CHAPTER 6

Discharge, resist and special styles

Clifford Berry and John G Ferguson

6.1 INTRODUCTION AND DEFINITIONS

Discharge and resist styles have been important since the earliest days of textile printing. Knecht and Fothergill gave an excellent account of the many processes, often developed with considerable ingenuity, that provided a wide range of effects without the advantages of modern dyes [1]. In recent years, modern techniques have made the use of direct printing practicable for many more designs and reduced the necessity of using these styles, but they will always be of significance because the effects obtained are often different and aesthetically superior.

In the direct printing style, the final effect is obtained in one operation, with the proviso that fixation and washing may also be necessary. Originally the term 'direct' indicated that no prior step of mordanting or following step of dyeing was required. In the discharge style, the fabric must first be dyed with dyes that can be destroyed by selected discharging agents. The discharge paste is printed on to the dyed fabric and, usually during subsequent steaming, the dye in the pattern area is discharged. A white discharge is thus produced. It is also possible to add a discharge-resistant ('illuminating') dye to the discharge print paste, to produce a coloured discharge. The area of dyed fabric surrounding the pattern areas is described as the 'ground', because it is a background from which the illuminating colours (often called head-colours) shine. This is especially true when the ground is black, when the colours seem to have extra brilliance. The use of the term 'ground' is naturally extended to describe the dyed fabric before printing.

Resist printing can be used to produce similar effects, but in this style the fabric is first printed with a resist agent and then dyed. Ground colours can, therefore, be obtained with nondischargeable dyes. Resist mechanisms may be chemical or physical, the maximum effectiveness being ensured by using a mixture of both types of resist agent. A physical resist inhibits absorption of dye, and a chemical resist inhibits fixation. Coloured resists require the addition to the print paste of dyes or pigments that are satisfactorily fixed in the presence of the resist agent, either before the fixation of the ground colour or during the process.

If the ground colour is not too dark, it may be that the required effect is obtainable by ‘overprinting’. This is simply direct printing on to a predyed fabric. Tone-on-tone effects, which use colours of similar hue, are often produced in this way, but contrasting colour combinations are also possible. For example, blue dyes may be printed on to a yellow fabric to obtain green areas. Overprinting requires no elaboration, but discharge and resist styles must be considered in more detail if the full range of possibilities and problems are to be appreciated and understood.

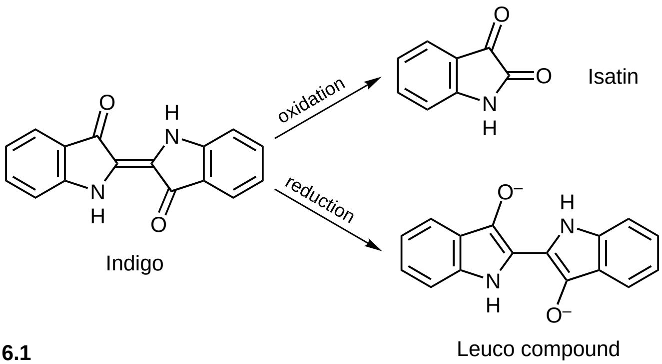
6.2 DISCHARGE PRINTING

With any industrial process there must be sound technical and commercial reasons for its conception and continuation. In the case of discharge printing, the following considerations determine the usefulness of the process compared with other printing techniques.

1. Printed materials with large areas of ground colour can be produced, the depth, levelness and penetration of which would be difficult, if not impossible, to obtain by a direct printing process.
2. Delicate colours and intricate patterns can be reproduced on grounds of any depth, with a clarity and sharpness that have become the hallmarks of this style. Intricate white patterns lose their crispness if left as unprinted areas in a direct, blotch print, because the print paste spreads unequally in different directions. In addition, a coloured motif fitted into a blotch print either leaves unprinted white margins or forms a third colour where fall-on occurs. In some cases such effects are acceptable, but they can be eliminated by using the discharge technique.
3. The extra processes required and the additional costs of discharge pastes mean that production costs are higher, but the aesthetically superior results give the product a higher value and enable profit margins to be maintained or even improved. The higher costs of discharge printing are often offset when applied to long-lasting designs used for scarves, ties, cravats and dressing gowns.

As already indicated, in discharge styles the pattern is produced by the chemical destruction of the original dye in the printed areas. The discharging agents used can be oxidising or reducing agents, acids, alkalis and various salts. An early and, one might say, classical example is the discharge printing of cotton dyed with indigo, the characteristic colour of which can be destroyed either by oxidation or reduction (Scheme 6.1).

In the former, an oxidising agent, such as a thickened 10% solution of sodium

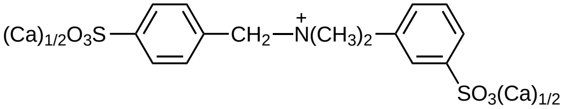


Scheme 6.1

dichromate, is printed on to the indigo-dyed material and dried. When this is passed through a hot bath of sulphuric and oxalic acid, chromic acid is liberated and the indigo in the printed areas is oxidised to isatin. The oxalic acid reduces any excess chromic acid which might be formed and which would otherwise gradually discharge the ground colour. Since isatin is soluble in alkali, the final step is to run the fabric through an alkali bath – in an open soaper, for example – whereupon the isatin is removed to give a white discharge pattern. The main problem with this process is the adverse effect of the oxidising agent and the acids on the cotton substrate, which can easily be tendered under these conditions.

To produce a white discharge effect by reduction, the indigo-dyed fabric is printed with a thickened paste containing a stabilised reducing agent, together with sodium carbonate, anthraquinone and Leucotrope W (*6.1*). When the dried print is steamed, the reducing agent is activated and reduces the indigo to its leuco (colourless) form. The Leucotrope W combines with the leuco compound to form an alkali-soluble orange product which will not reoxidise, and which can be washed out to give a good white. Zinc oxide can also be added to assist the discharging action and to give a white pigmentation effect. If Leucotrope O is used instead of Leucotrope W, an insoluble orange complex is formed which remains fixed to the fibre and is used in some styles to give a coloured discharge (Scheme 6.2).

These examples indicate the importance of an adequate knowledge of the structure and properties of the dye and print paste ingredients, so that the most effective



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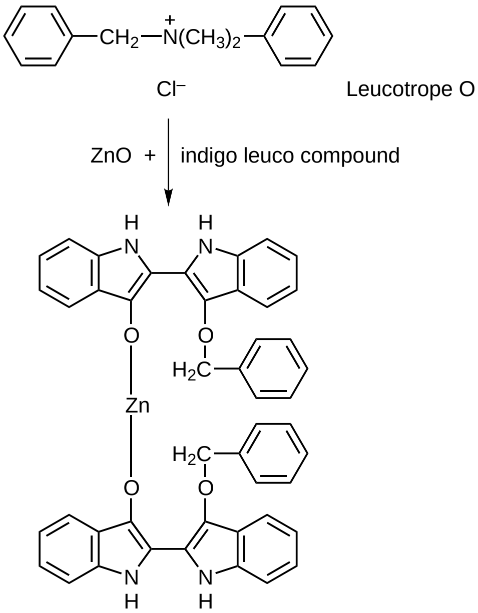


Scheme 6.2

technique can be chosen to produce a satisfactory discharge on whatever type of fabric is to be printed.

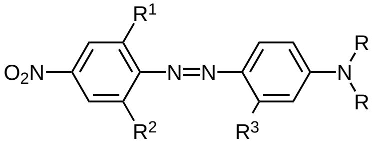
6.2.1 Print pastes for discharge printing

A typical print paste for discharge printing would contain dye (for a coloured discharge), discharging agent, other chemicals and auxiliaries, thickener and water. Each component requires detailed consideration.

Dye selection

The correct choice of dye is of fundamental importance in successful discharge printing, with respect to both the dischargeable ground and, where required, the illuminating, discharge-resistant dye. Fortunately, most modern dye ranges offer a reasonably adequate selection of both types.

Dyes which are suitable for the dischargeable ground usually contain azo groups that can be split by reduction. Even so, there are great differences in dischargeability between individual dyes. For example, many monoazo dyes in the disperse dye range, which are derivatives of azobenzene and have the general formula shown in structure 6.2, can be readily discharged. Their suitability as dyes for the production of discharge grounds is, however, dependent on the substituents in the *ortho* position to the azo group, particularly in the R^1 and R^2 positions. The common substituents in the R^3 position have less influence on dischargeability. A dye with a chlorine atom in the *ortho* position at R^1 or R^2 is more readily discharged than one with a bromine atom in the same position. For example, CI Disperse Orange 5 (6.3) on acetate fibres shows excellent dischargeability.



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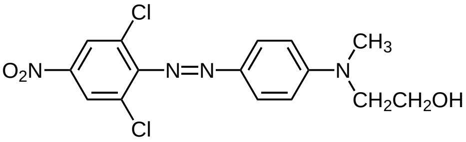
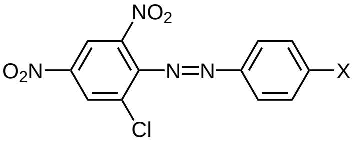


6.3

Dyes with two nitro groups and one chlorine atom, of the general structure 6.4, are more difficult to discharge than those with only one nitro and one chlorine substituent (6.5).



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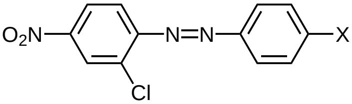

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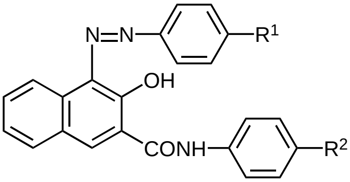
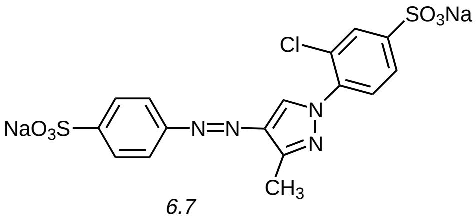


6.6

Dyes having the general structure 6.6 are difficult to discharge and can, in fact, be used as illuminating colours if some loss of tinctorial strength is accepted. In such structures the formation of internal hydrogen bonds would seem to produce a stabilising effect towards the discharge agent. Other examples of dischargeable dyes are CI Acid Yellow 17 (6.7) and CI Basic Blue 41 (6.8).

In addition to dischargeability, the colour of the amines produced by reductive cleavage is important. The ease with which the cleavage products can be removed from the discharge print during subsequent washing should also be taken into



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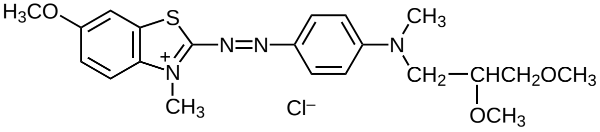


6.8

consideration. If they are not completely removed these residues will slowly darken, due to oxidation, and a white discharge that was initially satisfactory will become unacceptable. With a coloured discharge this point is less critical, as the illuminating colour will tend to mask any slight discoloration.

The great majority of discharge-resistant dyes are not azo dyes but are of the anthraquinonoid, phthalocyanine or triphenylmethane type. The choice depends upon the colour required, the reducing agent being used and the substrate.

The choice of dyes is facilitated by the dye manufacturers, who usually classify their products on a dischargeability scale ranging from 1 to 5. A dye which is classified as 5 or 4–5 on this scale would be suitable for a white discharge. For a coloured discharge, a dye classified as 4 would be acceptable or even 3–4 with very deep illuminating colours. Those dyes which have a dischargeability of only 1 are virtually undischargeable and, therefore, are suitable as the illuminating colours in coloured discharge styles. Only a trial under actual working conditions can provide full and final information on the suitability of a dye for discharge printing.

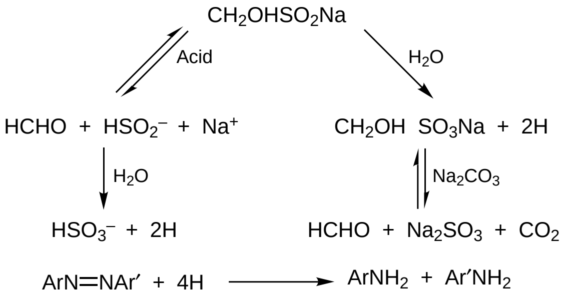
Discharging agents

Clearly, the most important methods of discharging are based on reduction. This general method can be varied and adapted to give discharges with most classes of dye in use and on most types of fibre. Indeed, to many printers the terms 'reducing agent' and 'discharging agent' are synonymous.

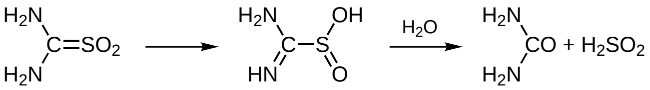
The most widely used reducing agents are the formaldehyde sulphoxylates. The stability of these compounds is such that only limited losses of sulphoxylate occur during printing and prior to steaming. The use of sodium formaldehyde sulphoxylate (CI Reducing Agent 2, sold as Formosul or Rongalite C) was established as long ago as 1905, when it was recognised that methods based on this reducing agent offered many advantages. Other products are the insoluble zinc formaldehyde sulphoxylate (CI Reducing Agent 4), water-soluble zinc formaldehyde sulphoxylate (CI Reducing Agent 6) and the water-insoluble calcium formaldehyde sulphoxylate (CI Reducing Agent 12).

A considerable amount of work has been carried out to show the manner in which the formaldehyde sulphoxylates decompose when used for discharge printing and on the effect of different conditions on the resulting prints [2,3]. A much simplified explanation of the process is shown in Scheme 6.3.

Thiourea dioxide (CI Reducing Agent 11), sold as Manofast, has been used successfully in certain sectors. Although chemically inert to many reagents, an irreversible rearrangement takes place when it is heated with alkali and water with the formation of formamidine sulphinic acid. Decomposition then takes place, one of the products being sulphoxylic acid, and it is this which is the active reducing agent (Scheme 6.4). Another reducing agent, which has been used since the earliest times, is tin(II) chloride. It is a readily soluble compound which reacts with an azo dye as shown in Scheme 6.5. It is important that tin(II) chloride solutions are used quickly since hydrolysis, which gives a turbid solution, occurs on standing. The hydrochloric acid produced will attack unprotected metal. The steaming equipment is particularly



Scheme 6.3



Scheme 6.4

$$Ar{-}N{=}N{-}Ar' + 2SnCl_2 + 4H_2O \longrightarrow ArNH_2 + Ar'NH_2 + 2SnO_2 + 4HCl$$

Scheme 6.5

vulnerable in this respect, and even the squeegee holders on printing machines may have to be protected with resistant lacquer.

The importance of tin(II) chloride diminished considerably on the introduction of the sulphoxylates, but it has now regained some significance in the discharge printing of synthetic fibres. It should be noted, however, that tin salts are undesirable in effluents.

The choice of reducing agent is determined largely by the fibre to be printed and, to some extent, by the dyes used. The soluble sulphoxylates can give haloing problems on the synthetic fibres, caused by capillary movement of solution along the yarns. This problem can be overcome by using the insoluble formaldehyde sulphoxylates or thiourea dioxide (CI Reducing Agent 11). This latter product has had a considerable success in the discharge printing of acetate and triacetate, due to its low tendency to haloing and also because it is effective under acid conditions, which do not saponify the fibres as an alkaline reducing system can do.

Printing pastes containing a high proportion of insoluble matter can, however, give rise to the difficulties of ‘sticking in’, scratching of copper rollers and blocking of screens unless finely ground powders with soft particles are used. In this respect, certain forms of calcium formaldehyde sulphoxylate are considered to be better than the insoluble zinc formaldehyde sulphoxylate, as they have a softer, ‘talc-like’ consistency as well as being more stable.

Generally, the sulphoxylates are stronger reducing agents than tin(II) chloride, and can be used to discharge a greater range of dyes. On the other hand, since very few dyes are absolutely resistant to reducing agents, tin(II) chloride is preferred with illuminating dyes. It would, therefore, seem logical to use both types of reducing agent for a pattern with white and coloured discharges, but most printers prefer to use only one reducing agent for simplicity of operation.

The actual amount of reducing agent required for optimum discharge will depend upon:

- the dyes to be discharged
- the depth of the ground
- the fabric being printed.

The use of insufficient reducing agent will, of course, give an incomplete discharge, whereas too much results in flushing or haloing during steaming, as well as being wasteful and uneconomic. Flushing of a white discharge results in blurred edges and a loss of fine detail, whilst in coloured discharges it is usually seen as a white halo around the printed areas. This is due to migration of the soluble reducing agent which, if the ground fabric has been dyed with a mixture of dyes with differing dischargeability, may produce a coloured halo. That is not to say that haloing and flushing must be avoided at all costs, since some styles actually depend upon the various effects which can be achieved in this manner – the so-called 'bleeder styles' (section 6.5.2).

Other chemicals and auxiliaries

Anthraquinone is often used to improve the discharge effect of a reducing agent, and is therefore used on fabrics dyed with the azo dyes which are more difficult to discharge. During steaming it is reduced to hydroanthraquinone which, in turn, reduces the dye and is itself reconverted to anthraquinone. This cycle of reactions continues until reduction of the dye is complete. The anthraquinone might, therefore, be considered to be acting as a catalyst. The presence of anthraquinone improves the whites and renders them more stable in air by retarding any oxidation of fission products. It also promotes reproducibility in fluctuating steaming conditions but, to prevent subsequent discoloration, all anthraquinone must be removed in the washing process that follows.

Leucotropes are compounds of certain tertiary bases with benzyl chloride and its substitution products. Their use has already been mentioned in the context of the discharge printing of indigo; Leucotrope W can be used in other cases to improve the discharge effect.

It is often necessary to employ *penetrating agents* during steaming, especially with white discharges, to ensure that the discharge paste thoroughly penetrates the fabric and to prevent any 'grinning' or show-through effects, especially on knitted fabrics. Additives of this type include glycerol, ethylene glycols and thiodiglycol. They are effective mainly because of their humectant properties. The actual amounts used must be carefully determined under local conditions as too little would give a poor discharge effect, but too much could result in flushing and haloing. A penetrating agent is not always necessary with coloured discharges as the illuminating dye tends to mask any incomplete discharge. In fact, any auxiliary that improves penetration of the fibre can improve the discharge effect. Therefore, *carriers* and *fixation accelerators* are often added when printing illuminated discharges on synthetic fibres; in some cases, they improve a white discharge on such substrates.

Wetting agents are also necessary when printing on fabric of low absorbency which may be coated with dried film of thickener from the preliminary dyeing operation, as in the 'discharge-resist' process (section 6.3.6).

A wider range of illuminating colours can be used if they can be protected from the reducing agent; the anthraquinonoid pink and blue disperse dyes are particularly prone to attack if CI Reducing Agent 6 is used. Experience has shown that one of the best additives in this respect is *urea*, which adequately stabilises such dyes during steaming.

White discharges are usually improved by additions of *titanium dioxide* or other white pigment, and when thiourea dioxide is being used as the discharging agent the white is improved by an addition of *zinc sulphate*. Discharge-resistant *fluorescent brighteners* are, of course, also very useful in improving white discharges, and are selected to suit the fibre being printed.

Thickeners

In discharge printing the correct choice of thickener is of even greater importance than in direct printing. Not only must all the requirements for direct printing be met, but the thickener must also have good stability to the reducing agent used, tin(II) chloride being particularly difficult. In this case, coagulation can occur if there is any incompatibility between the thickener and the tin(II) ions. Thus nonionic thickeners are necessary and anionic thickeners, such as the carboxymethylated types, should be avoided. The low pH (2–3) of tin(II) chloride solutions can also bring about hydrolysis of thickeners, with subsequent loss in viscosity. A low pH can also give rise to specky prints, due to aggregation or precipitation of certain dyes, notably some disperse dyes.

Specky prints can also be caused where particular dyes are absorbed by insoluble or acid-gelled materials in the thickener. Soluble dyes, such as basic dyes and acid dyes, can be precipitated by a high concentration of inorganic salt in the printing paste.

Since sharp and intricate patterns are characteristic of a discharge style, it is essential to minimise flushing and bleeding. It is, therefore, often necessary to use the low-viscosity thickeners and a high solids content. Thickeners that have been used include nonionic locust bean gum ethers, sodium carrageenates, starch ethers and crystal gums.

As already indicated, an essential criterion for successful discharge printing is the correct balance between penetration of the fabric and control of flushing and haloing. The control of penetration with humectants and the use of high-solids thickeners have already been mentioned. Other factors affecting the balance are:

- the viscosity of the discharge print paste
- the amount of print paste applied (controlled by factors such as mesh size, squeegee setting, engraving depth and so on)
- steaming conditions (discussed in Chapter 8).

6.2.2 Problems in discharge printing

There are certain practical problems associated with the actual printing of discharge styles. One of the most difficult is the location of the design on the fabric. This is because the print pastes are often almost colourless and, when applied to a dark ground, are virtually invisible, especially in roller printing with the machine running at speed. The incorporation of white pigment improves visibility; fugitive, contrasting sighting colours help, as do fluorescent agents used with ultraviolet lights. This is perhaps an inevitable difficulty of the discharge style, and one reason why the resist approach may be preferred.

Controlled rapid drying of discharge prints is imperative if loss of reducing agent is to be minimised. This may mean wrapping the first drying cylinders to prevent boiling and, on the other hand, the use of hot-air blowers to accelerate drying on hand-screen tables.

Another problem encountered is that of ‘facing’ or ‘scumming’, which is due to partial discharge of the unprinted areas of the dyed ground. This occurs mainly in roller printing and arises if the thin film or ‘scum’ of discharge paste left on the unengraved surface of the printing roller is transferred to the fabric. In subsequent processing, the full bloom of the ground colour is lost. The reductive atmosphere existing in the steamer can similarly affect the dyed ground. These problems are avoided by meticulous attention to the basic printing techniques – factors such as careful maintenance of doctor blades and correctness of engravings – and by the application to the fabric before printing of a mild oxidising agent, such as sodium nitrobenzenesulphonate or sodium chlorate, which is preferentially reduced by the reducing agent and thus protects the dyed ground. Since such mild oxidising agents inhibit undesired reduction, some are referred to as ‘resist salts’, but should not be confused with resisting agents.

6.3 APPLICATION PROCEDURES IN DISCHARGE PRINTING

The application of these general principles to specific examples of discharge printing on various substrates can be illustrated through a selection of recipes and processing recommendations.

6.3.1 Vat discharges on cellulosic fibres

The coloured ground is applied using selected azoic, direct or reactive dyes, while the illuminating colours are selected vat dyes. When considered necessary, the dyed ground is prepadded with 10 g l^{-1} ‘resist salt’ and dried, to prevent fading. After printing and drying the prints are steamed for 5–8 min at 102–104 °C in an air-free steamer. Washing and aftertreatment are carried out immediately, preferably in an open-width washing range, the first rinse being cold and the second hot.

When printing vat head-colour discharges, the first boxes of the washing range are used for oxidation of the vat dye. Initially the goods are washed in cold water with overflow and then oxidised at 40–50 °C with a suitable oxidising agent, such as hydrogen peroxide. Hot soaping is then carried out with additions of suitable detergents and soda ash, if necessary. The formulations used are shown in Table 6.1.

Table 6.1 Formulations for stock pastes/g kg^{-1}

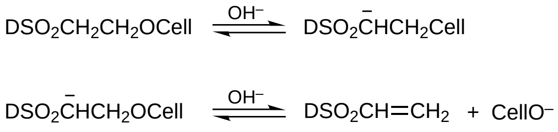
	1	2	3	4	5	6
CI Reducing Agent 2	100–200	100–200	120	200	200	200
Glycerine	50					
Soda ash		50–100				
Caustic soda (38 °Bé)				50	175	200
Anthraquinone paste		20				
Leucotrope W conc.					80	
Cold water	200	140	280	150	120	20
Thickener[a]	600	600	500	500	400	400
Fluorescent brightener	5		5		5	5

[a] Generally guar/starch ether blend; for whites and fine definition, blends of crystal gum with high-solids starch derivatives, such as Diatex SL (Diamalt), are sometimes required

Notes

1. Formulations 1, 3, 5 and 6 are typical for white discharges. The Leucotrope W should not be used in coloured discharging as it can adversely affect the illuminating vat colour. It is also desirable to add a pigment white to the discharge paste to give the best possible contrast; for example, 80–100 g kg^{-1} titanium dioxide is often used. When discharging direct dyes, formulation 1 can be used, whilst formulation 2 is typical for an azoic discharge. Formulations 3–6 are used for discharging reactive dyeings, vinyl sulphone dyes being especially important, as the bond with the fibre can be hydrolysed in the presence of caustic soda. The severity of the discharge increases from formulation 3 to formulation 6.
2. To obtain a coloured discharge, it is normal to add vat dyes to the formulations indicated in the table (formulations 2 and 4). As can be observed, the formulae are very similar to those normally used for printing ‘all-in’ vats. In discharge printing, however, the reducing agent has to destroy the ground dye as well as to reduce the vat dye, so in some cases additional reducing agent may be required. Other adjustments from the standard formulation are made to prevent halo formation. The amount of glycerol, which is hygroscopic, may be cut down and it is normal to use soda ash, which is less hygroscopic than potash.
3. With reactive dyes, the discharge can be achieved either by splitting the chromophore or by splitting the covalent link with the fibre. In the former case, which occurs under neutral or weakly acid conditions, discoloration of the white discharge can be instigated by reoxidation of the dye fission product, which is still linked with the fibre. Therefore, for permanent white discharges, it is advisable to use reactive dyes whose link with the fibre can be broken, thus leaving no linked residue. Vinyl sulphone reactive dyes are particularly suitable in this application as their ether linkage with the fibre can be broken by hydrolysis under strongly alkaline conditions. This is shown in Scheme 6.6.

With regenerated cellulose, it should be borne in mind that the alkalinity should be controlled so as not to affect the physical properties of the fibre.



$$DSO_2CH_2CH_2OCell \xrightleftharpoons{OH^-} DSO_2\overset{-}{C}HCH_2Cell$$

$$DSO_2\overset{-}{C}HCH_2OCell \xrightleftharpoons{OH^-} DSO_2CH{=}CH_2 + CellO^-$$

Scheme 6.6

6.3.2 Pigment-illuminated discharges

These are applied to cellulosic substrates dyed with selected azoic, direct or reactive dyes, the illuminating colours being selected pigments. A sulphoxylate discharging agent is used (CI Reducing Agent 4 or 6). The fabric is dyed using conventional methods with dyes selected as being dischargeable.

Preparation of the dyed ground fabric is carried out by padding with a mild oxidising agent. This helps to prevent the formation of haloes around the printed areas. Mild oxidising agents based on sodium nitrobenzenesulphonate are commonly used at concentrations of between 5 and 30 g l^{-1}.

There are potentially two printing systems, one of which is based on an emulsion system with white spirit. Nowadays, however, for environmental reasons a spirit-free thickener system would normally be employed, based on a colloidal thickener or a synthetic thickener of high stability to electrolyte (Recipe 6.1).

Fixation and finishing of the prints

After printing and drying the fabric is steamed for 5–10 min in saturated steam to facilitate the discharge. Thermosoling for 5 min at 150 °C is carried out to fix the pigment head-colours. The prints are then rinsed cold and soaped at 50 °C with nonionic detergent, followed by a further rinse. Washing-off is necessary to ensure brilliant prints with optimum fastness, which do not contain discharge decomposition products.

6.3.3 Discharges on wool and silk

The coloured ground is applied using selected acid or reactive dyes, while the illuminating colours are selected basic, acid or (for silk only) disperse dyes (Recipe 6.2). The print pastes indicated are very general formulations and the actual compositions used are highly dependent upon local factory conditions.

Discharge printing of wool and silk is a very specialised form of printing, with substantial add-on value in terms of profitability being a key consideration. Due to the high fabric value, the principle of ‘right first time’ should apply. Probably the principal European markets for this form of printing are Italy and France; the only other significant world contender is Japan.

One of the limiting factors in this process is the small number of dyes which can be used as illuminating colours with good fastness due to the requirement that they must be stable in the presence of reducing agent [4]. The most popular reducing agent used is CI Reducing Agent 6, although the paste form of CI Reducing Agent 12 is also used.

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Recipe 6.1

Emulsion system

Stock paste	(per kg)	Print paste	(per kg)
CMC[a] thickener	75 g	Pigment	25–70 g
Emulsifying agent	10 g	Stock paste	*x* g
Water	115 g	Zinc formaldehyde sulphoxylate	50 g
Urea	50 g	Diammonium phosphate (1:2)	25 g
Acrylic binder	100 g		
White spirit	650 g		

White-spirit-free system

Discharge paste	(per kg)
Pigment	27–70 g
Bean flour thickener (low solids, nonionic, acid- and electrolyte-resistant)	400–500 g
Acrylic binder	110–175 g
Glycerol	15 g
Defoamer	5 g
Zinc formaldehyde sulphoxylate/bean flour thickener (1:1)	100 g
Diammonium phosphate (1:2)	25 g
Water or thickener	x g

[a] Carboxymethylcellulose

Notes

1. This process is used to produce crisp and brilliant coloured discharges on dyed grounds that are dischargeable under neutral or acid conditions. Not all pigments are suitable for this process and nondischargeable ones should be selected.
2. Pigment concentrations must not be too low (in general, not less than 10 g kg^{-1}), as the reducing effect of the reducing agent could have a detrimental effect on the shade. Shading of head-colours with low amounts of pigment should also be avoided for the same reason.
3. To optimise the pigment fastness, the amount of acrylic binder should be increased with increasing amounts of pigment used.

CI Reducing Agent 2 can be used in combination with zinc oxide, which behaves as a pigment white and a buffer [5].

After printing the fabric is dried as quickly as possible and steamed with minimum delay for 10–20 min at 100–120 °C. This is followed by a cold rinse, soaping at 50 °C, a warm rinse, and then finally a further cold rinse.

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Recipe 6.2

	White discharge	Coloured discharge
Thiodiglycol	40 g	40 g
Hot water	100 g	200 g
Thickener	500 g	500 g
Zinc formaldehyde sulphoxylate (CI Reducing Agent 6)	100–150 g	100–150 g
Titanium dioxide (1:1)	75 g	
Discharge-resistant dye		20–40 g
Sodium *m*-nitrobenezenesulphonate		5–20 g
	1000 g	1000 g

6.3.4 Discharges on secondary cellulose acetate

The coloured ground is applied using selected disperse dyes, while the illuminating colours are selected basic, vat or disperse dyes (Recipe 6.3).

The fabric is prepadded with resist salt (10 g l$^{-1)}$ and dried, then printed, dried and steamed at atmospheric pressure for 20 min. It is rinsed well and then soaped at 50 °C. For vat-colour discharges, after cold rinsing, the fabric is treated with hydrogen peroxide (35%; 5 ml l^{-1}) at 50 °C to oxidise the vat dye, rinsed and dried.

6.3.5 Discharges on cellulose triacetate

The coloured ground is applied using selected disperse dyes, while the illuminating colours are selected vat, disperse or basic dyes (Recipe 6.4). Ground and illuminating dyes are fixed by high-temperature fixation; reduction clearing is the preferred aftertreatment. After printing and careful drying, the goods are steamed for either:

- 20–30 min at atmospheric pressure, or
- 20 min at 70 kPa (10 lbf in^{-2}) excess pressure, or
- 6–8 min at 170 °C (high-temperature steam).

After steaming, a cold rinse is followed by soaping at 50 °C and rinsing. If a vat head-colour is being printed then the leuco compound must, of course, be oxidised in the usual way.

6.3.6 Discharge and discharge-resist processes on polyester fibre

The coloured ground is applied using selected disperse dyes, while the illuminating

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Recipe 6.3

White discharge

Thiourea dioxide	100–200 g
Thickener (crystal gum, gum arabic, etc.)	500 g
Thiodiglycol	50 g
Water	100 g
	1000 g

A coloured discharge is obtained by adding disperse, basic or vat dyes to the above paste.

Notes

1. If very bright head-colours are required basic dyes can be used, but their fastness properties are limited on this fibre.
2. Nondischargeable disperse dyes are more often used than vat dyes for head-colours, to avoid the extra process of oxidation. The largest range of suitable disperse dyes stable to reducing agent is available when tin(II) chloride is used; as printers prefer not to use tin(II) chloride, however, a rather yellowish colour is often obtained. Thiourea dioxide is the most acceptable reducing agent. In practice formaldehyde is often added (50 g kg^{-1}) as more stable colours are thereby obtained.
3. Blends of diacetate and nylon can be discharged in the same way, but dyeings on nylon are more difficult to discharge than those on diacetate, and the efficiency of the discharge is reduced with increasing proportions of nylon in the blend.

Recipe 6.4

	White discharge	Coloured discharge
Thiourea dioxide	100–150 g	100–150 g
Thickener	500 g	500 g
Thiodiglycol	50 g	50 g
Water	100 g	100 g
Discharge-resistant dye		*x* g
Carrier		20 g
	1000 g	1000 g

Notes

1. Discharge of dyeings on triacetate is more difficult than on secondary acetate as the fibre is more hydrophobic and more highly crystalline. It is more difficult for the reducing agent to penetrate the fibre and destroy the dye, and subsequently the reduction products are difficult to remove. This accounts for the relatively severe conditions used at all stages of processing. Due to the problems encountered, a discharge-resist style is often preferred, as described overleaf for polyester substrates.
2. On triacetate/nylon blend fabrics the above recommendations apply, but with increasing amounts of nylon, satisfactory results are more difficult to obtain.

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colours are selected discharge-resistant disperse dyes. The discharging agent can be either a reducing agent or an alkali.

Dyes that have diffused into polyester fibres in conventional dyeing are virtually impossible to discharge, because the hydrophobic properties of polyester make penetration of the reducing agent and removal of the reduced disperse dye extremely difficult. Results obtained are not acceptable commercially except for lightweight fabrics. Consequently the discharge-resist process was developed.

Polyester fabric is impregnated with dischargeable disperse dye, by pad mangle or lick roller, and dried at low temperature to keep the dye on the fibre surfaces. Discharge pastes containing CI Reducing Agent 6 or tin(II) chloride are printed on to the fabric and the dye is destroyed during drying and subsequent processing (Recipe 6.5). The safest approach is low-temperature (102 °C) steaming, which will not fix the ground colour, followed by a high-temperature fixation of ground and illuminating dyes.

An alternative method is to produce a discharge-resist effect using alkali on disperse dyes containing diester groups [6]. These groups hydrolyse in the presence of alkali to produce a water-soluble carboxylate salt (Scheme 6.7). The soluble sodium carboxylate form has no affinity for polyester. In practice, the diester disperse dye is padded on to the fabric, low-temperature dried and then overprinted with a print paste containing alkali. As with the process involving a reducing agent rather than alkali, the fixation is with high-temperature steaming followed by a reduction clear process.

$$\mathrm{Dye{-}N(R_1COOR_2)_2} \xrightarrow{\mathrm{NaOH}} \mathrm{Dye{-}N(R_1COO^-)_2} \longrightarrow \mathrm{Dye{-}N(R_1COONa)_2}$$

Scheme 6.7

A variation, apparently a resist method but in fact a discharge-resist technique using diester disperse dyes, was developed in 1980 [7]. This process uses the polymerisation properties of sodium silicate solutions of differing pH values. In the process, the coloured illuminant is locally polymerised when in contact wet-on-wet with the ground shade, which contains the disperse dye diester and a nonvolatile acid (Recipe 6.6) [8]. The sodium silicate in the illuminated head-colour is of a specific grade (ICI Mond Division grade 0100) to provide maximum effectiveness.

For the best definition, the fabric is dried as quickly as possible, and is fixed in high-temperature steam for 6–8 min at 165–175 °C. After cold-water rinsing a hot alkaline reduction is carried out, followed by rinsing in hot and cold water.

Discharge on dyed lightweight polyester

With the development of lightweight polyester fabrics, problems were encountered using the conventional discharge-resist styles concerning the printing of fine lines,

Recipe 6.5

Pad liquor for ground	
Disperse dye (dischargeable)	*x* g
Water at 20–30 °C	*y* g
Thickener (locust bean ether)	500–100 g
Wetting agent	2 g
Resist salt (1:2)	30 g
	1000 g

	With reducing agent	With alkali
White discharge paste		
Locust bean ether thickener	500 g	500 g
Zinc formaldehyde sulphoxylate	80–150 g	
Caustic soda solution (38 °Be)		50–80 g
Discharge-stable FBA		5 g
Carrier	10 g	
Polyethylene glycol (r.m.m. 300–400)		50–80 g
Glycerol		5–80 g
	1000 g	1000 g
Illuminated discharge paste		
Discharge-resistant disperse dye	*x* g	*x* g
Water at 40 °C	200 g	200 g
Locust bean ether thickener	500 g	500 g
Zinc formaldehyde sulphoxylate	60–120 g	
Polyethylene glycol (r.m.m. 400)		50 g
Urea	20 g	
Carrier	10 g	

Notes

1. Tin(II) chloride may be used as an alternative to CI Reducing Agent 6.
2. Formaldehyde (methanal) is incorporated to stabilise the reducing agent after printing, but before steaming.
3. Urea has been found to protect some discharge-resistant dyes, especially the anthraquinone pinks and blues, from attack by the reducing agent.
4. To prevent diffusion of dye into the fibre before discharge can occur, low-temperature steaming should precede fixation. Of the three alternative methods described below, the first two are to be preferred. The third is used when only a high-temperature steamer is available.
    - (a) Initially, to destroy the dischargeable dye, the fabric is steamed for 5 min at atmospheric pressure. The pressure is then raised to 140 kPa (21 lbf in^{-2}) and steaming carried out for 20 min to fix the discharge-resistant illuminating colours and the coloured ground.
    - (b) Steam for 5–8 min at atmospheric pressure in saturated steam and then for 6–8 min at 175–180 °C in superheated steam.
    - (c) Discharge and fix in one high-temperature steaming operation for 6–7 min at 175–180 °C.

Recipe 6.6

Print illuminant	
Thickener	500–600 g
Glycerine	60–80 g
Polyethylene glycol (r.m.m. 300)	60–80 g
Sodium silicate	160 g
Alkali-stable FBA (white only)	5–15 g
Alkali-stable disperse dye	*x* g
Water	*y* g
	1000 g

Print ground	
Sodium alginate thickener	350–500 g
Citric acid (to pH 4.5)	5 g
Diester disperse dye	*x* g
Water	*y* g
	1000 g

levelness and colour migration. As a result a new process was introduced based on the alkali-dischargeable diester disperse dyes and two auxiliary products, Zetex PN-AD (Zeneca) (a blend of ethoxylated products and polyols) and Zetex PN-DG (Zeneca) (based on an ethoxylated product) [8]. These products are said to provide a synergistic auxiliary combination which makes the new process possible. With the use of Wyoming bentonite in blends with conventional thickeners, fine lines can be obtained in the design. Thickeners containing sodium alginate are not recommended.

The lightweight fabric is dyed conventionally using recommended diester disperse dyes and after washing-off is stentered at low temperature to remove creases. Printing is carried out according to Recipe 6.7.

Recipe 6.7

	White	Coloured
Thickener	400–600 g	400–600 g
Matexil PN-AD (Zeneca)	120–200 g	120–180 g
Matexil PN-DG (Zeneca)	60–100 g	60–80 g
Sodium carbonate	60–80 g	60–80 g
Alkali-stable FBA	5–15 g	
Alkali-stable disperse dye		*x* g
	1000 g	1000 g

Fixation and simultaneous discharge of the ground shade is carried out by steaming for 6–8 min at 175–185 °C, followed by a washing process incorporating a reduction clear. This process is dependent on fabric dyeing and fabric construction, and it is essential to perform preliminary trials before beginning bulk production.

6.3.7 Discharges on nylon

The coloured ground is applied using selected acid, disperse, basic or direct dyes. The illuminating colours are selected acid, direct or basic dyes, and the discharging agent used is zinc formaldehyde sulphoxylate (CI Reducing Agent 6) (Recipe 6.8).

After printing and drying, steaming is carried out for 10–30 min at 102 °C, and the prints are then rinsed and soaped at 50 °C.

Recipe 6.8

Dye	*x* g
Thiodiglycol	20–40 g
Hot water	200 g
Crystal gum solution (1:2)	500 g
Zinc formaldehyde sulphoxylate (added after cooling)	100–200 g
	1000 g

Notes

1. Basic dyes are often used for blue ground colours.
2. Disperse dyes have limited light and wet fastness properties.
3. An addition of zinc sulphate should be made for white discharges.

6.3.8 Discharges on acrylic fibres

The coloured ground is applied using selected dischargeable basic dyes, while the illuminating colours are nondischargeable basic dyes. The discharging agent may be a sulphoxylate or tin(II) chloride (Recipe 6.9).

6.3.9 Discharges on polyester/cellulose blends

The direct printing of polyester/cotton blend fabrics with mixtures of disperse and reactive dyes presents problems (section 5.9.2) because of the low dye fixation levels obtained and problems of staining during the washing-off process. Discharge styles on

Recipe 6.9

White discharge

Crystal gum (1:3)	200 g
British gum (1:1)	200 g
Water	200 g
Fixation accelerator (normally organic compounds containing nitro groups)	30 g
Sulphoxylate	100–200 g
Potassium thiocyanate	0–50 g
Fluorescent brightener (stable to discharge)	5 g
	1000 g

Colour discharge

Basic dye	*x* g
Water	200 g
Locust bean gum ether (10%)	400 g
Fixation accelerator (normally organic compounds containing nitro groups)	20 g
Tin(II) chloride (1:1)	100–180 g
Tartaric acid or citric acid	10 g
Potassium thiocyanate	0–50 g
	1000 g

After printing and drying, the fabric is steamed for 20 min at 20–40 kPa (3–6 lbf in^{-2}) or 30 min at atmospheric pressure. After steaming, the prints are rinsed in cold water and then treated for 20 min at 40 °C with 1 ml l^{-1} ammonia (25%) and 1 g l^{-1} sodium hydrosulphite. This is followed by a further rinse at 40 °C and soaping in a fresh bath at 60–70 °C. Finally the prints are rinsed and dried.

Notes

1. Sulphoxylate is used only for the white discharge, as it is too powerful for the basic dyes employed as illuminating colours. Even with a white discharge careful control of the sulphoxylate must be exercised, otherwise haloing will result.
2. Excess fixation accelerator must not be used as this can also lead to halo formation; if pressure steaming is carried out the accelerator can be omitted. The potassium thiocyanate is a swelling agent for the acrylic fibre and has been found to give superior results, even in the presence of accelerator.
3. The washing-off procedure is critical for white discharges as the products of the discharge are not easily removed and oxidation in air can lead to tinting of the whites.

polyester/cotton have therefore been especially difficult. As in the case of 100% polyester substrates, a discharge-resist approach must be taken.

If pigments are used as illuminating colours, with a potential acid catalyst to crosslink the pigment binder, zinc formaldehyde sulphoxylate must be used as the

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reducing agent. Experience shows that extreme care must be taken in washing-off to prevent unfixed disperse dye from staining the binder film.

If a mixture of vat and discharge-resistant disperse dyes is used, the problem is that the alkaline conditions required for fixing the vat dye illuminating colours produce large colour changes and low colour yields of the disperse dyes.

The availability of alkali-dischargeable disperse dyes has provided new possibilities. Used with selected vinyl sulphone reactive dyes, which are not fixed in the presence of sulphites, white discharges are possible. Coloured discharges can also be obtained by adding alkali-resistant disperse dyes and chlorotriazine-type reactive dyes that are fixed by alkali in the presence of sulphites. Alternatively, reactive dyes that are not fixed under alkaline conditions can be used for the dischargeable ground [9].

The polyester/cellulose fabrics have not found a commercially significant place in the discharge styles, cotton being technically much easier to discharge. Cotton is also perceived by the fashion industry to be preferable to polyester/cellulose blends.

6.4 RESIST PRINTING

Resist or reserve printing is related to discharge printing in that the end-results are often indistinguishable. The resist style, however, offers the advantage that dyes of great chemical stability, which could not be discharged, can be resisted to give prints of high fastness standards.

The justification for both styles lies in the aesthetic appeal of a white or coloured pattern on coloured grounds, an effect that very often could not be reproduced by any other technique. The difference, therefore, between discharge and resist printing is not one of appearance, but of process. In discharge printing, the discharging agent is applied to the fabric after it has been dyed and the dye in the printed areas is destroyed during subsequent processing. In resist printing, the resisting agent is printed on to the undyed fabric and effectively prevents the fixation or development of the ground colour, which is subsequently applied by an appropriate ‘dyeing’ technique, such as dyeing, padding or overprinting. The result can be either a white resist or a coloured resist, where a selected dye or pigment is added to the resist paste and becomes fixed to the fibre during subsequent processing.

Virtually every class of colorant is capable of being resisted, as is borne out by reference to older publications on textile printing [1]. Many of the techniques they describe are too complex and time-consuming to be of commercial interest today, but they do illustrate the wide scope of the style, with the proviso that it has little application to synthetic-fibre fabrics.

The resisting agents employed, then as now, function either mechanically or chemically or, sometimes, in both ways.

The mechanical resisting agents include waxes, fats, resins, thickeners and pigments, such as china clay, the oxides of zinc and titanium, and sulphates of lead and barium. Such mechanical resisting agents simply form a physical barrier between the fabric and the colorant. They are mainly used for the older, coarser and, perhaps, more decorative styles in which breadth of effect and variety of tone in the resisted areas are of more importance than sharp definition of the pattern. A classical, and nowadays almost unique, example of a purely mechanical resist is to be found in the batik style, using wax applied in the molten state. In a true batik the wax is applied by hand, but the process has been developed and mechanised for the production of those styles which now come under the general heading of 'Africa prints'. It is not possible to apply an illuminating colour with a wax resist but, after removal of the wax, another colour can be printed within the resisted area. These styles often fall outside the experience of most commercial printers and will be dealt with in more detail in section 6.5.1. A mechanical resist is usually used in conjunction with a chemical resist, so improving the overall effect.

Chemical-resisting agents include a wide variety of chemical compounds, such as acids, alkalis, various salts, and oxidising and reducing agents. They prevent fixation or development of the ground colour by chemically reacting with the dye or with the reagents necessary for its fixation or formation. The actual choice of chemical-resisting agent depends, therefore, on the chemistry of the dye being used and its fixation mechanism. Consequently, as in discharge printing, a working knowledge of the relevant chemistry is necessary when choosing effective resisting agents.

A classical example of the style, using indigo for the ground, illustrates a combined mechanical- and chemical-resist effect. A typical resist paste to give a white effect would contain china clay, a copper salt, a high-solids thickener (British gum or gum Senegal) and, possibly, tallow. Before printing, the fabric would be pretreated with starch and calendered, to give a flat surface upon which the resist print would form a more perfect protective cover. After printing, the goods would be thoroughly dried to consolidate the resist barrier. The ground would then be dyed by dipping the fabric into the indigo vat as many times as required to produce the desired depth of blue. The protective action of the resist paste would be partly due, in this case, to its oxidising properties, which would have the effect of throwing the indigo out of solution before it could reach the fibres. The insoluble deposit so formed would reinforce the mechanical-resist effect of the china clay, thickener and tallow. The process is completed by oxidation of the indigo and washing to remove thickener, surface dye and chemicals.

Resist print pastes that contain a high proportion of insoluble mechanical-resisting agents impose certain restrictions during the printing process. In copper-roller printing, such print pastes are apt to 'stick-in' in the engraving, especially in very fine patterns, and to ensure good results a brush furnisher is indispensable in keeping the engraving clean. In screen printing it is important to ensure that the solid particles are not coarse enough to block the screen mesh. It is, therefore, customary in this case to strain the print paste through a sieve which has a finer mesh than that of the actual printing screen.

Not only must a resisting agent be able to prevent the fixation of the ground colour, but it must also be capable of surviving the actual dyeing process. It is therefore preferable to use materials that are not too readily soluble in water and to modify the dyeing process. Pad application of dye reduces the time of contact and therefore the bleeding of soluble resist agents.

Nip padding (Figure 6.1) is in fact usually preferred to immersion (slop) padding. Some thickening of the pad liquor may be necessary to increase the volume of liquor carried on to the fabric. The temperature of the dye solution must also be kept low, and it is often necessary to dry the fabric immediately after application of the dye. Use of an engraved cover roller, known as overprinting, provides an alternative to nip padding and one stage in the process may be eliminated if drying of the resist is not essential.

6.4.1 Resists under aniline black

Many of the points considered above are illustrated in the process of resist printing under aniline black. This particular colorant is formed on cellulosic materials by the

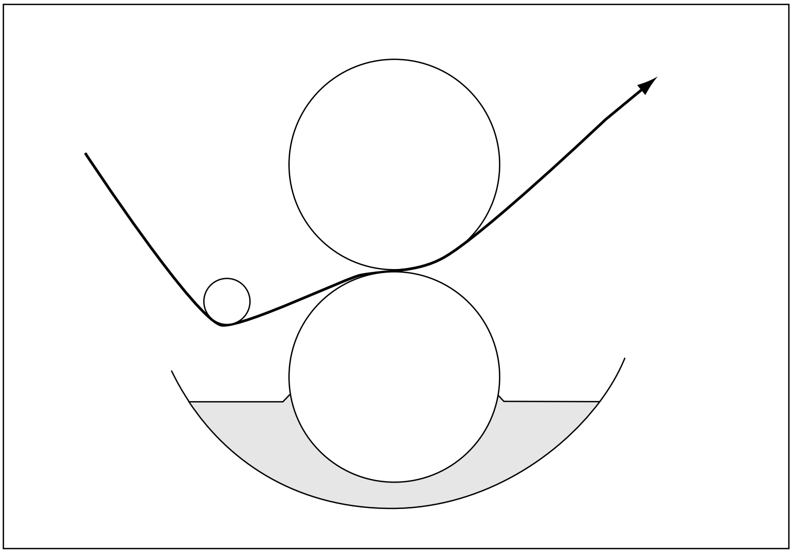

Figure 6.1 Nip padding mangle

oxidation of aniline; it is virtually indestructible and most certainly cannot be discharged. Unfortunately, some loss in fibre strength is incurred, due to oxidation of the cellulose. Nevertheless, the quality of the black so produced, its fastness properties and its low cost make it a highly desirable ground colorant for resist effects.

The first attempts in this direction were based on the fact that aniline black is an oxidation product; the earliest resists consisted of reducing agents. But it was later shown that the presence of mineral acid, either free or produced at a later stage during steaming by dissociation of an unstable salt, was equally essential in the development of the black. Alkaline salts and other neutralising agents can, therefore, be employed either alone or in combination with reducing agents, to prevent the formation of the aniline black in the printed areas.

A typical stock paste for resist printing of aniline black contains 125 g kg^{-1} sodium acetate, 125 g kg^{-1} zinc oxide paste (1:1), 10 g kg^{-1} sodium thiosulphate and a thickener based on low-viscosity alginate. This could be used to give a white resist; alternatively, a suitable dye could be added to produce a coloured resist. A typical aniline black liquor is prepared by mixing together the three solutions specified in Recipe 6.10 and bulking to 1 l. The actual process can then proceed in any of several different ways.

Recipe 6.10

1.	Aniline hydrochloride	80 g
	Aniline oil	5 g
	Tragacanth thickener (6%)	50 g
	Water	250 g
2.	Potassium ferrocyanide	50 g
	Water	200 g
3.	Sodium chlorate	30 g
	Water	200 g

Underprinting

The resist paste is printed on to the fabric and then overprinted with the black, which has been suitably thickened for printing. After drying the print is steamed to develop the black and oxidation is completed by an aftertreatment with hot acid dichromate solution. Such an aftertreatment also serves to reoxidise vat dyes used as illuminating colour.

Nip padding

The aniline black liquor is applied to preprinted and dried material by means of a roller which runs in the thickened aniline black liquor and forms a nip with a second roller (Figure 6.1). A slop padding process is not recommended, as the soluble resisting agents tend to bleed and so cause haloing. Development of the black is carried out as indicated above.

Discharge-resist or afterprint process

In spite of its name this is nevertheless a resist process, but it is so called because the aniline black liquor is applied to the fabric before the resist paste. This is a technique requiring very close control, but it is usually preferred for high-class work because when employed correctly it yields sharper and brighter colour effects than can be obtained from the preprint processes.

The importance of careful control over every stage of the process cannot be overemphasised. The aniline black liquors must be freshly prepared and, as in the discharge-resist style on polyester, drying of the padded material must be carried out with great care. On emerging from the drying machine, the goods ought to be light yellow without a trace of green. If they have been so far overdried as to become greenish they are unsuitable for light-coloured and white resists because the green is undischargeable.

After drying, the padded goods should be cooled to prevent oxidation and printed as soon as possible. After printing, overdrying must again be avoided and steaming, to develop the black, should be carried out without delay. The steam should not be too moist, as otherwise the colours are apt to run and the whites can become discoloured. The whole process from start to finish must be carried out without undue delays and with careful control at every stage.

As already indicated, coloured resists under aniline black can be obtained with vat dyes where the inherent alkaline and reducing nature of an ‘all-in’ print paste provide the desired resist effect.

Reactive dyes can also be used by fixing the print by one of the various two-phase processes after the black been developed. Pigments may be used to illuminate the resist, in which case a suitable quantity of pigment binder would be added to the print paste, together with zinc oxide, magnesium carbonate and sodium acetate. Such print pastes can be used to give both preprint and afterprint resists.

6.4.2 Resists under reactive dyes

Due to the wide range of available colours, brightness and good all-round fastness properties, reactive dyes are now very popular both for direct printing and for plain dyeings. Discharge printing can be carried out successfully on selected reactive grounds, particularly those produced with dyes of the vinyl sulphone type. There are difficulties with blue and turquoise dyes which are not azo compounds, however, and this makes the use of resist processes necessary.

Most reactive dyes can only be fixed on cellulosic fibres in the presence of alkali. Consequently nonvolatile organic acids (such as tartaric or citric acid) and acid salts (such as monosodium phosphate) may be used as resist agents for preprint resists under such dyes. Hence, the thickeners used should be acid-resistant. Hydroxyethylated and methylhydroxyethylated cellulose ethers, locust bean gum and tragacanth are suitable for this purpose. When printing with deeply engraved rollers the concentration of acid- or alkali-binding substance can be kept low, but an increase in the concentration may be required if sharp effects are to be obtained with shallow engravings. A typical preprint resist paste would have the composition shown in Recipe 6.11. The colourless resist print pastes may be made visible by tinting with a fugitive dye such as CI Acid Blue 1, or by adding a fluorescent brightener, which is detected with the help of a ultraviolet lamp.

Recipe 6.11

Citric acid	50 g
Thickener	600 g
Water to	1000 g

After the material has been printed and dried it is nip-padded, overprinted or padded with a solution of a high-reactivity reactive dye containing a minimum concentration of sodium bicarbonate. If the material is to be immersed in the dye liquor, it may be necessary to increase the acid concentration in the print paste to 80 g kg^{-1}. Long immersion times should be avoided for reasons already mentioned. Drying must follow immediately, then an appropriate fixation step, and washing.

A typical padding liquor is shown in Recipe 6.12. Certain alkali donors may be

Recipe 6.12

Reactive dye	20 g
Resist salt	7 g
Hot water	393 g
cooled to 40 °C and diluted with	
Cold sodium bicarbonate solution (3%)	500 g
Thickener	80 g
Water to	1000 g

employed instead of sodium bicarbonate, in which case the steaming time should be increased to 7–10 min to allow for adequate breakdown of such compounds and subsequent fixation of the dye.

An alternative preprint method for white resists, using a two-phase fixation process, can be carried out as follows:

1. Print the white material with acid-resist paste, and dry
2. Pad with a neutral dye liquor, and dry
3. Nip-pad the material with fixation liquor, fix, wash-off and dry.

The fixation liquor used for this method would be as shown in Recipe 6.13, and fixation is best carried out by steaming for 20 s.

An overprinting technique can also be employed to give white resists on a reactive pad dyeing. The material is first padded, using Recipe 6.14. After drying, the padded material is printed with an acid-resist print paste (Recipe 6.15). After printing, the material is dried carefully to avoid fibre damage. Fixation of the ground is carried out by any convenient two-phase process which would involve the application of an alkaline fixing liquid followed by steaming, or cold dwell, and the usual final wash-off and drying.

Very effective results can be achieved with a white pre-resist under overprints with reactive dyes. This can be done either with intermediate drying or by printing wet-on-

Recipe 6.13

Caustic soda (38 °Bé)	20 ml
Sodium sulphate (anhydrous)	200 g
Common salt	100 g
Water to	1000 ml

Recipe 6.14

Reactive dye	1–40 g
Water at 80–90 °C	300 g
Neutral thickener	50 g
Resist salt (1:2)	15 g
Lactic acid (50%)[a]	2 g
Water to	1000 ml

a Or 1 g tartaric or citric acid

Recipe 6.15

Citric acid (1:1)	200 g
Acid-resistant thickener	400 g
Water	400 g
	1000 g

wet. The acidic resist paste is made up as previously described and the overprint is based on a standard direct-printing recipe containing alkali. After the second printing, the goods are dried, then steamed to bring about fixation of the overprinted dye, and washed off as usual. A solids-rich thickener gives sharp outlines and should be used, particularly if the overprints are to be produced by printing wet-on-wet. In screen printing some of the acid-resist paste will be transferred from the fabric on to the underside of the following overprint screen. There it acts upon the acid-sensitive alginate thickener, precipitating it in the mesh of the screen as alginic acid. The screen, therefore, becomes blocked in these areas and actually assists the production of the desired effect. In roller printing, however, care should be taken to prevent the acidic print paste from being carried forward to contaminate the overprint paste, which would cause precipitated thickener to stick in the engraving. If necessary, one or more plain rollers can be inserted between the resist roller and the overprint roller as a precautionary measure.

Coloured resists under reactive dyes can be produced in several ways [10]. One of the most popular is to preprint the fabric with a pigment print paste containing an addition of acid to act as resist agent. The pigment binder should preferably be one that can be fixed by steaming. A typical stock paste will be made up as shown in Recipe 6.16. The actual print paste would be prepared from this stock paste by adding the requisite quantity of pigment. The sequence of operations would then be as follows:

1. Preprint with pigment paste containing acid
2. Pad with reactive dye, after intermediate drying, or overprint without drying
3. Steam for 2–10 min according to the reactivity of the dye used
4. Wash-off
5. Dry.

Recipe 6.16 uses an emulsion thickening system, but due to environmental legislation, restrictions as to the use of systems based on white spirit resulted in the promotion of

Recipe 6.16

Thickener (cellulose ether)	100 g
Emulsifier	8 g
Water	100 g
Pigment binder	120 g
White spirit	612 g
Tartaric acid (1:1)	60 g
	1000 g

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further developments using aqueous systems based on synthetic thickeners [11]. Prior to this, the synthetic thickeners used to prepare aqueous pigment thickeners were unacceptable as the acid required for the resist produced an unacceptable drop in viscosity.

Resists with Fast Colour Salts under reactive dyes can also be carried out, and give interesting results that exploit the economy and colour range of both classes of dye. When naphtholated fabrics are printed with Fast Colour Salts, alongside reactive dyes of the vinyl sulphone type, the reactive dye can be fixed by raising the alkalinity of the prepared fabric and by brief steaming after printing. The reactive print may be resisted to a greater or lesser extent by the acid in the Fast Colour Salt print in the areas where the two print colours meet or overlap. In many cases, the Fast Colour Salts contain so much alkali binder that the reactive dyes can be resisted completely. If not, the desired resist effect may be obtained by the addition of acid or acid salts. Naturally, the amount of acid or acid salt added must not be so high that the pH for the azoic coupling is significantly lower than the optimum value.

Half-tone effects under reactive dyes can be produced by mechanical and chemical methods. Such resists are obtained by, for instance, merely preprinting the material with a solids-rich thickener, which coagulates under the influence of the alkali in the reactive overprint. The resist effect can be emphasised by adding titanium dioxide or other white pigment to the resist paste. The reactive colour pastes which are to be partially resisted can be printed, wet-on-wet, on top of the resists and, after drying, the dye is fixed by a suitable two-phase process. If the reactive coloured ground is applied by a pad–steam process, then intermediate drying is necessary before the padding.

All-reactive resists

The wide colour range available makes the idea of the 'reactive resist under reactive ground' style particularly attractive, provided it can be achieved in a reliable manner [12]. One approach depends upon the fact that the fixation of vinyl sulphone-type reactive dyes can be prevented by the addition of sulphites, thiosulphates or thiourea [13,14]. The fixation of selected reactive dyes of the substitution reaction type is not affected by additions of these agents and they can therefore be used as illuminating head-colours. White- and coloured-resist pastes can be prepared by making 150 g kg^{-1} additions of the resist shown in Recipe 6.17 to standard stock pastes. The printed fabric can be overprinted, wet-on-wet, with a standard vinyl sulphone print paste. Drying is carried out below 120 °C and fixation brought about in saturated steam. The process is completed by the usual thorough washing. This process and other variants of the 'reactive under reactive resist' styles are summarised in Table 6.2.

Variant 1 is suitable for rotary-screen and roller printing but is not recommended for

Recipe 6.17

Sodium bisulphite (38 °Bé)	310 g
Sodium bicarbonate	500 g
Glyoxal (40%)	65 g
Water	125 g

Table 6.2 ‘Reactive under reactive resist’ styles

Overprinting wet on wet (variant 1)	Fixation of ground in one-step process (variant 2)	Fixation of ground in two-step process (variant 3)
Preprint white and coloured resists	Pad the ground with vinyl sulphone dyes and Remazol salt FD (sodium organic acid) (HOE)	Pad the ground with vinyl sulphone dyes (slightly acid liquor)
Overprint the ground wet-on-wet with vinyl sulphone dyes containing bicarbonate	Dry at 80 °C	Dry
Dry below 120 °C	Overprint the white and coloured resists Dry below 120 °C	Overprint the white and coloured resists Dry below 120 °C
Steam 6–8 minutes with saturated steam Wash-off	Steam 6–8 min with saturated steam Wash-off	Steam 6–8 min with saturated steam Fix ground by two-phase process Wash-off

Mixtures of vinyl sulphone and resist-stable reactive dyes

Variant 4A	Variant 4B
Print mixtures of vinyl sulphone and resist-stable reactive dyes Overprint white or coloured resists wet-on-wet Dry below 120 °C Steam 6–8 min with saturated steam at 120 °C Wash-off	Pad mixtures of vinyl sulphone and resist-stable reactive dyes Overprint monochlorotriazine dyes and/or Overprint vinyl sulphone dyes and/or overprint mixtures of vinyl sulphone and monochlorotriazine dyes Overprint white resists Steam 6–8 min with saturated steam at 120 °C Wash-off

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flat-screen printing because of problems related to this process, such as the pressing of the screen frame on the preprinted ground colours. The process does not give exactly the same effect as would be obtained if the ground was dyed, due to the difference in penetration.

Variant 2 produces the full dyed ground effect lacking in variant 1. Certain conditions must be maintained. In particular, the drying of the dyed ground must be carried out below 80 °C, as at higher temperatures the Remazol Salt FD would decompose and alkali would then partly fix the vinyl sulphone ground; a high-quality resist would then not be possible. Also the padded, unfixed fabric should not be stored for more than 24 h.

Variant 3 does not require the dyeing temperature to be limited because of slightly acidic conditions, and the fabric can be stored for longer periods. Two-phase steaming or two-phase cold-dwell processes can be employed, although there is a higher risk of mark-off during the cold-dwell process.

Variants 4 (A and B) are interesting for producing half-tone effects. Attractive multicoloured effects can also be obtained by mixing vinyl sulphone and monochlorotriazine dyes of different shades; for example, a vinyl sulphone yellow and a monochlorotriazine turquoise produce a green. On partially overprinting this combination with resist paste, a turquoise colour results.

An earlier approach made use of the very large difference between the rates of reaction of the dichloro- and monochloro-triazine dyes. Printing a dichlorotriazine dye with an addition of a colourless dichlorotriazine, but without alkali, followed by overprinting with a monochlorotriazine dye with minimum alkali, drying, steaming and washing can give effective coloured resists. In practice this approach was difficult and was not widely adopted.

When acid-fixing reactive dyes were used for the dyed ground, and were not fixed before printing, there was the attractively simple possibility of printing alkali only for a white discharge resist. The more stable alkali-fixing reactive dyes could be used for illuminating colours. This approach is not at present possible, however, as the dyes are no longer commercially available [9].

6.4.3 Vat resists under vat-dyed grounds

This is certainly not a widely used style, but it has been, and could be, used where the fastness properties associated with vat dyes are necessary. The material is first printed with a normal all-in vat print paste with addition of sodium thiosulphate. After steaming, to reduce the vat dye, the material is padded in a solution containing a vat leuco ester and sodium nitrite, followed by passage through a sulphuric acid solution. The alkali in the vat print neutralises the acid and the sodium thiosulphate is preferentially oxidised, preventing development in the printed areas. The goods are finally aftertreated in the normal manner prescribed for vats.

6.4.4 Resists under azoic colorants

A traditional style of clean whites and bright reds under navy blue (Variamine) grounds is economically produced entirely with azoic colorants.

The Variamine Blue salts couple with Naphtol AS (CI Coupling Component 2) less readily than all other diazo salts, and the reaction occurs at an acceptable rate only in the optimum pH range of 7–8 [15]. Thus it is not difficult to effect a resist by reducing the pH. A paste containing 50–100 g kg^{-1} of aluminium sulphate is printed on to naphtholated cotton, which is then dried and padded with Variamine Blue salt solution and allowed about 40 s air passage (or a short steaming) for coupling to take place; this produces a white resist on a navy ground. The aluminium sulphate reduces the pH to about 4, converting the naphtholate to the free Naphtol AS, which does not couple, and precipitating aluminium hydroxide, which acts as a physical resist. Naphtol AS is readily removed in the normal afterwashing, which is best preceded by a hot sulphite bath to destroy excess Variamine salt.

Any fast-coupling diazo salt could be printed, in excess, on to naphtholated fabric to give a coloured resist under the Variamine navy ground, because very little Naphtol AS would remain unreacted. Clean bright resists are only obtained, however, if no trace of blue is produced. By choosing one of the orange or red salts that couple most easily at pH 4–5 (CI Diazo Components 2, 6–9, 11, 34, 36 and 37), the required pH and resist effect can be obtained by adding aluminium sulphate. For example, the print paste shown in Recipe 6.18 might be used. Additional colours can be obtained with pigments or with solubilised vats, if an intermediate steaming is acceptable. In the latter case bisulphite can be used to resist the diazo coupling, and lead chromate to provide the oxidation in subsequent acid treatment.

Recipe 6.18

Fast Red Salt 3GL (CI Azoic Diazo Component 9)	80 g
Starch tragacanth thickener[a]	500 g
Aluminium sulphate (1:1)	100 g
Water	320 g
	1000 g

[a] Or hydroxyethylcellulose

It is not possible to produce resists under red azoics simply by pH control, but the use of phenylhydrazine *p*-sulphonic acid (Resist H, HOE) does give this possibility. The compound is printed on naphtholated fabric which is then overprinted, or dried and nip-padded, with one of a range of orange to bordeaux salts. Resist H reacts with the diazonium salt so rapidly that no coupling occurs and clean whites are obtained. Coloured resists are obtained by adding selected reactive dyes to the resist paste. Vinyl sulphone dyes are particularly suitable and should be used with sodium dihydrogenphosphate as a buffer. After printing and application of the Fast Colour Salt, it is recommended that fixation of the reactive dyes is achieved by the hot wet-fixation method. This provides an ideal start to the removal of unreacted coupling components in the subsequent open-width washing. Print pastes for these resists can be based on a stock paste prepared as shown in Recipe 6.19.

Recipe 6.19

Stock paste	
Resist H	200 g
Sodium hydroxide solution (37 °Bé)	100 g
Tylose H300 (powder)	30 g
Water at 70–80 °C	500 g
Tartaric acid (dissolved in 145 g water), added after cooling	25 g
Print paste	
Stock paste	400 g
Sodium dihydrogenphosphate	50 g
Tylose H300 (6% paste)	300 g
Reactive dye	0–80 g
Water to	1000 g

A specific example will illustrate the interesting possibilities this style presents. A fabric prepared with Naphtol AS is printed with a resist paste containing a Remazol yellow, then all-over printed (wet-on-wet) with a mixture of Fast Red Salt TR (CI Azoic Diazo Component 11) and Remazol Turquoise (Reactive Blue 21). In the yellow print areas the Resist H prevents formation of any red, and a bright green is produced. In the surrounding areas the red and turquoise produce an attractive brown colour. One printing run, drying and a wet-fixation process, therefore, gives a green resist under a brown ground, without the dark overlapping areas or white places that would be obtained by direct printing (unless the pattern fitting accuracy was perfect). Fees has discussed the general use of such economical and attractive styles [16].

6.4.5 Resist printing of wool

Over the years, various methods for resist printing wool have been investigated. Bell has reviewed some of these [4], of which two are of interest.

In practical terms, the chemical resist product Sandosperse R (S) is a reactive resist agent similar to a reactive dye, which is itself colourless. Bell and Lewis describe the reaction in which the resist agent reacts with the amino groups in the wool, blocking the reactive sites [17]. The resist also is complemented by anionic repulsion. In this process pale shades can be resisted to white, and varying effects are obtained with greater depth of shade.

Secondly, sulphamic acid used as a nonionic dye resist agent for wool was patented by Sandoz in 1955 [18]. Little progress was made until Bell *et al.* determined that the resist was effective against reactive dyes [19]. Sulphamic acid is used at a concentration of 150–200 g kg^{-1} together with similar quantities of urea in the print paste, which also incorporated thickener, nonionic wetting agent and antifoam. To prepare an illuminated colour, certain reactive dyes (covalent fixing) are added to the paste. After printing, thermofixing for 4–5 min at 150–160 °C is carried out to fix the sulphamic acid. Steaming follows for 30 min at 100–120 °C for fixation of the reactive illuminating colour. Full washing-off is carried out, including an ammonia wash at 70 °C for complete removal of unfixed dye, thus preventing subsequent cross-staining of unprinted areas during the final dyeing. This dyeing is carried out with selected reactive dyes from various ranges.

6.5 SPECIAL STYLES

This section is devoted to a selection of those printing styles which, although not now produced by the majority of commercial printing establishments, still have some interest and significance for specialised outlets. Some knowledge of the special techniques employed in the production of such styles leads to a deeper understanding and appreciation of the art of textile printing and stimulates the constant search for new effects.

Several related styles, still of considerable commercial importance, fall under the general heading of ‘Africa prints’.

6.5.1 Africa prints

The modern Africa print style is based on a popular selection made by African people from a large number of widely different textiles exported to that continent. Hence ‘Africa prints’ has become a collective term for various types of printed article which were, at some time, adopted by the African population for their tribal costumes. It is hardly possible to discuss Africa prints without some reference to their historical and geographical origins.

Some of the oldest Africa print styles have their origin in the tie-dyeing or Bandhana technique, which is a simple mechanical-resist process. How long this technique has been practised and how it came to Africa is outside the scope of this book, but the characteristics and designs produced by this method still have an influence on later African printing.

Another type of resist print is obtained by a mechanical resist, usually wax, to cover those areas of the fabric that are to be patterned, and then dyeing the fabric. This is known as the batik style and the wax is, of course, a true mechanical resist. Indonesia is generally regarded as the country of origin, but the Chinese too are thought to have used this method. In Egypt, wax resist prints were reputedly known as early as 1500 BC, and in South America relics of such prints were found to date back to the old Peruvian civilisation.

Which country is the true cradle of the wax printing method is still disputed, but the influence of the art of batik printing on the Africa print style is unquestioned, and the exquisite beauty of the prints that were produced by this method in different parts of the world has always been acknowledged. Today the Indonesian batiks are, perhaps, the most widely known and their influence can be traced in some of the patterned motifs encountered in Africa prints, motifs which are known to be South East Asian in tradition.

The Africans would appear to share with the South East Asians a gift for expressing their feelings in pictures and symbols and also a similar sense of colour. These are probably some of the reasons why such styles were readily accepted on the African continent when brought there by the Dutch and Portuguese traders from their South East Asian colonies. Although Indonesian in origin, many of the motifs found in these styles are now peculiar to the African continent, and it has become a truly African style. Nevertheless, traditional Indonesian batiks are still produced and a brief description of the processes involved forms a useful background against which the more up-to-date methods may be discussed.

An Indonesian printer may require as many as seven to eight days to produce a batik of a size sufficient for a sarong. The fabric is first scoured and kneaded with peanut oil or another vegetable oil to make it receptive to the print which should penetrate and adhere well. This treatment is also indispensable for the subsequent dyeing process, since it ensures satisfactory penetration and adsorption of the dye by the fibre. The oil was formerly removed by treating the cloth in a suspension of rice straw ash in water, but this process is now carried out with soda ash and has to be repeated several times.

The batik printer, usually a woman, sits cross-legged in front of the length of cloth, which hangs from a wooden or bamboo stand known as a Gawangan. The molten wax is applied to the fabric by means of Tjantings, that is, small vessels of calabash gourd or metal pierced by openings of various sizes, often fitted with small spouts. The worker pours the melted wax over those portions of the fabric which are required to remain uncoloured. Often the outlines of the pattern are first roughly sketched on the fabric before being drawn in wax, but experienced batik printers know their patterns by heart and draw them freehand. When one side is finished the fabric is held against the light and the pattern is drawn in wax on the reverse. The fabric is now ready for dyeing, the first colour generally being indigo. The dye recipes are traditional within families and many contain very peculiar ingredients, such as brown palm sugar, fermented cassava starch, various types of banana and even ground chicken meat.

After dyeing the wax must be removed from the fabric and this is done by mechanical treatment and by treating in boiling water. Sometimes alkali is added so as to form an easily removable emulsion. The whole sequence of wax application and dyeing operations is repeated as many times as are necessitated by the design of the article. A characteristic feature of a batik print is the appearance of fine veins of colour running irregularly across the reserved parts of the pattern. This is due to penetration of the dye liquor through cracks which have formed in the coating of wax.

Obviously, such a process could not cater for the many millions of metres of material that are required to be printed annually to African styles. Consequently, methods have been evolved to imitate the traditional batik styles by more up-to-date production methods.

Africa prints can be divided according to production techniques into the following groups:

- real wax prints
- Java prints
- green-ground prints
- imitation wax prints
- fancy prints.

Real wax prints

The prints found in this group are so called because the design is, indeed, produced by covering the patterned areas of the fabric with a wax resist and subsequently dyeing the areas left free. The resisting agent used is usually a rosin obtained from certain pine trees and, like wax, it must be applied in the molten state.

Special duplex machinery has been developed which prints both sides of the material. The printing is by engraved copper rollers which, together with the containers and other components associated with the rosin, are heated to keep it in the molten state. Immediately after printing, the fabric is quenched in cold water so that the rosin solidifies and the sharpness of detail is maintained.

The fact that the printer cannot dry the fabric in the normal way brings its own special problems during the subsequent dyeing processes. Moreover, since the dye most often applied is indigo, special precautions have to be taken when preparing the dyebath, to avoid removal of the rosin at the normal alkalinity. Consequently, the indigo is usually vatted with a zinc and lime recipe and dyed at room temperature. The characteristic marbling effect produced by fine lines in the resisted areas is ensured by deliberate cracking of the rosin print, either by passing through a pot-eye or by 'tumbling' the material in cold water, before the continuous dyeing stage.

After dyeing, but before going on to subsequent resisting and printing operations, the wax is partially or completely removed from the fabric by hot washing, depending upon the type of effect required. When removal is partial, spots of rosin are left on the fabric and resist the later colours. Such resist spots do not repeat exactly with the basic design, and this is considered to be a typical and valuable feature. Azoic colours are often used, both base printing and naphthol printing being practised. Reactive dyes are also used, printed as neutral pastes with subsequent wet fixation in hot alkaline liquors. The second, third and any other colours are almost exclusively printed by means of blocks or screens, with the colours fitted by hand into the original pattern because of the dimensional changes caused by washing and drying.

Mordant dyes usually accompanied indigo in classical real wax printing, but nowadays azoic colorants are widely used; they offer the same coloristic possibilities and are technically superior.

The characteristics of real wax prints can be summarised as follows. The basic pattern is dyed with indigo (tested by sublimation); the fabric displays a characteristic unprinted strip about 1 cm wide along each selvedge and an irregular marble or veined appearance (caused by the cracks in the wax resist coat) which does not occur in the normal pattern repeat. The indigo print shows the characteristic pale blue half-shadow on one side of the motif, which is reversed on the other side of the print (this arises because the original duplex wax print is never in exact register). As the dye penetration is good, it looks virtually the same on both sides. The handle is very soft, heavy and sticky; occasionally, the fabric has a lingering smell of rosin.

Real wax prints are inevitably very expensive, because of the number of separate processes. Attempts to imitate the style have therefore been frequently made. The real wax print is, of course, itself an imitation of the old batik prints, but of all the imitations, this is the one that comes nearest to the original article.

Java prints

The description 'Java print' is nowadays applied to a specific type of article which may have only a tenuous connection with Java. Typical of this type of print is a colour scheme consisting of brilliant dark green, lemon yellow, chocolate brown and golden yellow, although this can be varied to include, for example, pale blue or ruby red. Formerly, the design consisted of Javanese motifs, but today the term is essentially an indication of the colour scheme and the motifs are of only secondary interest. With a little expertise and knowledge almost any design can thus be made into a Java print.

The modern Java print has developed into a blotch print with one or two colours over a delicate filigree pattern. Originally, the filigree pattern was drawn in wax with the Tjanting, and the blotch print effect was obtained by dyeing the fabric with indigo or other natural dyes. In the modern Java print, the effect can be obtained by the use of a resist agent (Rapidamine Resist D, HOE), which is printed on to a Naphtol AS-G prepared fabric before overprinting with Rapidamine Blue G (CI Ingrain Blue 5) and other Fast Colour Salts.

The coloured resists are obtained by adding selected vinyl sulphone reactive dyes to the resist paste.

The Java print is a particular favourite in Africa and may be encountered throughout the entire continent, whereas other styles tend to be adopted individually by small populations or tribal units. Because of its general popularity, the Java print can be considered as a 'pan-African' style.

Green-ground prints

The green-ground print strongly resembles the Java print and is also essentially characterised by its colour scheme.

This article, which at one time played an important role in the African market, is produced by an elegant resist printing technique and is, coloristically, indeed a work of art. The Java print is generally considered to be the more beautiful of the two styles, however, and the green-ground print has now fallen into decline.

Imitation wax prints

The aim here is to imitate real wax prints without the lengthy wax resist printing procedure. Considerable ingenuity has been exercised to imitate the veining effects and other features of a real wax print by the use of engraved rollers and other modifications of a conventional printing process. These include duplex printing so that the veining effect appears on both sides of the fabric.

Another method is to print the veined effect on to the back-grey before it meets the actual fabric to be printed, so that marking-off occurs to give the desired effect on the reverse of the fabric. Another possibility is to print the veins in a second printing operation using a longer repeat.

Another characteristic of a real wax print that can be imitated is the half-shadow of indigo resulting from failure to fit the resist on the reverse face of the fabric. A carefully engraved additional roller is used to print the pale blue shadow on one edge of the motifs. This half-shadow effect is not due to bleeding of the indigo and must not be confused with the specific 'bleeder' style, described in section 6.5.2.

Fancy prints

The 'fancy print' style may, perhaps, be described as an Africa print whose pattern is composed of a motif that is particularly popular or contains a dominant colour that is currently much in demand. At first sight these prints have some, although very superficial, resemblance to true Africa prints, but generally they are produced with complete disregard of the characteristics of traditional Africa prints.

Any topical event, public occasion, inauguration, any political happening of nationwide importance, any new minister or president of state, or his birthday, may be regarded as important enough to be commemorated by the creation of a special fashion article incorporating a popular motif. These prints often display none of the characteristic features of wax prints.

6.5.2 Bleeder styles

This style, characterised by coloured haloes deliberately produced around the pattern, has recently been revived, following the introduction of several simple and economical techniques.

One technique uses mixtures of selected reactive dyes and Fast Colour Salts printed on fabric prepared with Naphtol AS. A thickener is chosen which coagulates on contact with the alkali in the prepared fabric, so that it releases a significant amount of water from the print paste. Part of this water and the reactive dye dissolved in it flows into the unprinted areas. The Fast Colour Salt couples almost instantaneously, and therefore produces sharp prints. Consequently, the reactive dye produces a halo around the mixed print produced by the combination of Fast Colour Salt and reactive dye. Cellulose ether thickeners are particularly suitable for this style, and the coagulating effect can be increased by the addition of salt to the impregnating bath, particularly salts of di- and poly-valent ions (Recipe 6.20). The addition of Leonil PAT (HOE) to the liquor improves the uniformity of bleeding of the reactive dye and gives a darker outline.

The colour specified in Recipe 6.21, for example, may be printed. Printing, drying and steaming then produces a brown print, resulting from a mixture of the red and the green, with a green halo.

In such styles, the greater the contrast of the halo the more impressive it appears. It is, therefore, an attractive proposition to add sufficient acid to the mixed reactive dye and Fast Colour Salt print paste in order to resist fixation of the reactive dye in the actual printed areas. If, for example, 30 g kg^{-1} of citric acid are added to the print paste in Recipe 6.21, a green halo is obtained around a red area, instead of around a brown one. On the other hand, if 10–30 g phthalic acid is used a green halo is produced around a brown area containing red dots, which are due to the phthalic acid crystals.

As can be imagined, this style offers the colourist wide scope for the production of different effects.

Recipe 6.20

Naphtol AS	15 g
Monopol Brilliant Oil	10 g
Caustic soda (38 °Bé)	30 ml
Trisodium phosphate	7.5 g
Leonil PAT	40 g
Glauber's salt	60 g
Water to	1000 ml

Recipe 6.21

Fast Red Salt TR	40 g
Selected green reactive dye	45 g
Urea	100 g
Water	310 g
Remol AS	50 g
Thickener	500 g

6.5.3 The 'crimp' style

This style is characterised by the appearance of alternate plain and crinkled stripes in the fabric itself. This effect can be brought about by localised fabric shrinkage with appropriate swelling agents. For example, if cotton fabric is printed in a stripe pattern with strong caustic soda, it shrinks in the printed areas and thus causes the unprinted areas to cockle or crimp. The greater the shrinkage or contraction of the printed areas, the more pronounced the effect becomes.

A typical print paste for this style on cotton would be made up as shown in Recipe 6.22. When the fabric has been printed with the crimping liquor, it is plaited down on a conveyor belt in the tensionless state and allowed to dwell for about 30 min, during

Recipe 6.22

Water	213 g
Caustic soda (50 °Bé)	750 g
Starch ether	35 g
Wetting agent	2 g
	1000 g

which time shrinkage occurs. The goods are then rinsed, neutralised with acetic acid, rinsed again in hot and cold water and finally dried without tension.

The scope of this style can be widened by printing the crimping liquor on to unmercerised cotton fabric which has previously been dyed with, for example, selected reactive dyes. In this case the colour deepens in the areas printed with caustic soda in a manner corresponding to the phenomenon observed in the mercerising process.

A coloured and white effect can also be produced by the addition of selected direct dyes to the alkaline print paste; the use of other printing styles in conjunction with the crimp style enables a variety of different effects to be obtained. A crimp effect can also be achieved on nylon fabric by printing a thickened solution of resorcinol, care being necessary in handling this hazardous chemical.

6.5.4 Burnt-out styles

As the name suggests, this seems to be rather a drastic process in that it involves the destruction of all, or at least part of the fabric in the printed areas of the pattern. This, of course, can happen accidentally in various styles if the chemical processes are not properly controlled, but in the burnt-out or *devoré* style, the removal of part of the substrate is essential to the desired effect.

The principle is quite simple and entails the use of a print paste containing an agent that is capable of dissolving or destroying the fabric in the printed areas during subsequent processing [20]. The effect can be employed alone or in conjunction with printed head-colours, but in either case the extent to which the 'burn-out' is used must be controlled, so that the physical strength and structural stability of the fabric is not unduly impaired.

Any fabric can be subjected to such a process provided that a reagent is used that can be adequately controlled during processing (for example, one that can be suitably thickened to give a print paste), and which is not harmful to operatives or machinery.

Polyester/wool blends, for example, can be printed with a paste containing sodium hydroxide [21]. After drying the fabric is pressure-steamed at 120 °C for 15 min; where the wool has been printed it is destroyed and removed during the washing process.

A convenient approach with cellulosic fabrics is to apply a reagent that generates a strong acid during heat treatment after printing. This style was originally used on cotton to give novel dress fabric effects, but the introduction of polyester/cellulose mixtures has widened the scope considerably. The polyester portion of such mixtures is virtually unaffected by the reagents used to destroy the cellulose portion and allows the production of sizeable burnt-out effects with adequate strength and stability retained. Fabrics resembling lace have been produced for shirtings and other fashion articles.

A further development is to overprint a burnt-out pattern on to a polyester/cellulose blend material which has been previously dyed or printed with disperse dyes only. Such dyes or prints have a distinctly ‘chalky’ or delustred appearance due to the undyed cellulosic portion, but in those areas where cellulose is removed by the burn-out the full depth of colour of the dyed polyester is revealed. This style can be extended further by overprinting a burn-out paste on to fabric which has previously been subjected to a discharge-resist process or in which the two fibres have been dyed to contrasting colours. Such a style offers a wide variety of possible effects.

A typical recipe for a burn-out print paste on cellulosic fabrics is shown in Recipe 6.23. After printing the fabric must be completely dried before the hot-air treatment. If the fabric is not completely dry at the carbonising stage the printed areas will not achieve the desired temperature for burning out and the result will be poor. If fabric for this style has been stored for a prolonged period, which may result in a degree of moisture gain, it should be redried before the burn-out procedure.

Recipe 6.23

Disperse dye	*x* g
Sodium hydrogensulphate	240 g
Water	120 g
Locust bean gum ether thickener	400 g
Glycerol	80 g
Carrier	0–15 g
Urea (only for colourless effect)	0–10 g
Water or thickener to	1000 g

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