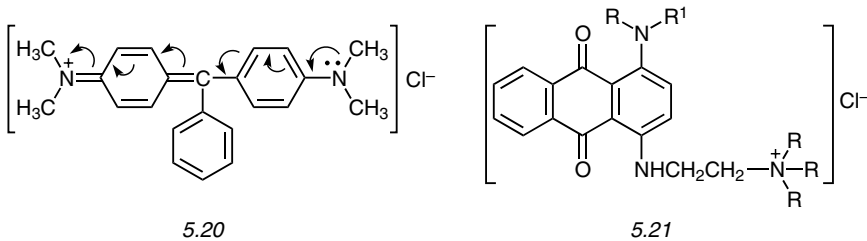
In pretreatment processes, alkaline conditions should be avoided as discoloration may occur in subsequent drying. Processes for desizing or removal of knitting lubricants

are best carried out at pH 5–6, and at temperatures below the glass transition point. Relaxation and, where necessary, bulking for about 20 min at 90–95 °C may be essential to obtain uniformly stable fabrics. To avoid setting-in creases, it is essential to cool slowly from 80 to about 50 °C, unless the fabric can be handled in open width at low tension.

5.6.1 Dyes

Selected disperse dyes may be used for pale colours, but the build-up and wash fastness attainable are limited.

Basic dyes have proved to be successful for the printing of acrylic fibres and offer brightness and good fastness to light and to washing. A wide range of colours is now available in this dye class, the chromophores being no longer restricted to the classical triphenylmethanes and oxazines. In the classical basic dyes the cationic nitrogen atom is an essential part of the colour-donating chromophore (5.20). Fluctuations in pH can therefore lead to colour changes and in some cases the dye forms a colourless carbinol base under alkaline conditions.



The newer dyes use azo, anthraquinone and phthalocyanine structures with the cationic nitrogen in a side-chain which insulates it from the conjugated double-bond system of the chromophore; compound 5.21 is an example. The colour of these dyes is therefore not so sensitive to alkali, but fixation will only occur under acidic conditions [40].

Fixation of prints of basic dyes on acrylic fibres follows the same mechanism as in dyeing processes. Adsorption on to the fibre occurs readily because of the high affinity of the dye cations for the negatively charged sites on the fibre surface, but diffusion to sites within the fibre is relatively slow. The fibre surface is usually saturated with dye, and therefore the speed of diffusion does not depend on the concentration of dye in the print paste. Dye mixtures may show 'blocking' effects if dyes of different affinity are used.

Dye solubility can have a significant effect on transfer from thickener film to fibre during steaming, and anions which form insoluble complexes with the dye should be excluded from the print paste. Dyes are available in liquid form, incorporating dye solvents. For use where powder brands are employed, Recipes 5.15 and 5.16 give typical stock print paste and reduction recipes respectively. The dye is pasted with the dye solvent and the acetic acid. Hot water (80–90 °C) is poured on to the paste to produce a solution, which is sieved and stirred into the thickener. Finally, the fixation accelerator is added; dicyanoethylformamide has been used successfully. It is extremely important that, during all the drying and fixation processes, the print is at an acid pH. For this reason the addition of a nonvolatile acid to the print paste is absolutely necessary.

Recipe 5.15

Basic dye	30–50 g
Thiodiethyleneglycol	3 g
Acetic acid (30%)	30 g
Hot water	x g
Thickener	500–600 g
Citric acid or ammonium sulphate	5 g
Fixation accelerator	10–20 g
	1000 g

Recipe 5.16

Thiodiethylene glycol	15 g
Acetic acid 30%	15 g
Hot water	450 g
Thickener	500 g
Citric acid or ammonium sulphate	5 g
Fixation accelerator	10 g
	1000 g

To obtain level colours in large area blotch prints, the addition of carboxymethylcellulose has proved successful, since this anionic thickening agent has a levelling effect on the absorption of the cationic dye. Similar effects can be obtained with other anionic materials. A pretreatment with alginate thickeners, sometimes used

to improve the handling of difficult knitted structures, has the same effect. In each case, however, changes in hue and depth of colour are to be expected.

The following dyes have become important in textile printing on acrylic fibres: CI Basic Yellow 28, 29, 51 and 63; Orange 27, 28, 30, 37, 42 and 43; Red 14, 18, 22, 24 and 110; Violet 7, 16 and 20; Blue 1, 3, 147 and 159; Green 4; Black mixtures.

5.6.2 Fixation

The dyes can only be fixed by steaming, and the ion-exchange mechanism presupposes that the dye can dissociate. When fixing water-soluble dyes on synthetic fibres, the importance of constant and correct steaming conditions can never be overstated. Unlike cotton and wool, synthetic fibres hold very little moisture; fluctuations in the moisture content of the steam are therefore not levelled out by changes in fibre regain. Where the steam is too wet the colours bleed, and where the steam is too dry the thickener is not adequately swollen.

The best results are obtained in saturated steam for 20–30 min at 0.1–0.2 MPa (14–28 lbf in⁻²) pressure in a star steamer. For continuous-filament acrylic yarn fabrics, a higher temperature (108–110 °C), at 0.14–0.15 MPa (16–21 lbf in⁻²), is preferred. Rapid agers are unsuitable for lightweight fabrics because of the permanent distortion produced by tension at temperatures well above the glass transition point. It would also be difficult to obtain acceptable colour yields at the usual, slightly superheated, steam temperatures. Tensionless steaming in festoon steamers is preferable, although yields are not as good as in pressure steamers.

It has been suggested that superheated steam may be used but, even when urea or similar hygroscopic substances are employed, the brightness and fixation are poor compared to optimum results [41,42].

Cold water rinsing and soaping at 50 °C, then at 70 °C with 2 g l⁻¹ anionic detergent, are required to ensure good fastness to rubbing and brilliance of hue.

5.7 POLYAMIDE FIBRES

These were the first synthetic fibres produced in commercially significant quantities. The development of knitting machinery led to the production of warp-knitted nylon fabric which could be heat-set, and dyed or printed to give materials with good easy-care properties.

Both nylon 6.6, made by condensation of hexamethylenediamine and adipic acid, and nylon 6, made from caprolactam, are used in substantial quantities. Nylon 11, made from aminoundecanoic acid, is of much lesser interest.

Scouring and setting should normally precede printing, the methods to be employed being selected according to fabric structure, cleanliness and dimensions required. It can be advantageous first to stenter to a width 4% greater than the stable width, if the fabric is to be gummed down directly on to the blanket of a screen-printing machine. This reduces the risk of blistering due to swelling and extension of the first printed areas.

5.7.1 Dyes

Dyes are selected from the ranges of acid, metal-complex acid and direct dyes, according to solubility, print paste stability, washing-off properties, and fastness properties. The use of both thiodiethylene glycol, to improve dye solubility, and thiourea, which acts as both a fibre-swelling agent and a dye-solubilising agent, is recommended. The amount of swelling agent, or carrier, required for printing nylon 6 need be only half that for nylon 6.6. For high colour yield it is essential to include an acid or acid donor, and both ammonium sulphate and citric acid have proved to be suitable [43].

A typical recipe for knitted fabrics of bulked nylon 6.6 is shown in Recipe 5.17. The coacervating agent has a beneficial effect on levelness and surface appearance of

Recipe 5.17

Acid or metal-complex dye	20–40 g
Thiodiethylene glycol	50 g
Water	x g
Thickening (8–14%) containing	500 g
Urea	50 g
Coacervating agent	0–10 g
Antifoam	5 g
Ammonium sulphate (1:2)	30–60 g
	1000 g

carpets and bulked-yarn fabrics. Ensuring the absence of uncoloured surface fibre gives an increase in apparent colour yield.

The choice of thickening agent must be made from products stable at low pH and providing satisfactory adhesion and film elasticity. Modified natural products based on guar, locust bean and karaya gums have been widely used.

5.7.2 Processing after printing

It is usually important that saturated steam is used for print fixation. By careful selection of dyes the steaming time required can be shortened, but 20–30 min is recommended at 100–103 °C. With many dyes, improved yields may be obtained by using a pressure steamer at 35–105 kPa (5–15 lbf in⁻²) excess pressure. High-temperature steaming, or thermofixation, may also be used for a few dyes.

During washing-off, great care must be used to avoid staining of unprinted white ground areas and pale printed areas. The high affinity and rate of adsorption of acid dyes, especially on nylon 6, make it essential to plan the washing process, bearing in mind the factors affecting dye sorption.

Because dye affinity is much lower under alkaline conditions, even the initial cold rinsing of the prints is preferably carried out in 1 g l⁻¹ sodium carbonate solution. Further washing may be at 40 °C, then at 60 °C with 1 g l⁻¹ sodium carbonate and 1.5 g l⁻¹ of a mildly cationic auxiliary agent to complex the anionic dye and hold it in the bath. Alternatively, an anionic retarding auxiliary may be used under acid conditions, but it may be necessary to use up to 6% on fibre mass of such an agent. Ideally, total washing times of 30 min are required.

Final rinsing in cold water may be preceded by a ‘backtanning’ aftertreatment with a synthetic tanning agent (Syntan), to improve the fastness to washing at temperatures up to 80 °C. Such aftertreatments are, however, less frequently used on prints than on dyed fabric because of adverse effects on the white ground, in addition to the 15 min extension of an already lengthy washing procedure.

The following acid dyes have been used: CI Acid Yellow 49, 79 and 222; Orange 95; Red 274, 276, 337 and 360; Violet 42 and 103; Blue 113, 205, 220, 221, 264 and 313; Green 81 and 84; Black 172. Suitable metal-complex dyes include CI Acid Yellow 232; Orange 107 and 166; Red 279 and 414; Blue 199 and 335; Brown 413 and 415; Green 91; Black 140 and 220.

5.8 PROTEIN FIBRES

Because the desirable appearance and properties of the natural protein fibres exceeds anything achieved by the synthetic-polymer fibres, they can be expected to maintain a secure place among the higher-priced luxury goods. Individually they are:

- sheep’s wool (by far the most important product)
- mohair (wool of the angora goat)
- alpaca (wool of the llama)
- cashmere (wool of the cashmere goat)
- camel hair

- mulberry silk (the most common natural silk)
- tussah silk (wild silk).

Since all are protein fibres, polypeptide chains are common to them all; however, in wool there are tangled side-chains, whereas the polypeptide chains of silk are elongated and have few polar side-groups, so that they absorb less acid. The presence of cystine sulphur bridges is also characteristic of wool.

These fibres can be broken down by hydrolysis into a mixture of numerous amino acids, the composition of which is characteristic of each fibre. The amphoteric nature of the protein fibres is due to the presence of amino and carboxyl groups, providing sites for acid and basic dyes as well as reactive and direct dyes. The formation of metal complexes, involving the fibre and dyes of suitable configuration, is also clearly possible.

Some other properties of these materials are also important for dyeing and printing. Protein fibres are particularly sensitive to the effect of alkali, to rubbing and to temperatures above 120 °C, which cause deformation, yellowing and impairment of handle. On the other hand, wool and silk are remarkably stable in the presence of dilute acids.

Wool has a well-known tendency to felting. Chlorination, however, changes the scaly layer of the wool fibre in such a way that the material wets out and swells more easily. The scales lie flat on the cortical layer, the wool no longer felts as readily and has increased lustre. Unfortunately it is extraordinarily difficult to carry out this process uniformly and irregular uptake of dye can result. Two approaches have been used to improve the uniformity of wet chlorination. Firstly, nitrogenous auxiliary agents may be used in the chlorination bath, which temporarily bind the free chlorine in the form of chloramines; these then react slowly with the wool (an example of this technique is the Melafix method, CGY). Alternatively, the sodium salt of dichloroisocyanuric acid is added (such as Basolan DC, BASF) and is slowly hydrolysed, liberating hypochlorous acid.

These processes, if carried out correctly, bring about such a substantial improvement in colour depth and brilliance, regardless of which dyes are used, that almost all wool piece goods for printing are pretreated in this way.

Natural silk also requires pretreatment. The silk moth (*Bombyx mori*) produces a double thread made of the protein fibroin, which is stuck together with a second secretion, sericin (silk gum). Textiles made from untreated 'raw silk' are coarse and hard to the touch. As a rule they are therefore 'degummed', by washing them in a soap solution. The resulting colloidal suspension of sericin in the soap, the so-called 'degumming liquor', acts as an excellent protective colloid and levelling agent in silk dyeing. After this treatment the material has improved lustre and absorptive capacity for dyes, and can be printed as described below, in principle, exactly as wool.

5.8.1 Acid, basic and direct dyes

As already mentioned, these dyes are all theoretically suitable for printing wool and silk; however, application is mainly limited to acid dyes. Basic dyes can provide extraordinary brilliance in some cases, but do not show adequate fastness. Acid dyes must also be selected to obtain acceptable light and wet fastness for each end-use, in addition to the desired brilliance of hue. This applies both to direct and to discharge printing.

The less soluble dyes of these classes need urea or thiourea to assist solution along with auxiliary solvents, such as thiodiethyleneglycol, and hot water. When printing wool, glycerol may be used to reduce the adverse effect of superheat in the steam during fixation; with silk, however, the addition of glycerol can cause 'flushing' problems.

Locust bean or guar derivatives are used as thickening agents, either on their own or in mixtures with cold water-soluble British gum. Crystal gum is used for printing silk, rather than tragacanth and mixtures of tragacanth with British gum or gum arabic, which were formerly the main thickening agents. Thickeners of high solids content are used for fine effects and outlines, whereas products of low solids content are preferred for larger areas because of their better levelling effect and the reduced possibility of crack marks occurring after printing.

The printing pastes contain an acid donor for fixation of the dye. This may be ammonium sulphate, ammonium tartrate, oxalate or even in some cases acetic acid or glycollic acid. Small amounts of sodium chlorate are added to counter the reductive effect of wool, and possibly the thickeners, during steaming. In the case of dyes 'sensitive to steaming', the addition of sodium chlorate is essential. Defoamers and printing oils are also usually necessary for smooth prints with sharp outlines. Coacervate-forming surface-active auxiliaries have proved successful for the prevention of 'frosting' effects on wool, especially where chlorination was not adequate and for particularly voluminous materials.

Relatively long steaming times of 30–60 min are usually needed to fix acid dyes on wool or silk. The most brilliant and fast prints can only be obtained in saturated steam fixation at 100–102 °C. For this reason it is most important to avoid overdrying the goods after printing (Chapter 8). Wool is even 'spray damped' sometimes before steaming, or put into artificially moistened steam. This, however, means that there is a danger of drop formation. In batch steamers, condensation spots and uneven fixation are less likely if a procedure of alternate steaming and evacuation is used. Festoon steamers, which allow sufficiently long steaming times, are often used.

The final wash of the printed goods usually takes place on the winch beck, but it can also be undertaken in one of the washing machines designed for knitted goods. Wool and silk should be treated very carefully, with as little mechanical strain as

possible. To prevent the staining of unprinted areas, as well as to counter the risk of bleeding, the use is recommended of polycondensation products of aromatic sulphonic acids, such as Mesitol HWS (BAY) or Erional NWS (CGY). These products improve the wet fastness on wool considerably. To obtain the best results, 5–6% on the mass of the goods should be used at 60 °C in an acetic or formic acid bath. Treatment for approximately 20 min in the final rinsing baths is required.

5.8.2 Metal-complex acid dyes

These dyes, both 1:1 and 1:2 complexes, offer higher fastness than acid dyes, particularly light fastness, but somewhat duller colours. The way in which metal-complex dyes are applied hardly differs at all from the method used for acid dyes, except that these dyes do not require the use of an acid or acid donor. At low pH, in fact, not only is the stability of the paste diminished but there is also a tendency for the dyes to aggregate and to give rise to specks. At the same time acid donors can adversely affect the levelness of prints, and these high-affinity dyes often give levelling problems in blotch printing anyway.

Otherwise both the dissolving process and the choice of print thickener, as well as fixing and afterwashing are the same as with acid dyes. It is possible, therefore, to mix acid and metal-complex dyes, but printing should be without acids or acid donors.

5.8.3 Reactive dyes

These products form true chemical bonds with the SH, NH or NH₂ groups in the polypeptide chains, in acid media (pH 3–5) at 80–100 °C. Such dyes can provide prints of good fastness and brilliant colours.

Additional expenditure is unavoidable when using these dyes, but this is justified by the high demands made, especially on goods which bear a Woolmark, as well as the durability of articles produced from these fibres. There is practically no difference in the printing procedure from that for metal-complex dyes, except that some acid donor is necessary in the paste to guarantee acidity. The fixation times can be reduced to 10–20 min in saturated steam at 100–102 °C. During afterwashing of the print, however, the degree of fastness expected can only be obtained if the unreacted dye on the fibre is removed completely. For this reason, after rinsing, the goods must be soaped in several baths at increasing temperature (40–60–80 °C), with 2 g l⁻¹ disodium hydrogenphosphate, enough ammonia to bring the pH to 9, and an anionic washing agent. In consequence, this energetic washing process does not allow any other class of dye, apart from reactive dyes, to be used in the print paste, and as far as printed goods are concerned, wet aftertreatment of this sort is possible only on nonfelting goods – that is, almost exclusively on chlorinated wool.

Recipe 5.18 indicates some general formulations for use on protein fibres.

Recipe 5.18			
	<i>Acid/g</i>	<i>Metal-complex/g</i>	<i>Reactive/g</i>
Dye	x	x	x
Urea	50	50	50
Thioethylene glycol	50	50	50
Water	y	y	y
Thickener	approx. 500	approx. 500	approx. 500
Ammonium sulphate 1:2	60		
Formic acid 85%			10
Sodium chlorate 1:2	15	15	15
	1000	1000	1000

5.9 POLYESTER/CELLULOSE FIBRE BLENDS

In recent years polyester and cellulose blends have become increasingly important, especially polyester:cotton mixtures in the ratios 50:50 and 67:33. Polyester fibres are also mixed with regenerated cellulose fibres in similar ratios. The popularity of these blends stems from the desirable balance of physical properties and the comfort in wear of articles made from them, such as shirts, blouses and other outer clothing.

Several techniques, dyes and dye combinations can be used for the printing of polyester/cellulose blends in the form of woven or knitted goods. Many variations have been tried out in practice and good results obtained, but always with some difficulty or undesirable complication [44,45]. The various processes described below refer to polyester/cotton mixtures; where necessary, information is given for mixtures of polyester and regenerated cellulose.

5.9.1 Processes using a single class of colorant

Pigment printing

Pigment printing is not complicated and does not present the difficulties that can arise when printing mixtures consisting of two different fibres, as one pigment colours both fibres and to the same hue. Moreover, no expensive treatment is required either before or after printing. Neither do the prints have to be washed. Most printed polyester/cellulose fabrics are therefore pigment-printed.

The process is essentially simple and safe. Pigments cover absorption irregularities in the substrate, and they can be used on substrates having different ratios of the two

fibres, as each fibre is equally covered by pigment. Slight variation in the recipe is required to achieve optimal fastness with different mixture ratios. The prints show very sharp outlines and the colour possibilities are almost unlimited. As no washing-off is required, it is also possible to print very delicate materials. Production costs are low.

There are certain offsetting disadvantages to pigment printing, however. The amounts of binder and crosslinking agent required for dark colours are so large that the handle of the goods is impaired. Application of pigment and binder to the surface of the fibres also reduces the natural lustre in the printed areas of the fabric.

Abrasion marks occur during wear on collars and cuffs of clothes made of pigment-printed polyester/cotton, especially on blouses and shirts. This has been shown to be caused by the action of body fat on the print. Abrasion at creases also occurs, especially if this kind of clothing is machine-washed. Dry-cleaning several times with chlorinated hydrocarbons is also likely to reduce the colour depth.

Insoluble azo colours

Certain CI Azoic Compositions which can be fixed under neutral conditions can be fixed on the cotton part of the blend and then given a later heat treatment during which some of the azo dye formed can diffuse into the polyester fibres. The fastness properties obtained are generally satisfactory. This process, however, is limited to a few hues. Polyester/cotton blends in the ratio 50:50 yield better results than mixtures in which polyester predominates.

Selected vat dyes

Chronologically, selected vat dyes of low r.m.m. were the first to be used for the printing of polyester/cotton. The dye is first fixed on the polyester, in hot air for 45–60 s at 200–210 °C. The vat pigment dissolves in the polyester part of the blend, acting like a disperse dye. The vat dye is then fixed on the cotton, using a two-stage fixation process. The Polyestrene dyes (HOE) were a small range of vat dyes selected for use in this way. The prints had very high fastness, but the brilliance and depth of colour was restricted.

Selected disperse dyes

In 1972 it was shown that selected disperse dyes (Dybln dyes, DUP) could be applied to polyester/cotton with the help of water-miscible high-boiling solvents, in hot air at temperatures of at least 210 °C [46]. The function of the solvent is to maintain the cotton in the swollen state and dissolve the disperse dye during fixation, so that the dye

can enter the fibre. Washing then removes the solvent and leaves insoluble dye within the cotton. The process is impressively simple in that only one class of dye is used, with one-stage fixation followed by a simple washing process.

When the process was introduced, however, few suitable dyes were available; a very low solubility in water was essential. There were no clear, brilliant red and blue dyes in the original range. A further disadvantage was that the fixing temperature needed to be very high, otherwise fixation was incomplete. Fixation is, moreover, less satisfactory in the superheated steam festoon steamers that are now widely used in print works. Blends with regenerated cellulose cannot be printed because the solvent swelling effect is inadequate. The printing paste had to contain about 10% solvent, which increased costs. The division of dye between cotton and polyester depended on the amount of solvent, and on the volatility of the dye. Finally, the fastness became less satisfactory on blends containing larger percentages of cotton; the process is limited to blends of ratio 67:33 or higher.

A range of similar dyes, Cellestren (BASF), was introduced, but has been withdrawn.

5.9.2 Processes using two dye classes

In processes using two dye classes the component for the polyester portion is always a disperse dye, whereas the dye for the cotton can belong to any one of several classes. In textile printing (in contrast to dyeing), only mixtures of disperse and reactive dyes have achieved significant success. For the sake of completeness, and because requirements vary with time and place, the other possibilities will also be described.

Pigments and disperse dyes

The limitations that affect pure pigment printing of polyester/cotton have already been discussed. By adding selected disperse dyes to the pigment printing paste, it is possible to get dye into the polyester fibres. This reduces the loss of colour and appearance on abrasion marks during wear and washing. Some dye manufacturers offer ready-mixed blends of pigment and disperse dyes. When using this kind of product, a certain amount of the disperse dye remains in the binding film. Those prints which require to be fast to dry-cleaning must therefore be given a controlled clearing process before they are sold to the customer. This also means another drying process, and careful selection of pigments for resistance to reduction. The simplicity of pigment printing is lost because of the additional operations. In some markets, however, these mixtures have met with limited success.

Azoic compositions and disperse dyes

After application of the dye mixture, neutral or acid steaming effects fixation of the azoic dye on the cotton portion of the blend. The disperse dye is then fixed on the polyester fibre using hot air. Most of the azoic dyes are susceptible to reduction, so that mild clearing conditions must be applied, and limitations on colour depth or rubbing fastness accepted.

Vat and disperse dyes

The two components can be mixed in the colour shop or they can be obtained from dye manufacturers as a ready-mixed product. The procedure for printing is the same as that described in section 5.9.1 for vat dyes alone. The goods are printed in the absence of alkali, treated so as to fix the disperse dye, and then subjected to a two-stage fixation in order to fix the vat dyes on the cotton. The pad-steam fixation stage is a reductive treatment, which removes much of the unfixed disperse dye, and makes the final washing of the print is easier. Prints produced by this method have very good fastness properties.

The vat and disperse dye combination has secured a safe place for the dyeing of polyester/cotton, but has not been introduced into printing to a great extent.

Soluble vat and disperse dyes

Selected vat leuco ester dyes, such as Anthrasols (HOE), and selected disperse dyes can be prepared as separate printing pastes. The two printing pastes are then mixed in a ratio of 1:1. After printing, the disperse dye is fixed in hot air and then the soluble vat dyes are oxidised during washing, using the same method as the nitrite process (section 5.3.4). The combination has only secondary importance because the costs are high and technical merits inadequate.

Reactive and disperse dyes

The application of disperse and reactive dyes in textile printing has met with worldwide interest. This combination can be fixed in a single process, as in pigment printing. The problems that may arise are fewer than with other dyes and this combination offers more scope as regards the colour range that may be produced. Ready-mixed dye blends are used and recommendations are also made for the mixing of disperse and reactive dyes:

- ready-mixed dye combinations, such as Drimafon R (S), Procilene (Zeneca), Remaron Printing Dyes (HOE) and Teracron (CGY)
- recommended separate disperse and reactive dyes, such as Dispersol PC–Procion PC (Zeneca).

When choosing dyes for this kind of combination, it is necessary to take into consideration the two different kinds of fibre in the substrate to be printed, and then to consider it as a blend. The reactive dye should give as high a degree of fixation as possible, since it plays an important part in obtaining full depths on the fibre blend. This is evident when unmercerised blends are printed.

There will, of course, be significantly more unfixed dye than for single-fibre fabrics. This will result in additional problems when washing the print. Unfixed disperse dye that cannot be removed in cold water, or solubilised in hot alkali, is likely to stain unprinted polyester in the hot washing stage. Finally, when selecting from the two different dye classes, one should consider the possible reaction of these dyes with each other and possible reactions with the chemicals and auxiliary agents used for printing and washing.

The following points must be kept in mind:

- washing the print should present as few problems as possible
- build-up of dye on the two fibres should be similar in yield and hue, producing as solid a colour as possible
- no reaction should take place between the disperse and the reactive dyes.

These points are discussed below.

Washing the print: Strongly alkaline washing treatments, as recommended for Drimafon and Dispersol–Procion PC dyes, have a particularly good clearing effect. The disperse dyes used possess alkali-sensitive groups, such as ester groups; in a strongly alkaline medium these dyes are solubilised and no longer stain polyester fibres [47]. Special nonionic washing agents may assist the washing effect substantially [48]. It must also be possible to wash off the reactive dyes used in the dye combination both quickly and completely, and the reactive dye must form a dye–fibre bond of high stability in the presence of alkali.

Build-up of dye: The build-up properties of disperse and reactive dyes on the two fibre components differ from one dye to another, and must be taken into account when selecting dyes. Just as important is the maintenance of the correct proportion of reactive to disperse dyes, to ensure that the ratio of the fibres to be printed does not significantly influence the hue and washability.

The stability of the dye–fibre bond is important, particularly when printing pale colours, for which alkaline print pastes are used because one-stage fixation is practicable. To ensure that the print can be easily reproduced, appropriate reactive dyes must be chosen.

Reaction between disperse and reactive dyes: When the fixation takes place at high temperatures in the presence of sodium bicarbonate, there is a danger that reactions may be take place between the reactive and the disperse dyes – for example, with amino groups. To avoid this, dyes must be selected with extreme care. The amount of alkali in the thickening agent should also be kept at a level that effects minimum decomposition of disperse dye.

The use of sodium formate, instead of bicarbonate, has been shown by Hoechst to give better colour yields, because the alkalinity required for the fixation of reactive dye is developed only at a late stage in the process. The use of reactive dyes fixed in acid conditions, such as the Procion T (ICI) dyes, achieved optimum yield of fixed disperse dye. Mildly acid conditions are ideal for disperse dye application. (These dyes have, however, been withdrawn.)

Urea is necessary for optimal fixation of reactive dyes in hot air or superheated steam. Urea also reduces the yellowing of cellulose under hot, dry, alkaline conditions, and it thus helps in the production of bright colours. It acts as a solvent for the reactive dye and accelerates migration of the dye from the thickener film into the cellulose fibre. When using some reactive dyes of good solubility, 50 g kg⁻¹ urea is sufficient. If higher amounts are used, the disperse dye stain on cotton is increased and the yield of fixed reactive dye may decrease, especially with dyes of the vinyl sulphone type.

When printing polyester/cotton fibre blends with combinations of disperse and reactive dyes, it is important that the goods undergo a suitable pretreatment process (Table 5.2). These differ from the usual processes for pretreatment of cotton in that the singeing process is delayed.

Singeing in the presence of sizing agents can cause fibre damage. Careful drying is necessary, because the dye absorption capacity of cellulose fibres can be adversely affected by overdrying. Regenerated cellulose fibres can present problems with regard to their absorption of reactive dyes, depending upon their origin. Correct pretreatment of regenerated cellulose blends is essential.

The safest method is to give the fibre blend an alkaline pretreatment with caustic soda of approximately 6 °Bé. This opens up the fibre structure and improves dye fixation. Should the singeing and bleaching be unnecessary because of the composition of the substrate, alkaline pretreatment should follow the desizing of the goods.

The mixtures of reactive and disperse dyes available on the market are produced in such a way that they can be sprinkled directly into the thickening paste. This applies

Table 5.2 Pretreatment processes for polyester/cellulose blends

Polyester/cotton	Polyester/viscose
Desizing	Desizing
Mercerisation	Drying
Drying	Singeing
Singeing	Alkaline pretreatment
Bleaching	Bleaching
Drying	Drying

both to printing pastes on a pure alginate base and to those on a half-emulsion base. When producing a printing paste containing alkali-sensitive disperse dyes it is important to ascertain whether the reaction of the alginate thickener is neutral before processing, so that the correct amount of alkali is present in the printing paste. The thickening agent must be able to withstand the very high temperatures used for fixing the dyes. A complexing agent for calcium, such as hexametaphosphate, should be added to the printing paste, to ensure that the thickener can be washed off quickly. Fixation accelerators may be preferred as alternatives to urea, which can sublime on to the machinery.

Prints with disperse and reactive dye combinations are fixed in a one-stage procedure, in either hot air (30–70 s at 190–205 °C) or superheated steam (6–8 min at 175–180 °C).

Washing-off the print

As far as the reactive dye in the combination allows, an alkaline washing process is used. This kind of washing process can consist of five steps, and a suggested procedure is given in Recipe 5.19.

The high washing temperatures are desirable in order to achieve good washing effects. This washing process can be applied in open width or in rope washing machines. The washing time for continuous washing depends upon the weight and density of the goods. The efficiency of the washing effect can be tested by acetone extraction. A 4 × 4 cm sample is cut from a corner of the print where the colour is strongest; it is placed in a test tube containing 5 ml of acetone and shaken for a short time. If washing has been satisfactory, the acetone remains unstained. Unfixed disperse dye which has not been washed off dissolves in acetone; if the acetone sample is strongly coloured, then the washing process must be repeated. The acetone test also makes it possible to assess the general level of fastness to be expected from the print.

Recipe 5.19

		<i>Auxiliaries</i>
Step 1	Rinsing (cold)	—
Step 2	Washing at 40–60 °C	3 g l ⁻¹ complexing agent 3 g l ⁻¹ soda ash 3 g l ⁻¹ caustic soda 38 °Bé 2 g l ⁻¹ washing agent (nonionic)
Step 3	Washing at ca. 95 °C	3 g l ⁻¹ complexing agent 3 g l ⁻¹ soda ash 3 g l ⁻¹ caustic soda 38 °Bé 2 g l ⁻¹ washing agent (nonionic)
Step 4	Rinsing at ca. 95 °C	
Step 5	Rinsing (cold)	0.5 ml l ⁻¹ acetic acid 60%

If the goods need to be washed again, it is advisable to divide the process up, so that the goods are batched in an alkaline state prior to the repeat process.

In the finishing stage, care should be taken when choosing the catalyst for resin finishing of the fabric. Catalysts that are activated at temperatures of 120–125 °C are to be preferred. At these temperatures thermal migration (the desorption of dye from the fibre to the surface) of disperse dyes is not significant. When the rub and wet fastness values deteriorate after resin finishing, thermal migration is a likely explanation.

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