

CHAPTER 3

Transfer printing

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3.1 INTRODUCTION

Transfer printing is the term used to describe textile and related printing processes in which the design is first printed on to a flexible nontextile substrate and later transferred by a separate process to a textile. It may be asked why this devious route should be chosen instead of directly printing the fabric. The reasons are largely commercial but, on occasion, technical as well and are based on the following considerations.

1. Designs may be printed and stored on a relatively cheap and nonbulky substrate such as paper, and printed on to the more expensive textile with rapid response to sales demand.
2. The production of short-run repeat orders is much easier by transfer processes than it is by direct printing.
3. The design may be applied to the textile with relatively low skill input and low reject rates.
4. Stock volume and storage costs are lower when designs are held on paper rather than on printed textiles.
5. Certain designs and effects can be produced only by the use of transfers (particularly on garments or garment panels).
6. Many complex designs can be produced more easily and accurately on paper than on textiles.
7. Most transfer-printing processes enable textile printing to be carried out using simple, relatively inexpensive equipment with modest space requirements, without effluent production or any need for washing-off.

Against these advantages may be set the relative lack of flexibility inherent in transfer printing: no single transfer-printing method is universally applicable to a wide range of textile fibres. While a printer with a conventional rotary-screen printing set-up can

proceed to print cotton, polyester, blends and so forth without doing a great deal beyond changing the printing ink used, the transfer printer hoping to have the same flexibility would need to have available a range of equipment suited to the variety of systems that have to be used for different dyes and substrates using transfer technology. In addition factors such as stock costs, response time and so on do not always apply and unlike dyers, most printers are able to operate without steaming or washing by using pigment-printing methods. Thus a balance exists which not only permits but even requires the coexistence of direct and transfer printing. The relative importance of the two methods consequently varies with fluctuations of the market, fashion and fibre preference.

A great many methods of producing textile transfer prints have been described in the literature. Many of them exist only in patent specifications but several have been developed to production potential. They may be summarised most conveniently as below.

Sublimation transfer

This method depends on the use of a volatile dye in the printed design. When the paper is heated the dye is preferentially adsorbed from the vapour phase by the textile material with which the heated paper is held in contact. This is commercially the most important of the transfer-printing methods.

Melt transfer

This method has been used since the 19th century to transfer embroidery designs to fabric. The design is printed on paper using a waxy ink, and a hot iron applied to its reverse face presses the paper against the fabric. The ink melts on to the fabric in contact with it. This was the basis of the first commercially successful transfer process, known as Star printing, developed in Italy in the late 1940s. It is used in the so-called 'hot-split' transfer papers extensively used today in garment decoration.

Film release

This method is similar to melt transfer with the difference that the design is held in an ink layer which is transferred completely to the textile from a release paper using heat and pressure. Adhesion forces are developed between the film and the textile which are stronger than those between the film and the paper. The method has been

developed for the printing of both continuous web and garment panel units, but is used almost exclusively for the latter purpose. In commercial importance it is comparable with sublimation transfer printing.

Wet transfer

Water-soluble dyes are incorporated into a printing ink which is used to produce a design on paper. The design is transferred to a moistened textile using carefully regulated contact pressure. The dye transfers by diffusion through the aqueous medium. The method is not used to any significant extent at the present time.

These different methods are considered separately in this chapter since they introduce different scientific and technical factors, and their use is best discussed in the context of the rather different commercial environments.

3.2 SUBLIMATION TRANSFER

Commercial sublimation transfer printing can be traced back to 1929–30 when disperse dyes were under close investigation at British Celanese Ltd during one of those periods of intense creativity that mark the history of dyestuff and coloration research. The investigators at Celanese picked up an observation by Kartaschoff, made during the early development of disperse dyes, that cellulose acetate became coloured when heated in contact with the dye powders [1]. They prepared papers impregnated with aqueous dispersions of the dyes and dried them, and heated them in contact with a cellulose acetate fabric. The fabric became strongly dyed. This observation was developed into a patented process which differs little in principle from that which is the present basis of sublimation transfer printing, namely ‘a process of coloration in which a volatile dye applied to a paper transfer sheet is passed, with the dye layer in contact with the fabric to be coloured, between hot calender rolls’ [2].

But the only textile substrates available in the 1930s for sublimation transfer printing were the cellulose acetates, which were not very stable at the required process temperature. This limitation, combined with the poor heat fastness of the dyes that had been developed at that time, prevented further progress being made.

The appearance some 20 years later of poly(ethylene terephthalate) (polyester) fibres changed the situation and created the conditions for a revival of the early process. With the new fibres came new application methods, notably thermofixation [3], which involved padding fabrics with an aqueous dispersion of suitable disperse

dyes, drying and heating the fabric at temperatures near to the softening temperature of the polyester. It was soon recognised that thermofixation involved sublimation of the dyes and adsorption on to the fibre from the vapour phase. At the high temperatures involved diffusion into the polymer was sufficiently rapid for a practical process to be devised. Based on these developments, a re-examination of sublimation transfer printing was begun, notably by de Plasse of Filatures Prouvost Masurel. Based on this work patents were taken out to cover aspects of ink preparation for printing transfer papers and a new company, Sublistic SA, was formed to commercialise the system [4]. It is worth noting that the formation of Sublistic SA involved the collaboration of dye-manufacturing, paper-printing and textile interests since vital technical inputs were needed from all three industries.

The introduction of transfer papers by Sublistic SA, backed up by sophisticated design and marketing as well as the development of suitable transfer equipment, occurred at the start of the 'polyester boom' and, indeed, contributed to it. Thus the new technical development found unusually few impediments to commercial success. Not surprisingly, other producers found ways of evading the terms of the Sublistic patents and new collaborative ventures appeared around the world. By 1970 some 24 million metres of transfer papers had been produced. Three years later, production had risen to 300–400 million metres per annum, and approximately one-third of printed polyester was being printed by transfer [5]. At that time there were forecasts of annual production levels of 1–2 billion metres by the 1980s; these, however, can now be seen to have been very optimistic, failing to allow for market saturation, fabric preferences and fashion. The serious decline in the popularity of polyester and changes in the relative production costs of natural and synthetic fibres led to extensive contraction in the sublimation transfer print industry. The process itself remained important, however, because the factors favouring this approach to printing did not change. A recent survey, confined to the printing of continuous web, found that some 10% of printing is carried out by transfer [6], while another has noted a marked increase of transfer printing during 1990 [7].

One response of the industry to its problems has been to seek ways of using sublimation transfer for the printing of natural fibres, particularly cotton. These have had some success and will be considered separately.

In the production of sublimation transfer papers and prints, four factors must be considered:

- selection of the paper
- printing methods
- dyes and inks
- the mechanism of sublimation transfer
- producing transfer prints on both man-made fibres and natural fibres.

3.2.1 Selection of the paper

Normally the selection of a paper for printing is governed only by considerations which apply to printing alone: the printing process, the printing machine, the printing inks and the appearance of the final product. In producing a sublimation transfer printing paper these, apart from the last, remain of great importance but to them are added the factors of the transfer process itself and the behaviour of the inks during that process. These extra factors impose some special limitations on the types of paper that may be used [8].

Papers weighing from 35 to 115 g m⁻² have been used, depending on the printing method. Since the cost of the paper represents a significant proportion (25–40%) of the cost of the product (and, additionally, since unprinted paper is purchased by the tonne and sold by the metre), it is important to use as light a paper as is consistent with the other factors that have to be taken into account. The lighter-weight papers are used in high-speed gravure or flexographic printing, while the heavier papers are used in sheet-fed systems such as flat-screen or lithographic printing where the mechanical handling of light papers is difficult. Essentially a smooth printing surface is required on which a sharp image can be produced. The paper has to be dimensionally stable during the printing process in order to preserve register, and also during the transfer process in order to avoid image distortion. This means that a highly calendered paper based on a kraft pulp is generally favoured. The paper may contain fillers such as china clay or titanium dioxide to assist manufacture or printing. For some specialised applications the paper may also incorporate unusual ingredients such as thermoplastic resin [9]. A certain amount of care is needed in selecting additives as some may interact with the dyes in the ink, restricting transfer or even causing chemical degradation.

In order that sublimation transfer of the dyes to the fabric shall be as rapid and efficient as possible, it is generally desirable that the paper should exhibit good 'hold out' – that is, the liquid ink should not penetrate the paper surface more than is essential for the stability of the image. Excessive penetration will also lead to a loss of definition. Consequently the surface of the paper may be modified by the application of a size which allows the ink to wet the surface but penetrate it slowly. Unsized paper can present special problems when water-based inks are used, due to dimensional changes which occur due to water absorption and difficulties in drying fully between printing stations. On the other hand a considerable amount of transfer paper has been produced using spare capacity on regular rotary-screen textile-printing machines. Since such machines do not provide for drying between printing stations, printing is carried out 'wet-on-wet' using water-based inks. In these circumstances rapid absorption of water from the ink is desirable so that sufficient loading of the ink may be allowed. By controlling the pore size during manufacture of the paper and adding

rosins, waxes or synthetic sizes to modify water contact angles, water absorbency can be controlled in such cases to within close tolerances.

At the transfer stage the paper requires several additional characteristics:

- good release of dye vapour from the ink layer
- stability to heat
- low permeability to dye vapour
- good dimensional stability during transfer.

The release of dye vapour during transfer is dependent not only on the vapour pressure of the dye at the transfer temperature but also on the rate of diffusion of the vapour through the surface layers of the paper and the affinity of the dyes for the cellulosic substrate or the thickener, binder or other additive used in making the paper or the ink.

It is probable that the primary effect on the paper itself of heating it to the transfer temperature for the few seconds required is to remove water and thus tender it irreversibly. Some chemical degradation of the paper may also occur, especially if it has been left in an acid condition. Care must be taken to select a paper in which there are no reducing agents or other chemical residues which may attack the dyes. Paper tendering may occur even with a long-fibre paper of high initial tear strength, such as a kraft paper (made from softwood by alkaline chemical pulping), but by selecting the right paper-making conditions the loss of strength may be kept within practical bounds.

The permeability of the paper to the dye vapour is a vital factor. Where transfer printing is carried out at atmospheric pressure or when vacuum assistance is used, low permeability is an obvious advantage ensuring that the direction of dye migration is always towards the fabric. Hence achieving maximum 'hold out' is clearly important in minimising the distance dye vapour has to travel through the paper surface. On the other hand, when transfer is assisted by an induced air flow the paper support has to be permeable to the air and free from pinholes [10]. In all methods some dye inevitably penetrates the paper, but papers have been developed empirically which give a very high efficiency of transfer when used correctly.

The properties of the back or unprinted face of the paper are also important, since when papers are stacked or rolled for storage the front (printed) and back faces are in close contact and dye may therefore mark off. If papers contaminated in this way are easily permeable to the dye, diffusion can take place over time, leading to a ghost image on the face and defective transfer prints.

The loss of water during transfer can in some cases lead to a dimensional change. This can be sufficient to cause relative movement of fabric and paper during transfer, with consequent loss of clarity. The fabric itself may also show a dimensional change

with the same consequences and this is considered in discussing the production of sublimation transfer prints at a later stage.

3.2.2 Printing methods

Any of the commercial processes employed in the printing industry may be used for the production of sublimation transfer printing papers [11]. In practice web offset and letterpress printing are not used; production is effectively restricted to gravure, flexographic and rotary-screen printing for continuous web production, while flat-screen and lithographic printing are used for the production of transfer sheets.

Gravure printing

This method of printing uses solid metal rollers engraved with a design or wooden rollers carrying an engraved metal wrapper. Ink is delivered via a series of rollers to the engraved printing roller and excess ink is removed with a doctor blade, leaving ink only in the engraved areas. When the inked roller is brought into contact with paper using an applied pressure the ink is almost completely transferred to give a print. The amount of ink delivered, which controls the colour depth, is determined by the depth of the engraving. The efficiency of transfer of ink from roller to paper is sometimes enhanced by establishing an electrostatic potential across the interface, which ejects the ink from the roller. Using a series of rollers with varying depths of engraving and allowing successive inks to overprint and produce 'fall on' effects, very complex designs with a large tonal range can be produced with high definition and subtlety. Very high printing speeds can be achieved ($60\text{--}120\text{ m min}^{-1}$) but the paper must be dried in between print stations in order to avoid smudging or marking-off. In this respect the gravure printing of paper differs from that of textiles, in which the absorbency of the fabric allows wet-on-wet operation. The need for rapid drying when printing paper by gravure makes it necessary to operate with highly volatile solvents such as toluene or ethanol, and in many countries this is leading to increasing pressure from environmental protection agencies.

A commercial gravure printing machine has as many as ten print stations and is fitted with automatic registering devices of great efficiency. The capital investment is very considerable, and in addition a large stock of expensive print rollers has to be maintained. For a stock in trade of 50 designs perhaps 300 rollers will be required, each costing several hundred pounds. But apart from this important commercial factor, gravure printing of transfer paper has come under some competitive pressure from other methods since in order to avoid distortion of the print rollers a limit has to be imposed on the width of the paper to be printed, and this is generally less than the

widths of textile fabrics. Nevertheless, due to the very high quality of printing and the subtlety of shading in design which it makes possible, gravure printing of transfer papers remains of considerable importance.

Flexographic printing

Also a roller-printing method, flexographic printing has the advantage over gravure printing that it is less capital-intensive with regard to both machinery and stock design roller costs. Moreover, it uses water-based inks and is suitable for printing wide papers. On the other hand flexographic printing offers less sophistication in design, especially with regard to tone effects, although these are possible to some degree.

The flexographic print roller, also called the stereo, is covered with rubber or composition, and carries the design in relief. The design is cut out using standard techniques but in recent years laser cutting has introduced new high standards of precision which have led to great improvements in print quality. By laser cutting the raised portions of the stereo may be cut in such a way that tone effects, albeit somewhat coarse, can be produced. The printing ink is delivered to the stereo roller by an engraved metering roller to which ink is delivered from the print trough. Thus the raised portions of the roller are effectively gravure coated, and by controlling the depth of engraving the amount of ink supplied can itself be controlled.

The stereo rollers (normally there are six, sometimes eight) are arranged around a large drum carrying the paper. Since only the raised portions of the stereo come into contact with the paper there is no need for drying between print stations; as the paper is dried only once, there is no problem of dimensional change on drying and slower-drying solvents can be used. Relatively low printing pressures are needed, and this enables wider papers to be printed. If the paper is dried between stations fall-on effects can be produced, but this is unusual in the production of sublimation transfer papers.

Normally flexographic printing delivers relatively little ink to the paper, and for transfer printing paper production it is frequently necessary to apply heavier than usual ink loadings in order to achieve the required shade depth on the fabric. In practice this means that in the production of transfer paper by flexographic printing output is frequently slower than when gravure printing is used or when flexography is used for normal paper printing.

Rotary-screen printing

When rotary-screen printing became widely available in the textile industry, a demand naturally developed for it to be used also for the production of transfer paper, thus creating the possibility of 'in house' manufacture cutting out the commercial paper

printer. Rotary-screen printing also has many intrinsic attractions from the point of view of transfer paper production, such as relatively low capital cost and the capability of printing very wide widths. In addition, the ability of screen printing to deliver heavy ink loadings can be useful for the production of papers for transfer printing heavy fabrics or thick materials such as carpet tiles.

Production of transfer paper by rotary screen does not differ in principle from textile printing by the same means. Paper is less compressible and less absorbent than fabric, however, and careful control of conditions is very necessary. The paper used has to be more absorbent than that used for gravure or flexographic printing since it is necessary to operate wet-on-wet. It has to have the capability of draining the water from the ink layer, but must be only minimally penetrated by the essential ingredients (dyes and binder).

Lithographic printing

Lithography offers the potential of producing photographic quality reproduction. As its name suggests, it originally depended on the properties of particular kinds of stone, but modern lithography (also known as 'off-set' printing) is based on modifying the surface properties of coated metal plates. A zinc or aluminium printing plate is coated with a light-sensitive oleophilic (hydrophobic) material. When the plate is exposed to light through a photographic colour separation negative the exposed areas become 'cured' so that the film can be washed off in the unexposed areas. Thus the design becomes reproduced on the plate in a pattern of oleophilic and hydrophilic areas. When the plate is wetted with an aqueous (or substantially aqueous) 'fountain liquid' the contrast between the two areas becomes so marked that an oil-based ink applied to the plate adheres only in the oleophilic regions, allowing the design to be printed on to paper. Generally, but not always, lithographic printing is carried out using four colour process inks giving yellow, magenta, cyan and black. This enables a very broad shade gamut to be produced with great shading subtlety. Depth of shade is controlled by printing each colour in dots rather than as an even coating. All the dots have the same colour intensity, but their size and density is controlled so as to present the observer with an image made up of coloured dots and the white paper substrate showing in between. Thus the colour physics of white and colour blends applies, rather than that of mixtures. This has important repercussions for the production of sublimation transfer printing paper by lithography, because the dot sizes produced on the paper by printing are not those produced on the fabric by transfer due to the lateral diffusion of the dye. By adjusting the dot size in accordance with the sublimation characteristics of the dyes the situation can be controlled [12].

The amount of ink delivered to the paper by the plate is small; the ink layer in the

dots has a thickness of only 1–2 μm . The colour content of the inks has therefore to be of the order of 50%, leading to very high viscosity relative to the inks used in other systems of printing.

The inks are oil-based. Originally drying oils such as linseed oil were used so that the printed image was oxidatively cured on standing. Today the principle is much the same although synthetic products are used. Since the printed ink films (or dots) are very thin, the different colours are applied successively without intermediate curing or drying and high printing speeds are possible.

Although initiation costs (such as plate production and machine setting) are high, production is cheap and for longer print runs the process is very attractive. As a process lithographic printing is used to print both sheets and continuous web but as far as transfer paper production is concerned only the sheet-fed version is used.

Flat-screen printing

Although flat-bed textile screen-printing equipment can be used for the production of transfer paper in the same way as described above for rotary-screen printing, the use of flat screens is limited effectively to the production of transfer sheets in standard paper-printing machines. These are designed to print large sheets which are cut up later for the production of placement designs or logos for garments or garment panels. The machines print at higher speeds than textile machines (1000–2000 sheets per hour) but each colour has to be applied separately in a single pass. Dimensional changes occurring during the drying of the paper can make the maintenance of register very difficult so that dimensional stability is an important requirement in selecting a paper.

The machines are generally fed automatically and the devices used require a flat sheet with a clean edge. Additionally the paper has to be dried while being carried on a moving belt without being blown about. This means that sheet-fed transfer papers are fairly heavy, in practice at least 75 g m^{-2} and normally 100–110 g m^{-2} . The inks may be solvent- or water-based.

3.2.3 Dyes and inks

The essential ingredient for a sublimation transfer ink is of course the colouring matter, which must be volatile at the transfer temperature that is appropriate for the textile being printed. This means that the molecules of the dyes used must be relatively small and contain as few as possible ionic substituents, which would limit or inhibit volatilisation. The dyes used are consequently chosen from the disperse dye class; not all dyes possessing appropriate volatility are suitable, however, since other considerations are important. Solvents are varied: a volatile liquid such as toluene in a

gravure printing ink, an ethanol/water mixture in a flexographic ink, a drying oil for lithography or a water-based system for screen printing. The degree of dispersion must be appropriate for their use with gravure rollers in gravure or flexographic printing. Normally disperse dyes are supplied as an aqueous paste or a powder containing dispersing agents and other diluents, which are frequently found to be unsuitable for incorporation into an ink. Consequently the dyes used for sublimation inks are obtained at the press-cake stage before other diluents are added and are selected to have very low solubility in the ink solvents and to be free from any tendency to crystallisation on standing.

The ink will also contain a binding agent which holds the dye on the paper. This is chosen to give the ink the right rheological properties for printing without inhibiting migration of the dye to the fabric during transfer. In water-based inks the binders are often alkylcelluloses, while in solvent-based inks poly(vinyl acetate) or acrylic polymers may be used [13]. An interesting variant is the use of a hydrophilic binder such as hydroxymethylcellulose in an emulsion ink based on water and toluene.

Inks are prepared by standard milling methods to reduce particle size to a suitable level. Because of the relationship between particle size and solubility, overmilling yielding very small particle sizes can be counter-productive, as it may lead to flocculation or subsequent particle growth.

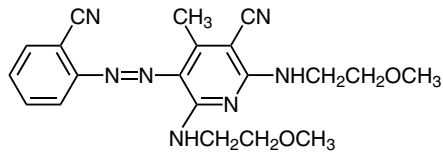
Structural features of suitable dyes

Due to the limitations of the market, even at the height of the popularity of sublimation transfer printing there was little incentive for dye manufacturers to synthesise dyes specifically for transfer print applications. Instead, their approach has been largely empirical, based on selection from existing ranges of disperse and solvent dyes, and batches of selected dyes have been taken out of the regular manufacturing programme to be specially finished for ink manufacture.

Most of the dyes used for transfer printing are based on monoazo or aminoanthraquinonoid chromophores. It has been claimed that particular nitrodiphenylamines and disazo [14] and cyanovinyl [15] dyes are sufficiently volatile, but these claims have not been accompanied by any parallel commercial activity. It has been established empirically that suitable dyes should preferably possess an r.m.m. of no more than 350, with a molecule containing a minimum number of polar auxochromes such as NO_2 , CN , SO_2R , NH_2 or NHR , and no ionic groups such as SO_3H or COOH . These broad considerations mean that only selected disperse dyes can be used for sublimation transfer printing and only those fabrics which have sufficient affinity for these dyes (polyester, polyamide, triacetate or acrylics) can be so printed. Since the cohesive forces in the solid disperse dye are of the same kind as those bonding the dye

molecule to the fibre, easy volatilisation will be related generally to the heat fastness of the transferred dye. This relation is, of course, conditioned by the relative ease of escape of a dye molecule from a dye crystal and the difficulty of such a molecule diffusing through the polymer matrix.

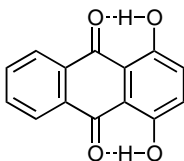
There are, however, two structural features that can enhance the volatility of the dye without reducing the heat fastness. First, the presence of bulky substituent groups can prevent close packing of the dye molecules in the solid and limit the strength of intermolecular bonding without having much effect on dye-fibre bonding; structure 3.1 is an example of such a molecule. This is shown by a lower latent heat of sublimation than would be expected for a dye of higher r.m.m. and a greater than expected affinity for the substrate.



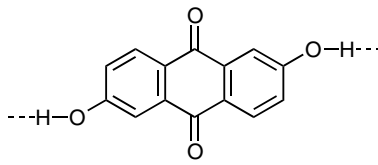
3.1

Secondly, when polar groups capable of hydrogen bonding with the polymer substrate, such as NH_2 , OH or NHR , are present as substituents in such a way that they become involved in intra- rather than inter-molecular bonding, they do not have as great an effect in reducing volatility but can still contribute to dye-fibre bonding. The effect is well illustrated by the data for two dyes (3.2, 3.3). At 200 °C the vapour pressure of compound 3.2, which is internally hydrogen-bonded, is 157 Pa (1.18 mmHg); compound 3.3, which has the same molecular mass but is not internally hydrogen-bonded, has a vapour pressure at 200 °C of only about 0.005 Pa (3.71×10^{-5} mmHg) [16].

Both polyester and cellulose acetate can be printed satisfactorily and with good fastness by sublimation transfer printing. Polyamide fibres can be readily printed, but the prints do not have good fastness to washing or heat. Acrylic fibres can also be



3.2

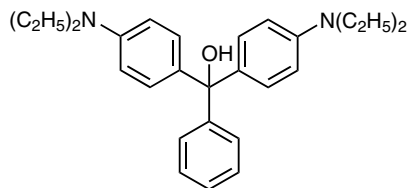


3.3

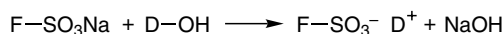
printed, but the prints lack intensity. To achieve better results on these substrates two novel approaches have been explored. The wet fastness of sublimation transfer prints on nylon is improved if a suitable reactive group, such as chloroacetyl amino or dichlorotriazinyl amino, is introduced into the dye molecule, thus increasing the extent of dye–fibre reaction [17]. The effect is real but not large. Much more effective is the incorporation into the molecule of azide groups, such as SO_2N_3 [18,19], which react by the generation of nitrene species inserted into the polymer on heating. This can give as much as 77% dye fixation – much better than the levels of fixation of other reactive dyes under these conditions [10]. There has, however, been no commercial exploitation of this system.

Attempts have been made to use modified basic dyes to provide a sublimation transfer system for printing acrylic fibres. The carbinol form of some basic triarylmethane dyes (for example, structure 3.4) can be volatilised from alkaline ink layers [20]. The dye interacts with sulphonate groups in the fibre to regenerate the coloured ionic form of the dye (Scheme 3.1).

The system is more efficient if the cation is an ammonium ion, as the ammonium hydroxide liberated can escape from the system. Ensuring that the transfer paper remains alkaline during storage is in this case difficult, however. Another approach uses basic dyes that can be deprotonated to yield a neutral volatile form. The dye is reprotonated after transfer [21,22]. The volatile species is usually an amine, which may be *N*-substituted. The basic dyes when applied by sublimation transfer using either of these options have lower wash and light fastness than when applied normally. This disadvantage, combined with the commercial difficulty of catering for the restricted market available for transfer printing acrylic materials, has resulted in a very limited exploitation of these methods. It is worthy of note that current interest in producing muted designs on garment panels made of blends consisting substantially of acrylic fibres is fully satisfied by the use of regular sublimation papers.



3.4



Scheme 3.1

Compatibility during sublimation transfer

Because of the multiplicity of factors involved in transfer printing (diffusion through the ink binder medium, sublimation, affinity for and diffusion through polymer matrix of the fibre) the shades produced under different production conditions are apt to vary markedly. The most important variable factor is temperature. Temperature variations occur not only between batches but also across the width of wide fabrics. With thick fabrics, and especially those with pile, temperature variations through the depth of the material can also be expected. Consequently it is important to select dye mixtures in which the components all behave in much the same way so that any variation that may occur will be limited to depth rather than differences in hue.

It has become customary to classify disperse dyes for sublimation transfer on the basis of empirical tests which are considered to reflect all the factors in a practical situation. In the UK several companies have adopted a classification of the dyes according to an A–D scale of decreasing transfer rate, and it is recommended that dye mixtures should be put together from dyes of the same group. In general, however, dyes of Group A are so volatile that prints have poor fastness, particularly to heat, and frequently poor definition; at the other end of the scale, dyes from Group D are difficult to transfer. Hence dyes are selected almost invariably from Groups B and C. Some care has to be exercised even within this narrow band, however. Generally speaking, compatibility and reproducibility of shade is quite easy with lightweight fabrics, which can be transfer printed with short treatment times; as the fabric becomes more difficult to penetrate and transfer times need to be longer, residual differences between the dyes in the mixture begin to show up. Vacuum-assisted transfer (see section 3.2.5) can be of some assistance in this connection. With pile fabrics variable penetration of the material has led to the successful use of dye mixtures that include dyes of both high and low volatility [23,24]. The more volatile dye migrates into the pile of the fabric while the other remains at the surface.

Another somewhat looser system of classification is the categorisation of dyes as ‘high, medium or low energy’ [25]. This uses a test in which is measured the temperature required for 90% colour development during transfer in a fixed (30 s) transfer time. The problem with this approach is that it does not allow for the variations in transfer time which occur in practice. If the dwell time is increased from the standard 30 s of the test, then obviously the temperature needed to produce 90% development will be reduced. But the change differs markedly from one dye to another and consequently the ‘energy’ system should be used with caution.

3.2.4 The mechanism of sublimation transfer

The physical chemistry of disperse dye adsorption from the vapour phase has been

considered in detail elsewhere [26]. In this chapter discussion will be confined to the particular conditions of transfer printing polyester and other man-made fibres. In conditions where polyester fibres are in contact with dye vapour the distribution of the dye at equilibrium is governed by a partition isotherm, in which the partition coefficient K is defined by Eqn 3.1:

$$K = \frac{C_f}{C_v} \quad 3.1$$

where C_f is the dye concentration in the fibre phase and C_v is the concentration in the vapour. It is conventional to assume that an instantaneous equilibrium governed by the isotherm is established between the vapour and the surface, so that the kinetics of achievement of the ultimate equilibrium are governed by the rate of diffusion of dye from the bulk of the vapour to the surface and by its rate of diffusion from the surface of the fibre into the fibre mass. Another consequence is that when the vapour is saturated then so is the fibre surface, and further adsorption can only occur as dye diffuses into the fibre to create free sites. Assuming that the dye vapour possesses ideal behaviour, the concentration in the saturated vapour is given by Eqn 3.2:

$$C_v = \frac{pM}{RT} \quad 3.2$$

where p is the saturation vapour pressure of the dye, M the molecular mass of the dye, R the gas constant and T the temperature. The data in Table 3.1 is based on Eqn 3.2. The values relate to an operating temperature of 200 °C (a typical transfer temperature) by extrapolation.

Although relatively few transfer printing dyes have a known vapour pressure, the data in the fourth column of Table 3.1 is sufficient to show that under transfer printing conditions the dyes are present initially in the vapour at a concentration of 10^{-3} to 10^{-5} g l⁻¹. Since cellulose acetate [33] and polyester [29] can adsorb approximately 10% of their own mass of dye, the value of K is of the order of 10^5 to 10^6 , which is much higher than that found in aqueous systems. This phenomenon relates to competition, possibly allosteric in nature, between dye and water for sites on the fibre, and has been discussed in detail elsewhere [26]. One important practical consequence is that fibres can be 'overdyed' during transfer printing if there is too much dye in the ink layer. Fibres overdyed in this way will slowly desorb dye on exposure to normal water-bearing atmospheres and will develop poor fastness to rubbing and washing.

The effect of the high distribution coefficient is that fibre saturation will develop at or just beneath the fibre surface as soon as the fibre/transfer paper interface reaches the

Table 3.1 Vapour pressures and concentrations of transfer printing dyes at 200 °C

Dye	R.m.m.	Saturated vapour pressure /Pa	Concn /g l ⁻¹	Ref.
CI Disperse Blue 14	266	8.2	5.56×10^{-4}	28
CI Disperse Blue 56	350	0.2	1.72×10^{-5}	29
CI Disperse Orange 3	242	21	1.29×10^{-3}	30
CI Disperse Red 9	237	136	8.23×10^{-3}	31
CI Disperse Red 15	239	48	2.94×10^{-3}	32
CI Disperse Red 60	331	6.4	5.38×10^{-4}	29
CI Disperse Violet 1	238	2.7	1.67×10^{-4}	28
CI Disperse Yellow 3	269	8.4	5.76×10^{-4}	27
CI Disperse Yellow 8	261	59	3.96×10^{-3}	28
CI Disperse Yellow 54	288	0.9	6.16×10^{-5}	29

operational temperature. The effect has been described in detail by Fenoglio and Gorondy [34] who devised the model shown in Figure 3.1.

This consists of a fabric F in contact with an ink layer I on a paper substrate P. The fibre and ink phases are visualised as planar slabs as shown. A gap G separates the fibre and ink layers, reflecting the fact that even under pressure the area of contact between the paper and the fabric surface will be small and most of the dye molecules will have to travel across an air space. The dimensions of the gap will depend on the applied pressure, the nature of the paper, the filament diameter of the fibres in the fabric surface and the fabric construction. Clearly the Fenoglio and Gorondy model is a gross simplification of the true transfer-printing situation but may be regarded as applying in the sense of a differential. Prior to heating (Figure 3.1a) the dye is contained in the ink layer. When the paper is heated on the reverse side (Figure 3.1b) dye sublimates into the gap and transfers by diffusion down a concentration gradient to the fibre surface. Initially there is also a temperature gradient across the gap, which may for a short time lead to dye condensing on the fibre surface, but after a brief delay a uniform steady-state system will be established which can be considered in detail. The length of this delay will depend on the size of the gap as well as on the thermal properties of the paper and the fibre, but it may be assumed to be short relative to the full transfer time. At the steady-state transfer temperature dye will diffuse from the fibre surface inwards down a second concentration gradient within the fibre.

In order that diffusion within the fibre may be as rapid as possible, the operating transfer temperature needs to be such that segmental motion in the polymer is rapid. Provided the flux of dye vapour from the paper continues, adsorption and diffusion will

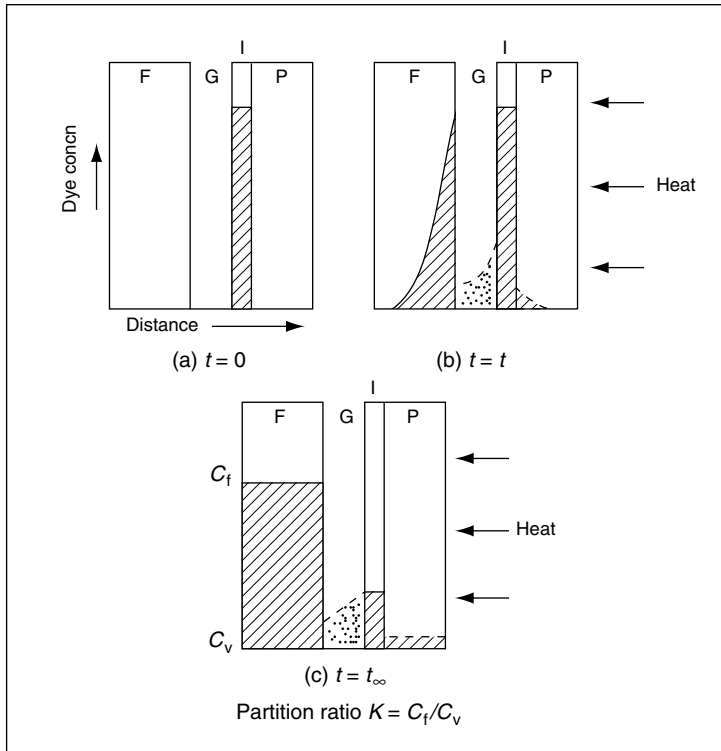


Figure 3.1 Model system describing vapour transfer-printing mechanism

proceed until a thermodynamic equilibrium is established between the three phases F, G and I as shown in Figure 3.1c. In a practical system the distribution of the dye will be strongly in favour of the fibre phase; a little dye will be retained by the paper phase, however, due to the small affinity of the dye for the paper surface and the ink binder as well as a degree of back-diffusion into the paper during transfer. Naturally paper and binders are selected to keep this effect to a minimum.

There are thus four potential rate-determining steps in the situation:

- diffusion from the ink layer into the vapour
- diffusion across the gap between paper and fabric
- adsorption at the fibre surface
- diffusion into the fibre.

Initially the first of these will predominate, but once the steady state has been established it is the slowest process that will control the situation. Generally it may be assumed that adsorption at the fibre surface will always be rapid, provided the surface is

not saturated, so that it is the three diffusion processes and the factors affecting them which must be considered.

The production of a transfer-printing paper requires the dye to be dispersed or dissolved in a printable medium containing a binder that will hold the dye on the paper until it is used in the transfer process. When the paper is heated in contact with the fabric, the escape of the dye from the binder will depend on its affinity for the binder and its rate of diffusion through the binder layer. Thus selection of the binder material involves considerations beyond those normally involved in formulating a printing ink. Binders and associated solvents have been selected largely on empirical data, and relatively little has been published comparing different materials. However, the wide differences that can arise have been illustrated by Bosnakyan's work on the rate of transfer of the disperse dye Sublaprint Blue 70032 (LBH) from ink layers of a fixed thickness formed using different binders at different dye concentrations on metal foil [35]. (Foil was used to ensure that no penetration of the support was possible and that the transfer temperature was achieved very rapidly.) The results are illustrated in Figure 3.2.

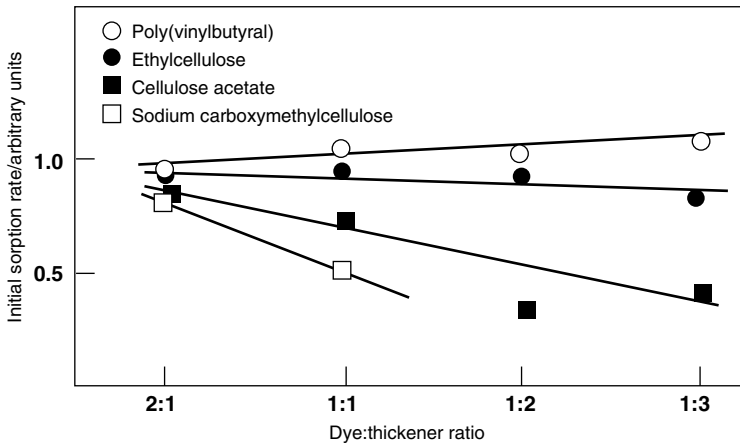


Figure 3.2 Changes in initial sorption rates at different dye:thickener ratios for Sublaprint Blue 70032 (LBH) at 200 °C

The marked differences that exist between binders are evident. At high dye:binder ratios the different binders behave similarly but as the ratio falls the affinity of the dye for the binder and its permeability become increasingly important. Poly(vinylbutyral) and ethylcellulose clearly offer greater flexibility than cellulose acetate or sodium carboxymethylcellulose. Ethylcellulose is generally favoured because inks that incorporate it have good printing properties and are easy to make. A new factor has

been introduced by the adoption of wet-on-wet rotary-screen production of transfer papers using fairly absorbent paper to allow sequential printing without intermediate drying. Inevitably this gives a rather higher degree of paper penetration than, say, the use of solvent-based inks printed by gravure on a highly compressed paper. The choice of a binder in these circumstances involves consideration of the paper construction and the differential diffusion of water and dispersed binder from the wet ink, in addition to the factors considered already.

Once the dye has escaped from the paper surface it must migrate across the gap G . The Fenoglio and Gorondy model relates to the penetration of dye into a single fibre from a paper surface where the gap G is easily defined. With a real fabric consisting of an assemblage of fibres the magnitude of the gap will vary considerably. Fibres near to the paper will compete with fibres further away. Thus the rate of penetration of the fabric will depend not only on the rate at which a high surface concentration can be achieved but also on the ease with which molecules move within the spaces between individual filaments [36]. This is governed by the collisions between dye molecules and any others present, such as those from the ambient atmosphere, and is related to the average distance or mean free path λ_d . When only dye molecules are present (that is, in the absence of air), λ_d is given by Eqn 3.3:

$$\lambda_d = \frac{1}{\pi n \sigma_d^2 \sqrt{2}} \quad 3.3$$

where n is the number of dye molecules per unit volume and σ_d is the closest distance between centres of approach when the molecules collide.

Typical values of n can be obtained from Table 3.1. For example, 1 mol CI Disperse Yellow 3 contains 6.023×10^{23} molecules (i.e. Avogadro's number) and weighs 269 g. At 200 °C the saturated dye vapour concentration is $5.76 \times 10^{-4} \text{ g l}^{-1}$. Thus for a unit volume of 1.0 ml n is given by Eqn 3.4:

$$\begin{aligned} n &= \frac{6.023 \times 10^{23}}{269} \times \frac{5.76 \times 10^{-4}}{10^3} \\ &= 1.29 \times 10^{15} \end{aligned} \quad 3.4$$

Substituting this value for n in Eqn 3.3, and using the approximate dimension of $1.5 \times 10^{-7} \text{ cm}$ (based on the length of the CI Disperse Yellow 3 molecule) for σ_d , gives a value of $7.8 \times 10^{-3} \text{ cm}$ for λ_d .

In the course of transfer printing, however, the vapour contains other molecules

besides those of the dye. The presence of air, at pressures normally atmospheric but sometimes less, will supply other molecules which interfere with the movement of the dye molecules. Eqn 3.3 can be adjusted to allow for the presence of another kind of molecule as shown in Eqn 3.5, which gives a value λ_{da} for the mean free path of the dye molecules in the presence of another kind of molecule a:

$$\lambda_{da} = \frac{4V}{[\pi n_a (\sigma_d + \sigma_a)^2] \sqrt{[(M_d + M_a)M_a]}} \quad 3.5$$

where the unit volume V may be taken as 1 ml as before. The subscripts d and a refer to the dye and the other molecule respectively, and M is the r.m.m. For simplicity the atmosphere may be regarded as consisting of only one kind of molecule having characteristics somewhere between those of oxygen and nitrogen, so that Eqn 3.5 can be used for the dye-in-air situation. One important effect of a large excess of air molecules is that the mean free path of the dye molecules becomes virtually independent of temperature. Jones has applied Eqn 3.5 to the situation when the ambient pressure is varied at a constant temperature to produce the relationship shown in Figure 3.3 [37].

Figure 3.3 shows calculated values for three dyes of distinctly different r.m.m. It can be seen that it is only at low atmospheric pressures that this parameter is significant. At pressures above, say, 10 kPa the influence of the air swamps any effects due to variations in the dye molecules.

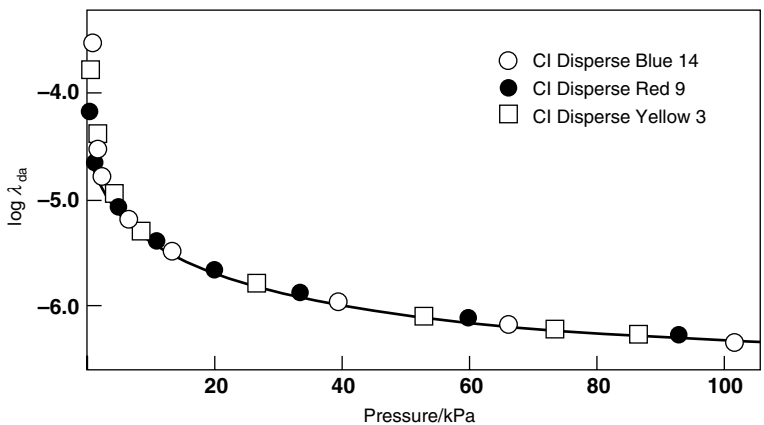


Figure 3.3 Changes in λ_{da} with ambient air pressure at 160 °C

Figure 3.3 shows the logarithm of the mean free path. Calculation of actual values shows that the ratio of the mean free paths at 3.3 kPa (25 mmHg) and at 101 kPa (760 mmHg) is 2.37×10^{14} . This has a very powerful effect in a practical situation, as has been confirmed by Dawson, who has measured the penetration of different dyes into thick carpet panels during transfer printing with four dyes of different volatility [38]. The results are shown in Table 3.2. The letters A to D in Table 3.2 relate to the volatility scale already mentioned and indicate the different dye properties exemplified. Dawson's results show that penetration is approximately doubled when the ambient pressure is reduced by two-thirds.

Table 3.2 Effect of ambient pressure on dye penetration during transfer^a

Dye	Dye class ^b	Pile penetration at different ambient pressures (in kPa)/%					Transfer/%
		100	66	50	33	3	
CI Disperse Red 15	A	30	35	50	70	100	83–92
CI Disperse Orange 25	B	15	25	45	60	85	73–87
CI Disperse Violet 33	C	5	15	35	40	50	53–55
CI Disperse Blue 122	D	5	5	10	15	25	25

a Transfer conditions: 45 s at 210 °C

b See text for explanation

An alternative to reducing the ambient pressure in order to increase the mean free path is to create conditions which impose a directional constraint on the molecular movement. Normally the sum of the free mean path motions is zero, but if the conditions are arranged so that the mean free paths become additive in a particular direction (by compelling the ambient molecules to move in the same direction away from the transfer paper towards the fabric), then collisions between dye and air molecules will tend to assist rather than impede migration in the desired direction. The effect of a hot (220 °C) air stream through a permeable transfer paper on dye diffusion through a multilayer polyester assembly during a 20 s period has been reported and is shown in Figure 3.4 [10,39].

The rate of air flow is closely related to the magnitude of the pressure difference across the paper/fabric composite. At low values there is little effect in the particular system studied, but as the difference is increased to 29.3 kPa (220 mmHg) the dye becomes fairly evenly distributed through as many as 16 layers of fabric. From the

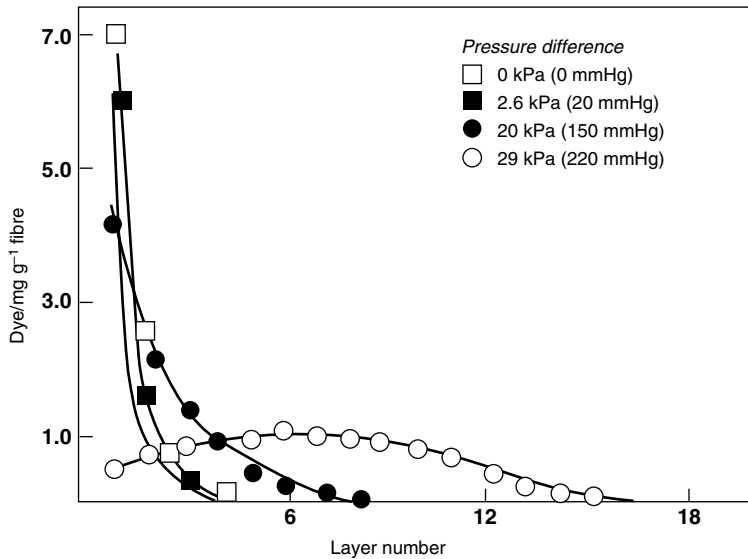


Figure 3.4 Distribution of CI Disperse Yellow 3 with continuous air flow

earlier discussion of the effect of the ambient pressure on the mean free path it is clear that the pressure difference of 29.3 kPa was needed in the particular situation studied to impose a dominant direction on the air molecules and is analogous to stirring a dyebath.

3.2.5 Producing transfer prints

Three considerations are paramount in establishing methods of production of transfer prints by sublimation. First, conditions have to be established that will lead to the rapid sublimation of the dyes and their diffusion into the fibres. Secondly, the gap between the paper and the fabric to be printed has to be minimised. Thirdly, the process must result in a fabric with substantially unchanged textile properties.

Clearly, the first of these requirements is met by using as high a temperature as possible, subject to not exceeding a level at which the fabric would be liable to be damaged or distorted. A similar compromise is involved in selecting conditions which achieve close contact between fabric and paper. Contact is maximised by applying a pressure to the fabric/paper composite, but fabrics will show deformation when compressed while being heated, especially at higher temperatures. Thus machinery designed for the production of sublimation transfer prints has to operate over a range of conditions which is determined by the properties of the fabrics to be printed and of the transfer papers themselves.

Machines for man-made fibre fabrics

Sublimation transfer printing was introduced initially for polyester fabrics, which soften in the region of 210–220 °C. Depending to some extent on the fabric structure, they are easily heat-deformed under pressure as the softening point is approached, and this can result in the fabric becoming glazed. In serious cases some spot welding may occur between fibres, leading to stiffening of the fabric. Nylon 6.6 fabrics behave similarly. Transfer printing of both nylon 6.6 and polyester fabrics can, however, be perfectly satisfactory in the temperature range 190–210 °C. Nylon 6 and acrylic fabrics must be handled at lower temperatures and are thus in general less suitable for the process.

Machines for producing sublimation transfer prints take many forms depending on the way in which the textiles are presented, whether as continuous webs, garments, garment panels, ribbons or tapes, hosiery and even caps. Apart from vacuum-assisted transfer, however, today's machines are little changed in principle from those developed originally for the process. The pressure bringing the paper into contact with the fabric is exerted either by a blanket under tension (in the case of continuous-web machines) or a hydraulically operated hotplate (in the case of unit printing of, say, garments).

Continuous-web transfer machines were developed from a type of machine common in the textile industry for preshrinking and setting, in which the fabric is passed around a heated drum under a continuous blanket. A typical arrangement is shown in Figure 3.5.

The size of the heated drum in the centre of Figure 3.5 determines the production rate of the machine. Thus a drum of 2 m diameter with a feeding system designed to

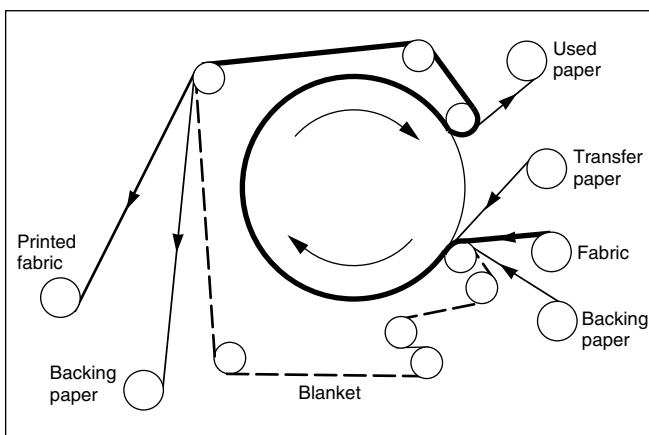


Figure 3.5 Continuous transfer printing

cover 80% of the surface will allow production of 900 m h^{-1} with a 20 s contact time. Production rates as high as 1300 m h^{-1} have been claimed in such machines with either larger drums or shorter contact times. The machine is operated with the reverse side of the transfer paper in contact with the cylinder and the face of the fabric against the printed side of the paper. The paper may be slightly wider than the fabric and a backing strip of paper is fed in to prevent dye being transferred to the continuous blanket. The blanket has to be made of material that can withstand temperatures in the region of $200 \text{ }^\circ\text{C}$ for long periods, and Nomex fabric is commonly used. This is made from an aromatic polyamide, poly(1,3-phenyleneisophthalamide), which because of the high cohesive forces developed from the aromatic system in the polymeric chain has a glass transition temperature of $275 \text{ }^\circ\text{C}$ and a softening temperature above $350 \text{ }^\circ\text{C}$ [40]. It is an expensive material but very suitable for sublimation transfer printing. The pressure between paper and fabric is controlled by adjusting the tension on the blanket. The effective pressure is not high (ca. $1.4\text{--}2.1 \times 10^3 \text{ kg m}^{-2}$) and even so at the upper limits of operating temperature glazing of fabrics may be observed. Since the applied pressures are low there are no major difficulties in the way of devising machines for printing wide fabrics up to 3.5 m.

It is essential to have a uniform temperature across the width of the transfer machine in order to have a constant rate of transfer and uniform colour. Special measures are normally required to achieve this. In machines by Hunt and Moscrop and by Kannegiesser the cylinder comprises a hollow shell containing a heat-transfer liquid; a biphenyl/diphenyl ether mixture is often used. The shell is only partially filled and the remaining space is evacuated before the system is sealed. The liquid is heated electrically and the vapour from the boiling liquid condenses on the internal surfaces to supply heat to the drum. Natural equalisation of the internal pressure ensures uniform heating and, providing the machine is sited sensibly so that there is no accidentally uneven cooling, uniform transfer temperatures are maintained. Other methods of heating, including the use of oil, gas and electricity, have been used with appropriately designed arrangements. A typical continuous-web transfer print calender is shown in Figure 3.6.

Transfer machines for garments and garment panels have been developed on very similar lines to conventional presses. A typical arrangement is shown in Figure 3.7.

In this version the paper is laid on the garment or garment panel on the continuous belt. This is then moved under the heated plate B by a drive operated by a foot pedal switch. The heated plate automatically lowers on to the paper/fabric composite and is held there for a preset time and at a preset pressure. The plate then lifts and the belt moves forward to allow the paper to be removed from the printed article, which is added to a stack. Meanwhile a fresh garment or panel is arranged for the next print.

An alternative arrangement is to have a moving flat bed which moves in and out



Figure 3.6 Rollingstatic MVZ 986, 3200 mm working width transfer-printing machine (Lemaire)

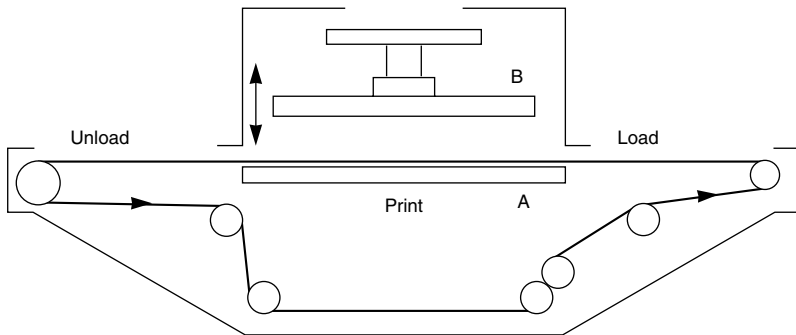


Figure 3.7 Flat-bed press (Kannegiesser)

from the plate. This allows loading and unloading to be carried out on both sides of the heated zone, giving higher productivity. There are several variations on this arrangement, designed to print caps, hosiery and other preformed articles. One variant, which is used for printing such garments as T-shirts and sweaters, is fitted with a continuous feed for the transfer paper. The unsewn garment is laid out with front, back and sleeves in a cruciform arrangement on the movable belt and is carried into the plate zone. The plate is lowered, bringing the paper into contact with the garment to produce an overall print. The plate then lifts and the garment is carried forward for removal, while at the same time the paper is advanced for the next print. When the garment is sewn together the print pattern extends over its whole surface.

Both continuous and unit printing machines have been redesigned to provide vacuum-assisted transfer. This is less easy with continuously operated units, but

nevertheless reliable and successful units are available. Vacuum assistance may take two forms. Either a pressure differential may be set up within the machine so as to promote a flow of hot air which assists the migration of the dye molecules, or the machine may be designed to produce a reduced pressure in the dye transfer zone.

By using a perforated hollow drum or plate and establishing a pressure differential, air can be made to flow through the system. The air flow holds the fabric in contact with the drum, and the paper is held in place without the need for a blanket. Although there may be some benefit in this arrangement in having the drum or plate heated, it is much more effective to have the heat supplied to the reverse side of the paper as in the conventional transfer machine. In a flat-bed machine this is easily arranged by using a perforated hotplate, while in a continuous machine external heating equipment such as infrared heaters gives the best results. One big advantage from this kind of arrangement in continuous-web printing, apart from more rapid transfer in certain difficult cases, is the absence of compression and consequent glazing of the fabric.

It is clearly much simpler mechanically to design a discontinuous low-pressure transfer machine, and several such machines are available. They operate in much the same manner as a flat-bed transfer machine, with the provision of a sealing system and a pump to evacuate the transfer zone rapidly. Such machines are useful for difficult fabrics such as Lycra stretch fabric for swimwear, which will not stand severe transfer conditions and yet requires to be printed with above-average penetration because it is naturally stretched in wear and stitch marks at the seams are unsightly. This type of machine is also of value in transfer printing carpet tiles, which must be printed without crushing while requiring good penetration down the pile or into the felt.

The difficulty with continuous vacuum transfer machines is in establishing a reliable seal with a continuous feed of fabric and paper. One solution is, in effect, to wrap the transfer drum in an evacuable skin. This approach has been used by Kleinewefers in a system in which the fabric and paper are held in contact with the heated cylinder surface by a perforated flexible metal band in place of the conventional blanket (Figure 3.8). On the outside surrounding 78% of the circumference is a continuously maintained vacuum chamber with the entrance and exit seal-operated. A major advantage of this arrangement is that the vacuum enables transfer to be achieved more quickly, even when operating at the 10.7 kPa (80 mmHg) pressures which can be used, so that the drum diameter can be reduced from the normal 2 m. This makes a system of this kind easier to construct. Production rates of 1800 m h⁻¹ have been claimed.

A more direct solution to the problem has been implemented in the Stork vacuum transfer system, which encloses the entire feeding and heating system inside a vacuum chamber (Figure 3.9).

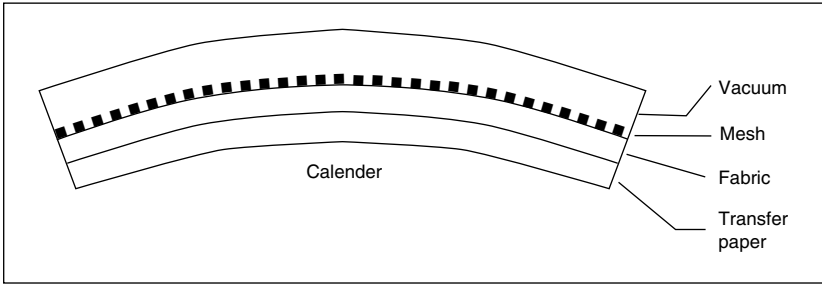


Figure 3.8 Continuous transfer printing under vacuum conditions (Kleinewefers DSV 1200 machine)

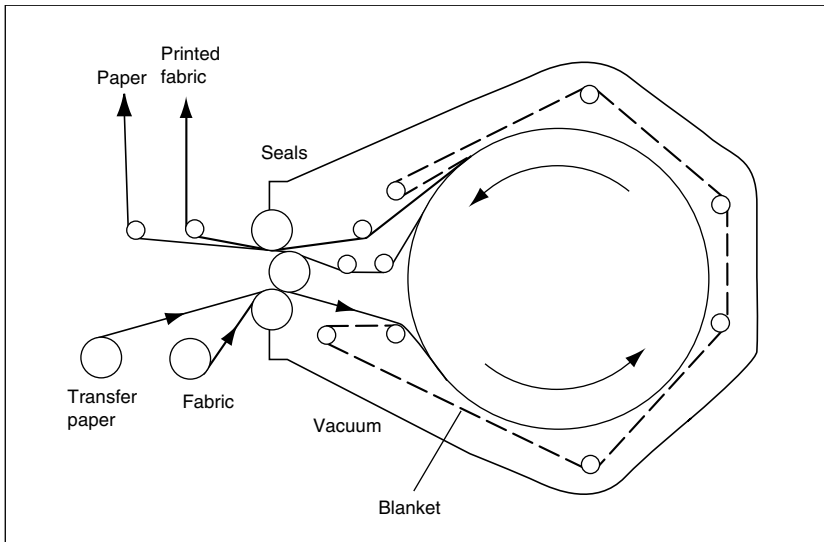


Figure 3.9 Flow diagram of vacuum transfer printer (Stork TC451 machine)

Vacuum transfer machines are particularly useful for heat-sensitive fabrics such as acrylic materials, since the transfer temperature may be reduced by as much as 40 degC. Alternatively dyes that sublime less readily can be transferred, with corresponding benefits in heat fastness.

3.2.6 Sublimation transfer on natural fibres

It is possible to use sublimation transfer papers to print fabrics made from blends of polyester or polyamide fibres with cellulosic fibres such as cotton or viscose. The dyes

will transfer to only a slight degree to the cellulosic component, although it is advisable in such cases to check the fastness achieved since some sublimable disperse dyes can stain cellulosic materials to a significant degree but with poor fastness. Since the cellulosic component is only weakly coloured, however, the quality of the result depends on its proportion in the blend, the extent to which the fabric structure presents it to the view, and the depth of shade to which the polyester or polyamide component is printed. At higher print strengths the prints have a somewhat milky appearance, due to the visual contribution of the weakly dyed cellulosic component. Consequently there has been for many years great interest in the possibility of using sublimation transfer papers to print cellulosic or substantially cellulosic materials, in addition to the general interest in developing transfer print systems for such fibres in competition with regular printing.

Two approaches to the problem have been explored commercially. One is to modify the cotton chemically to make it receptive of disperse dyes without significantly changing its textile behaviour, and some systems have been developed which exploit this to a limited degree. An alternative is to exploit the affinity of many sublimable disperse dyes for certain durable aminoplast resin finishes, and to treat the cotton appropriately before printing.

Cellulose acetate was the substrate in the first explorations of sublimation transfer printing [2], and this has been the starting point of many of the studies of chemical modifications of cellulose which have been undertaken with the aim of producing a cotton that is printable with sublimation transfer dyes. But there are limits to the degree of chemical modification that is permissible before the cotton loses the properties which make it the most important textile fibre. Thus alkylation using acetic, propionic or butyric acid has been of some use in relation to polyester/cotton blends but not for the printing of pure or substantially cotton fabrics [41,42]. A method for the introduction of propane sulphonyl groups by exposing cotton to propane sulphone vapour for 60 minutes at 60 °C has also been examined [43].

Consideration of the physical chemistry of the situation suggests that the most effective modification would involve the introduction of substituent groups with high binding potential in their own right, such as aryl or aroyl groups, rather than alkyl substituents which have the primary effect of blocking hydrophilic centres in the cellulosic chain. The degree of substitution of cellulose by benzoyl groups which is needed to produce significant affinity for disperse dyes is quite small, and if the process is carefully controlled benzylation of cotton can be used to produce an excellent transfer-printable cotton [44]. Another avenue which has been explored has been pretreatment with vinyl monomers [45].

Physical (rather than chemical) modification of cotton has also been investigated. In this connection investigations have been carried out on pretreatment of cotton

with high-boiling ($> 150\text{ }^{\circ}\text{C}$) swelling agents to open up the structure to disperse dyes, which become entrapped [46].

But while chemical or physical modification pretreatment processes may be of scientific or technical interest, they do not fit well with the structure of the textile print market. One of the advantages of transfer printing is that the fabric is committed to a design as late as possible in the production chain, and only to the degree supported by potential sales. Pretreatments of this kind imply a commitment to future transfer printing, although not to any particular design, at a very early stage and consequently this has greatly limited commercial interest.

Pretreatment of cotton fabrics with resin preformers is well established in textile processing, and can be carried out by a simple padding and drying application just before printing. Thus it does not suffer from the major disadvantage of the more fundamental modifications discussed above. Resin finishing agents based on hydroxymethylmelamine, used to confer crease resistance to polyester/cotton or cotton fabrics, also provide a substrate that is fast to washing and has good affinity for disperse dyes. Thus by impregnating the fabric by padding with an aqueous solution of the resin precondensate and drying followed by sublimation transfer in the usual way, the resin is simultaneously printed and cured, to give a fast to washing result [44,47–52]. It is essential that the resin impregnation be uniform, as otherwise printing will be uneven. Thus the resin application requires more care than is usually required in the resin finishing of fabrics, where any defects tend to remain invisible. Also the drying conditions need to be controlled in order that the partial curing, which inevitably occurs during drying, takes place consistently.

During curing of the precondensate in the transfer printing, formaldehyde (methanal) is emitted. This has to be minimised for health and safety reasons and the operation needs to be carried out with suitable extraction. The amount of formaldehyde produced depends upon the particular condensate selected. The melamine molecule possesses six hydrogen atoms which can be replaced by reaction with formaldehyde to produce ultimately hexahydroxymethylmelamine (HHMM). All the condensates can be etherified to form a whole range of alkoxymethylmelamines. These products have different degrees of reactivity and yield free formaldehyde to different extents during condensation. From all points of view the best results are obtained in transfer printing when using fully substituted HHMM. Formaldehyde emission can be further reduced by partly replacing HHMM with a polyurethane. Although polyurethanes are of no value on their own as transfer-printing resins they condense readily with HHMM and similar products to give durable soft finishes without loss of effectiveness as an aid to transfer printing, while at the same time reducing the HHMM requirement.

The approach so far described is suitable only for the printing of continuous web.

Garments and garment panels cannot be pre-impregnated with the same convenience and consequently methods have been sought to transfer the resin binder at the same time as the dye. Since the resins and resin preformers used do not sublime, their transfer involves other mechanisms which it is more appropriate to consider in relation to melt and film transfer.

No satisfactory substitute for formaldehyde-yielding resin formers has been found and, in view of the drive by leading retailers to eliminate such materials from their ranges, it is likely that the use of the currently available pre-impregnation route to sublimation transfer printing cotton will decline.

3.3 MELT AND FILM RELEASE TRANSFER

These two approaches to producing a transfer print are closely related from a scientific and technical point of view and under some conditions it is not easy to distinguish one from the other. It is consequently more appropriate to consider them together.

Both melt and film release transfer papers are produced using inks to produce an image that softens or melts on heating, and which transfers to the fabric carrying the colouring matters. The colorants do not require to show any substantivity at the transfer stage, which is essentially mechanical. Both methods involve bringing the transfer paper and the fabric together with applied heat and pressure to form a composite shown diagrammatically in Figure 3.10.

Figure 3.10 shows a highly formalised picture of the situation and makes no allowance for the complex nature of the fabric 'surface'. It pictures the situation before the applied pressure has forced any of the softened or molten printed image or ink layer into the fabric or back into the structure of the paper. At this point there will be an adhesive force F_1 between the image and the paper and, if the process is to work, another force F_2 between the image layer and the fabric. Within the image layer there is a cohesive force F_3 . All three forces are temperature-sensitive. Suppose that an attempt is made to separate the paper from the fabric, to which it is now temporarily bonded. If both F_1 and F_2 are significant, a stress force will develop in the image layer. If the temperature is currently above the softening point of the ink then the film will

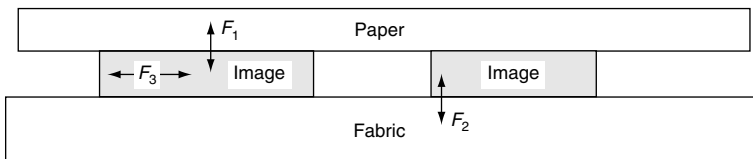


Figure 3.10 Schematic representation of melt/film release transfer

split, leaving an image on the fabric and a residue on the paper. The way in which the split occurs will depend on the relative magnitudes of F_1 , F_2 and F_3 at the time. Applying a high pressure and forcing the fabric into the softened or molten film effectively increases F_2 , and consequently reduces the amount remaining on the paper after separation. Alternatively, if the film melts and wets the fabric and consequently flows over the fibre surfaces, then little pressure will be needed to effect a high degree of transfer. The transfer will be affected also by the interaction of the printed image film in its normal, softened or molten state with the paper surface, in that this will determine F_1 .

A different situation arises where the force F_3 is relatively strong and F_1 is weak. Then the separation of the paper from the fabric will result in the image layer being transferred, substantially intact, to the fabric. This is pure film release transfer. In practice, the film is softened by heating at the same time as pressure is applied, and transfer will be accompanied with some degree of flow into the fabric. Pressure-induced flow and flow due to melting and wetting are closely related, so melt and film transfer are not always easy to distinguish. In both systems the transfer of colouring matter from the paper to the fabric is a mechanical process, rather than one of diffusion. Thus the paper must have sufficient adhesion to the print layer to allow it to be handled and, at the appropriate time and under the appropriate conditions, release it easily and efficiently to the textile. It is a feature of melt and film release transfer systems that coated 'release' papers are normally used to promote the efficiency of transfer to the fabric. The subject of such release papers is therefore one which must be addressed in this context.

3.3.1 Release papers

There is no body of published research concerning release papers, and what is known tends to derive from empirical experience. This is largely because release papers were developed primarily for the self-adhesive label trade. This has fairly simple requirements which can be met using silicone-coated or polyethylene-coated papers. The requirements for a transfer-printing release paper are more complex, however.

In the first place the paper has to be receptive to the printing ink while having excellent 'hold out' properties so that all the ink is drawn from the engraved gravure rollers or taken from the flexographic stereo roller. If screen printed the ink must not mark back on to the screens as they apply the different coloured components of the design. As the quality of the transferred print will reflect completely its quality on the paper (unlike sublimation transfer printing, where some lateral diffusion occurs to hide minor print faults), the print layer must develop a uniform film during drying; thus the paper must be wetted by the ink solvents to a sufficient degree either to allow the ink

to flow or to avoid reticulation. To some extent the performance during printing can be controlled by adjusting the ink formulation, taking into account the differing characteristics of the different printing processes, but clearly there is no point in selecting a release paper which unnecessarily presents problems. Gravure printing lays the ink down in dots reflecting the shape of the engraving and these have to coalesce to give a uniform film in the few seconds before the ink is dried. Flexographic printing lays the ink down in a continuous layer, but it must not flow under the pressure of the print roller to give edge outlining. Screen printing also lays down ink in dots defined by the screen mesh; however, screen inks dry more slowly than gravure inks do, they have greater viscosity and they are applied at heavier coating weights, so obtaining a uniform film is less of a problem. On the other hand the screen has to lift off (or 'snap') from the paper without taking ink with it.

The processes taking place immediately after printing a release paper and during drying are highly complex and have received little scientific study. During drying the ink composition inevitably changes. The various components reach their solubility limits at different times. The rheology and the interfacial tension between the ink and the paper change, and there may be some separation of the components. The surface energy of the release paper will affect the distribution of the separated components in the drying ink layer and, since release is determined by the interaction of the release coating and the component of the dried ink layer adjacent to it, the releasing potential is difficult to predict precisely from the respective properties of the paper and the ink.

Most commercial textile transfer release papers are coated with a solution of Werner chrome complexes of myristic or stearic acid, unlike those used in the label industry which tend to be silicone-coated. This is because silicone papers are difficult to print unless the surface properties are maintained within very fine limits, which are hard to control. On the other hand, the Werner complex coatings give a surface printable by litho, gravure, flexo or screen printing and the coating can be applied in line with paper manufacture if desired. The Werner chrome complexes are cationic and as the applied film containing the release coating material dries, the positively charged moiety is attracted to the naturally negatively charged paper surface; the molecules of the agent thus become oriented with the hydrophobic moiety pointing away from the surface. This provides a very effective release coating for a wide variety of ink systems of use in the production of melt or film release papers. Other release systems can be used in specific systems, including wax-based coatings, UV-cured acrylic materials, and solutions or dispersions of polyamides.

3.3.2 Melt transfer printing

The earliest commercial transfer-printing process for textiles was, in fact, a melt

transfer process, and it has continued to give excellent results for over 40 years. The Star printing process, developed by Star Stampa Artistici di Milano, uses a multicoated paper substrate as the transfer medium [53,54]. The paper is first sealed with an impermeable coating of, for example, nitrocellulose. It is then given a second coating of low-melting waxes based on oleic resins together with dispersing agents which assist the removal of waxes in the later stages of the process. The design is then printed on to the coated paper by gravure printing using an ink based on drying oils and waxes. Care has to be taken in selecting the materials so that the wax layer does not melt during the printing process and the paper does not adhere to itself under pressure in the printed roll, a phenomenon known as 'blocking'. Transfer is effected by bringing the paper into contact with the fabric and passing the composite between heated calender rollers at fairly high pressure. The ink and wax layers melt and are forced by the pressure into the fabric. The impermeable coating prevents the ink layer from migrating back into the paper, and the transfer is highly efficient. As the composite leaves the nip of the calender the paper is removed, leaving the image on the fabric. The process is then completed by treating the fabric by whatever means may be appropriate to fix the dyes in the transferred image; for example, fabrics transfer-printed using direct dyes may be nip-padded with a salt solution and steamed. If vat dyes have been used in the ink the fabric may be impregnated with caustic soda/hydros solution and steamed. The residual waxes from the transfer ink and coating are removed during final washing of the fabric. The efficiency of the transfer process is dependent upon the ease of release of the image layer and since this is achieved by the use of a high-pressure calender the process has not been widely adopted. The Star printing process is capable of producing very high-quality prints, however, and by the use of gravure printing outstanding design work is possible.

Many attempts have been made to develop processes analogous to Star printing which do not require high pressures to effect transfer. Sandoz have patented a process that uses an ink containing dyes that do not melt or sublime together with a polyglycol or an ether or ester derivative of a polyglycol which is transferable at 120 °C [55]. The agent is said to act as a 'transfer solvent' for the dye. The same concept of transfer by means of a melting-transferable solvent is the basis of transfer papers marketed by Sublistatic [56]. These are recommended for the transfer printing of silk, wool and cotton. They carry a coating that melts at 60 °C, and transfer is carried out using a modification of a standard sublimation transfer calender which applies a roller pressure of 59 kPa (6 kg cm^{-2}) to the paper/fabric composite as it is carried under the blanket to contact the heated drum. Although this pressure is not low, it is much less than that used in Star printing. As the dyes are not required to become fully penetrated during the dwell time in the transfer machine, operating temperatures can be, with advantage, lower for the printing of fibres such as silk.

After the transfer is completed the dyes are fixed, in the same way as for Star printing.

This transfer system lacks the simplicity that characterises sublimation transfer printing and as far as cotton printing is concerned it cannot be regarded as offering any advantage over pigment printing, which accounts for over 50% of printed cotton. It could, however, be a useful one if it can be adapted to be suitable for the printing of reactive dyes.

Melt-transfer systems for the printing of garments or garment panels have been available for some time. The successful ones have been developments on the theme of applying a resin binding system along with sublimation-transfer dyes using standard transfer-printing equipment. A typical product of this kind has been described by de Vries and Snyder [57,58]. Sublimation printing dyes are printed on to a paper with suitable release properties and then top-coated with a polymeric layer. Suitable polymers have a T_g between -20 and $+50$ °C, and may be chosen from a selection that includes poly(butyl methacrylate), acrylonitrile-butadiene-styrene terpolymers, a vinyl isobutyl ether-methyl methacrylate copolymer and similar materials. The incorporation of urethane groups in the polymer is stated to be advantageous. The de Vries company marketed transfer papers under the trade name CoTon, recommending transfer to be carried out using a standard transfer press for 15–20 s at 195–200 °C. The results had a soft handle and excellent appearance. The transfer mechanism involved the transfer of the polymer accompanied by the sublimation and/or dissolution of the disperse dye to produce a print on the cotton fabric. It is not necessary to employ resins of the kind used in the de Vries process and formulations of waxes mixed with acrylic resins and aminoplast precondensates or other crosslinking agents have also been used successfully. Of considerable interest in this connection has been the successful introduction of the so-called photocopy transfer papers such as Fabrika (CLC Fabrika) and Transphotron (Green Print International), all of which operate as melt release systems. These products offer a coated release paper on which a colour photocopy can be produced using a machine such as the Canon Laser Copier. The images are formed using 'colour formers', which are essentially pigments coated with a low-melting (80 °C) methacrylate resin. The photocopied image can be transferred on to a cellulosic fabric using a standard transfer press operating at 190–200 °C for 15–20 s. The results meet the normal commercial standards for washing fastness and the system is used both for design work and point-of-sale decoration. Since the photocopiers produce prints of photographic quality which are accurately transferred to the fabric, the image quality on the garment is excellent. The most advanced photocopiers can be modem-linked so that designs can be line-transmitted and reproduced on garments within seconds. The Fabrika system is based on the use of vinyl esters [59], but a variety of other resins can be used successfully as a basis for these papers, including acrylic and

other systems which can be formulated with modifying agents such as plasticisers or crosslinking agents.

3.3.3 Film release transfer printing

As the name implies, film release deposits the printed image as a virtually coherent film on the textile material. Such systems have been used for several years with great success worldwide for the decoration of garments; their use for printing continuous-web fabrics, which have to meet different criteria, has not so far proved commercially viable, although the technical problems presented are well understood.

The most widely employed transfers employed for the printing of cotton garments are based on plastisol inks. These consist primarily of finely dispersed vinyl chloride copolymers in nonvolatile plasticisers such as dioctyl phthalate, tricresyl phosphate or chlorinated paraffins together with pigment as colorant. Plastisol inks are used for both direct textile prints and the production of transfers. One of their most useful characteristics, as far as the printer is concerned, is that they do not dry. They contain no solvent and do not block screens by drying. When heated, however, they congeal or set by internal crosslinking and the prints become dry to the touch. The image remains thermoplastic and this property enables the prints to be used in transfers.

Two main methods are used for the production of transfers. One method is to print on to a release paper, usually one that is coated with a Werner complex, using a semidrying lithographic ink system and then to blotch screen print over the image using a white or grey plastisol backing coat. After application of the backing coat the print is passed down a drying oven to set the plastisol layer. Alternatively the image can be directly printed using fine screens and plastisol process inks. The image layer is thin and does not have high covering power, so an additional plastisol backing layer is normally required. Both methods enable images of high photographic quality to be produced. A third method of production is to make the image using screens which put down the full image layer in a single application.

The production of the transfer print may be carried out using a transfer press at 165–190 °C for 10–20 s, during which time the film softens and is forced into the fabric. After removal from the press the composite is allowed to cool and the image to reset. The paper can then be removed.

A variety of transfer equipment is used, ranging from standard transfer units such as that shown in Figure 3.7 to semicontinuous units such as the Reliant press shown schematically in Figure 3.11. In presses of this type the transfer is placed on to the garment on the moving belt, and passes into the machine. As the fabric enters the oven the top belt moves into contact, holding the cloth and paper together while they are heated. Just before the garment leaves the oven the pressure roller forces the two

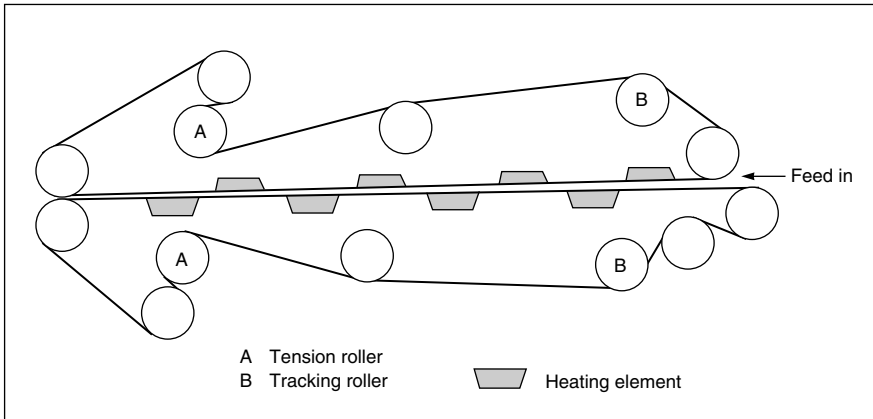


Figure 3.11 Rotary transfer press (Reliant)

closer together and the composite leaves along the belt for the paper to be removed when the print is cool. Continuous rotary presses are made by several manufacturers and employ different heat-input and pressure-application systems. They are characterised by high productivity compared with standard presses.

When an unmodified plastisol ink is used, the development of adhesion between the heated thermoplastic image and the cotton fabric is slow. There are two reasons for this. The first is that at the transfer temperature steam is generated from the fabric, due to regain moisture being released. This provides a barrier to contact between the hydrophobic plastisol and the fabric. The second is that the plastisol does not readily wet the hydrophilic fabric. Bonding can be increased by applying more transfer pressure (as discussed in relation to Figure 3.10), but this increases the risk of fabric being pushed through the image. Increasing the transfer time helps, but at the cost of a loss of productivity. Consequently an adhesive is frequently applied as the final coating layer of the transfers and this acts as a flux.

After transfer plastisol prints remain thermoplastic and consequently printed garments, though fast to washing, can be ironed only on the reverse of the fabric. Early versions of these prints gave rise to problems even in tumble drying, but the quality of contemporary transfer prints is much higher as a result of more informed formulation.

There are several variants of the plastisol transfer theme. Some plastisol transfer papers are made to be used in so-called 'hot-split' systems. Although the paper used for these is not a release paper it must have good 'hold out' properties. In these systems the paper is peeled away from the composite while it is still hot from the transfer press. In peeling, the image is split between the paper and the fabric. Referring back to Figure 3.10 and the relation between the operating forces, it is

clear that for a hot-split system the film must melt and flow into the fabric under the operating pressure more than would be required for a cold-peeling system; otherwise the splitting of the film on peeling would leave too much residue on the paper. Consequently inks for hot-split systems have to be formulated specifically for that purpose, and the vinyl polymers and plasticisers selected tend to melt or soften at slightly lower temperatures than those for cold peeling. The prints are somewhat softer than regular plastisol transfers and have less covering power when applied to coloured fabrics.

Another kind of plastisol transfer incorporates a so-called 'blowing agent', such as 1,1'-azobisformamide, which generates gas within the soft hot ink and causes it to expand. This process has to proceed more slowly than the development of adhesion, so that the print can expand to give a 'stereo' effect as it leaves the press without being blown off the fabric. Rapid release from the paper support is also needed. Plastisol transfers are not used for the printing of continuous-web prints because the market requirements differ. Whereas the application of plastisol transfers to garments takes the form of decoration to enhance market appeal, prints on continuous webs require to have soft textile handle and heat stability as well as fastness to washing, rubbing and so forth. Consequently the transferred film must be removed at the end of the process by washing, or be broken down during the transfer operation under the stress of the pressure used in application, or be thermally unstable so that it loses its film properties during dye fixation. The first approach suffers from the disadvantage of being a wet process. The second is quite easy to achieve as regular pigment-printing binders containing pigment can be easily transferred from a release paper on to cotton fabrics using moderate pressures [60]. The binder film transfers but breaks down under the transfer pressure. Unfortunately pigment-print binders are very strong film-formers and make unsuitable bases for printing inks for a variety of reasons. If applied in thin layers by gravure, they block the engraved rollers. They do not cause screen blocking when diluted, but screen printing with water-based inks on a non-absorbent release paper leads to problems of paper stability and maintaining register. Also pigment-print binders in the uncured state on paper have a tacky surface which makes the papers unsuitable for use. The third method exploits the potential energy stored in certain kinds of film formed by evaporation [61].

If a surface is coated with a solution of a film-forming polymer and then allowed to dry by evaporation, changes take place in the polymer solution as it becomes more concentrated. In the formation of the original polymer solution, the intermolecular cohesive forces were broken down by competition with solvent molecules. In the reverse process that takes place as the solvent evaporates these cohesive forces begin to reassert themselves, but as drying involves an increase in the viscosity of the film the ability of the polymer molecules to achieve optimum internal bonding or the lowest

energy state is limited in the time available, and further molecular migration becomes impossible.

The extent to which the lowest-energy (maximum-bonding) state is reached will depend on the length of the polymer molecules, their degree of flexibility and any steric hindrance provided by substituent groups. Consider poly(vinylbutyral) as an example: evaporation of a solution of this polymer on a release paper surface gives rise to a film which has considerable potential energy, as the bulky butyral groups severely restrict free motion of the polymer as the solution concentrates. If such films are removed from the supporting paper and softened by warming, polymer relaxation then becomes possible as the polymer segments become able to move. The result is considerable shrinkage. It is this property that can be exploited in transfer printing.

After printing an image on to a release paper by appropriate means it can be transferred on to fabric using a heated pressure calender with hot peeling. At this stage the film is intact, but is attached discontinuously at contact points to the rough fabric surface. If the fabric is now heated the film starts to relax but is partly prevented from doing so by virtue of the attachment points. Thus a tension builds up between these points which leads to rupture of the film as it becomes weaker with increasing temperature. The breakdown of the film means that it has little effect on fabric handle and need not be removed at the end of any dye or pigment fixation process. This approach can be used to apply disperse dyes or pigments which may be fixed by the simple application of heat.

It has proved possible to prepare successful printing inks containing reactive dyes and alkali in formulations which are quite stable in the ink solvent. The dye in these cases can be satisfactorily fixed by steaming directly after transfer. The fixation achieved by this means is rather higher than that obtained in much printing with reactive dyes and this factor, combined with easy removal of unfixed dye during washing-off and low dye wastage during the printing of the paper, makes printing reactive dyes in this way cheaper than direct printing. The reactive dyes used have to be free from many of the components added during their normal standardisation; as a result of the difficulty in ensuring supplies of dyes in a suitable form, the method has not been commercially exploited.

3.4 WET TRANSFER PRINTING

The principle behind wet transfer processes is the use of water as the medium through which dye diffuses in passing from the paper to the fabric. Thus it resembles sublimation transfer printing in that it is a diffusion-controlled system, but since water is used instead of vapour it is not restricted to the use of dyes that can sublime. The first commercial exploitation of this approach dates from the introduction of the Fastran

process in 1971 [62]. This involves padding wool garments with stabilised thickeners to obtain an expression of the order of 1:1 and then bringing the wet garment into contact with a transfer paper printed with acid or reactive dyes. The composite is then heated in a press for several minutes during which time the dye migrates to the fabric and becomes attached in the usual manner. The method is not highly productive but is quite suited for the printing of high-value articles such as knitted woollen garments, especially when novel design effects are obtained at the same time.

Several attempts have been made to devise continuous wet transfer systems. The DewPrint machine introduced in the late 1970s (shown schematically in Figure 3.12) offered an ingenious solution to the problems posed [63].

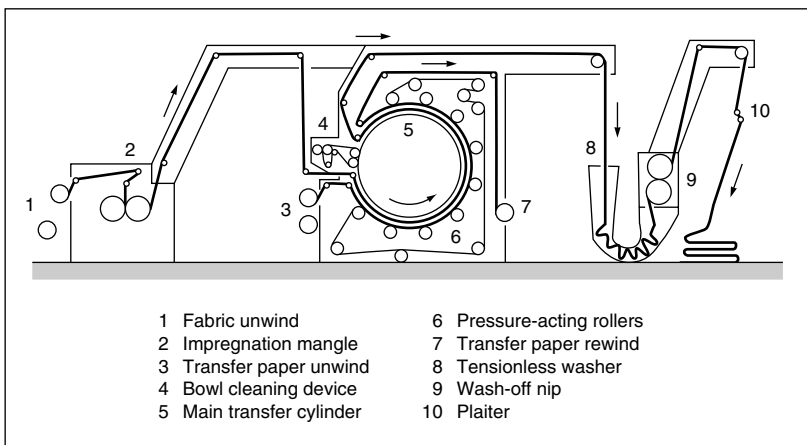


Figure 3.12 Wet transfer-printing machine (DewPrint)

The major difficulty to be overcome in a system of this kind is how to maintain the contact pressure holding the paper to the fabric continuously at the required level over a period of time. This cannot be achieved simply by using a stretched blanket as in sublimation transfer. Consequently the DewPrint machine was fitted with a series of pressure rollers around the heated transfer cylinder, which exert a steadily increasing pressure up to but not exceeding the pressure of the mangle used initially to impregnate the fabric. The major drawback of this solution to the problems was the capital cost involved, which seriously affected adoption of the approach.

Continuous wet transfer continues to be of interest, and new equipment has been recently introduced by Küsters in association with the Cotton Art process developed by Dansk Tranfertryk for transfer printing reactive dyes using their specially developed transfer paper [64].

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