Transfer printing

1 Background

1.1 Transfer printing

Transfer printing involves a number of processes in which designs are first usually printed onto paper and then in latter and separate process transferred to a textile. The most commercially important of the transfer-printing methods are Sublimation transfer and Film release. Other processes involve transfer of a meltable ink (Melt transfer) and transfer in an aqueous film (Wet transfer)

Transfer printing offers several advantages over conventional printing

1. Design may be easily printed onto the textile with relatively low skill using inexpensive equipment with modest space requirements and without any need for washing-off.
2. Designs are printed and stored on inexpensive paper, reducing stock holding costs.
3. Short-run and repeat orders are less costly and much easier to fill by a transfer process than by direct printing because the initial print set-up (e.g. screen/colour registration) have been completed on inexpensive paper.
4. Transfer printing allows the printing of complex designs, which may be overly expensive if printed directly onto textiles.

A common example of transfer printing is printing of T-shirts at market stalls. Often the Film release method is used. The customer chooses the T-shirt and the required pattern. The garment and paper holding the pattern are placed in a heated press and within a minute the customer walks away with the printed T-shirt. In this process both the coloured pattern and a polymer film are transferred to the textile.

Similarly, in the Sublimation transfer process, a roll of polyester fabric and a roll of paper printed with selected disperse dyes are held together for about 30s at 190-210°C as they pass around a heated roller. The dyes sublime from the paper and diffuse into the polyester. The design can be changed almost instantly and without stopping by interleaving a different paper against the polyester fabric. The exhausted paper is often used for gift wrap, while the printed polyester is ready for dispatch.

The principal of Sublimation transfer was first observed in the 1930s by investigators at British Celanese. They showed cellulose acetate fabric could be strongly dyed when heated in close contact with paper coated with disperse dyes. However, commercial application of the Sublimation transfer process only occurred with the growth in the use of polyester in the 1950's and the realisation that the thermofixation method of dyeing polyester involved sublimation of disperse dyes and dyeing of the fibre from the vapour phase. Sublistatic SA, was formed to commercialise the Sublimation transfer printing process and during the 1970's and early 1980's there was a massive growth in the use of this process to print polyester as many companies jumped into the market. Possibly due to its rapid growth, the ease with which inexperienced operatives could enter the market and printing inappropriate designs/fabric combinations transfer printed polyester developed a cheap and nasty image and the growth declined rapidly in the late 1980's

1.2 Transfer printing natural fibres

One of the worst examples of the application of transfer printing was probably the manufacture men's suits from double knit polyester fabrics printed with woven designs. While the fabric drape was wrong the fabric also often had a flat and somewhat glazed appearance. To answer these criticisms and to take advantages of the increased opportunities offered to natural fibres by transfer printing process organisations examined the possibilities for sublimation transfer printing natural fibres, particularly cotton.

It is possible to use sublimation transfer papers to print fabrics made from blends of polyester and natural fibres such as wool and cotton. Under the hot dry transfer conditions, the disperse dyes will usually only transfer slightly to the natural component, which is only weakly coloured. This gives good

colour fastness to the blend as the dye is strongly bound to the polyester, while the loss of colour from the natural fibre makes little change to the appearance of the print. Depending on the colour strength and contrast of the print, blends containing up to 30% natural fibre may be printed using this approach.

While it is technically possible to sublimation transfer print fabric manufactured wholly from natural fibres with disperse dyes there has been little commercial application of these processes, which generally involve substantial modification of the natural fibre with reactive monomers. These compounds either form polymers within the fibre or block the hydrophilic groups in cotton or wool.

The most practical of these processes exploited the affinity of many sublimable disperse dyes for the resins, typically used to confer crease resistance to polyester/cotton and cotton fabrics. The fabric was padded with an aqueous solution of the resin and dried followed by sublimation transfer printing in the usual way. This not only cured the resin but gave a transfer print fast to subsequent washing.

Esterification of the hydroxyl groups of cotton improves the affinity for disperse dyes. Treatments involving benzoylation were particularly effective. Similarly the amino groups in wool could be reacted with benzoic anhydride in dimethylformamide to achieve a 30% weight increase. This modified wool was readily sublimation transfer printable, shrink-resistant and heat settable.

Wet transfer processes were developed for printing wool with acid or reactive dyes. The Fastran process involves bringing garment panels saturated thickened paste into contact with the transfer paper and holding in a heated press for several minutes. The method was not highly productive but proved practical for printing of high-value articles such as fully fashioned knitted woollen garment panels.

The DewPrint machine was an attempt to develop a continuous wet transfer process. The major difficulty with this process was to maintain steady contact between the paper and the saturated fabric during the dye transfer process. Evolution of steam and dissolved gasses as the paper and fabric passed around the heated roller may have been responsible for blurred and patchy prints. Pressure rollers were subsequently fitted around the heated transfer cylinder to maintain the pressure on the impervious blanket but with little improvement in print quality. In hindsight it may have been better to use a porous blanket to allow these gases to escape.

2. Wool Transfer printing research

2.1 Introduction

The wool fabric used for printing is an expensive substrate, because it is usually a light weight worsted knitted or woven fabric prepared from fine micron wool. Printing wool using conventional means is a complex, expensive and risky process involving four critical steps.

1 In order to achieve sharp bright even prints the fabric is usually chlorinated. It is notoriously difficult to get an even treatment with this process due to the high reactivity of chlorine. The best approach is probably to use open width chlorination with a Kroy machine. Recently CSIRO have released SiroFlash as an alternative to this step.

2 Wool prints are often in short run lengths (70m) printed using flat screens on a long table, although rotary screens and continuous printing can be used. It is essential therefore to quickly register the different colour screens to avoid wastage of the expensive fabric.

3 After printing the fabric must be carefully dried and conditioned before steaming. To obtain the maximum brightness and sharpness from the prints the wool must rapidly achieve saturation regain on entering the steamer. If the wool is too dry or the steam too hot (104°C or above) maximum colour yields will not be achieved. Likewise if the wool is damp and the steam very wet condensation can occur and the prints will be blurred.

4 Removal of the chemicals, unfixed dyes and thickeners after printing is the final critical step. To achieve bright prints with the required wet fastness reactive dyes must be used. While there is a high level of reaction between wool proteins and the dye, deactivated dye and dye which has reacted with soluble wool proteins can stain undyed areas of the print.

The use of transfer printing offered obvious advantages to wool printers and the potential to increase the amount of wool printed. The wool industry decided to investigate methods to transfer print wool and research began at both the International Wool Secretariat (IWS) Ilkley U.K. and at CSIRO Textile Industry.
At IWS Dr David Lewis and Dr Veronica Bell investigated methods to improve the printability of wool using commercially available transfer papers. This involved both disperse dyes used for polyester printing and basic dyes used for printing acrylic fabric. While simple treatments gave bright prints on wool the fastness of the prints to washing and light was generally very poor. Only reaction of wool with a 60% solution of benzoic anhydride in dimethylformamide to achieve a 30% weight gain in the wool proved effective but this was clearly impractical. IWS were also involved with the development of Fastran and Dewprint processes.

2.2 - Wool Transfer printing research at CSIRO

At about the same time a team lead by Dr Rex Brady, with Dr Peter Cookson and Keith Fincher was formed at CSIRO Division of Textile Industry to develop alternative methods for transfer printing wool. The melt transfer printing process used available textile dyes and machinery However, a more ambitious sublimation transfer process latter named Keratrans quickly showed more commercial potential. This process more akin to the polyester process required the development of a new range of disperse dyes, which formed chrome complexes during heat transfer.

2.2. 1 Melt transfer printing

Melt transfer printing involved mixing conventional wool dyes and chemicals required for printing with a transfer medium and printing transfer paper. The paper and chlorinated wool were pressed together and heated in a calendar to transfer this mixture to the wool. The printed wool was steamed to develop the print followed by washing-off to remove unfixed dyes and chemicals. This process only eliminated one (step 2) of the four critical steps in conventional wool printing.

The focus of the research in this project was paper printing and achieving a high level of transfer from the paper to the wool fabric. The transfer medium needed to be water soluble so that it could be easily removed after completion of the printing process but must also melt or soften at a reasonable temperature to allow good transfer to the wool fabric. A high molecular weight polyethylene glycol (PEG) was chosen as the transfer medium. PEG did not significantly increase the viscosity of the printing chemicals and conventional thickeners could not be used as they interfered with the melt transfer step. The transfer printing paste was thickened by preparing an emulsion of the printing solution with white spirit and printing the transfer paper. Considerable effort was expended in evaluating and developing emulsifiers, which would give the right viscosity to the printing ink. This was essential in the production of good prints particularly, uniform blotches on the transfer paper and the final wool print.

The melt transfer printed paper needs to be a good compromise between stability during handling and storage and release of the print during transfer. With some release papers complete ink transfer could be achieved but the dry transfer ink tended to easily peal off the paper. If the paper was too absorbent little ink transfer occurred in the calendar. A high quality coated paper offered a good compromise. The Melt transfer printing process could be used to print a range of natural and synthetic fabrics with appropriate selection of dyes and chemical auxiliaries.

Print transfer occurred in a calendar between a heated (100-120°C) polished metal roller and a nylon roller under extreme nip pressure. While this is conventional textile machinery used in finishing cotton it is expensive specialised equipment unlikely to be available to wool printers especially for short production runs. This plus the use of flammable solvents in printing the paper, the limited reduction in processing steps offered by melt transfer and the potential of the developing Kertrans process lead the team to refocus its effort.

2.2.2 The Keratrans Process.

The Keratrans Process involved printing transfer paper with a conventionally thickened paste and sublimable dyes. A straight forward pad-dry treatment prepared the wool for transfer printing, which

was carried out in an inexpensive transfer calendar. The printed wool was steamed to develop the print but washing-off was not required. This process eliminated three (steps1, 2 and 4) of the four critical steps in conventional wool printing.

A major commercial challenge with the Keratrans process was the need to manufacture a new range of dyes. Although, the chemistry was well known it is always difficult to promote a process that requires the manufacture of new chemicals. Peter Cookson had synthesised a range of reactive and chelatable disperse dyes, which included a yellow with a reactive chloroacetylamino group and an orange, red and reddish navy all with alpha, alpha di hydroxyl azo groups, which could form chrome complexes. These dyes were heat transfer printed onto wool prepared with a soft acrylic polymer and potassium dichromate. The theory was that the disperse dye would transfer to the polymer and during steaming the dye and dichromate would diffuse into the wool to form a chrome dye which are known to be stable to light and washing. Muted prints were obtained; however while Keith Fincher was optimising the pre-treatment he found that the surfactant used to wet the wool during polymer application was most important component in obtaining good dye transfer and in fact the new disperse dyes formed complexes with the reduced dichromate during the transfer step. Many surfactants and chrome three salts were then evaluated. Chromic acetate gave the best results but commercial samples were variable. The pre-treatment using an anionic surfactant, chromic chloride, urea and lactic acid was subsequently patented.

At about this time David Lewis joined the group from IWS. The weak link in the process was the availability of dyes. Dyes based on acetoacetanilide pigments and the Petramin dye range used to dye nickel modified polypropylene were evaluated. Keith Fincher scoured the Colour Index and tested many likely structures without success. He suggested preparing a yellow dye based on salicylic acid to replace the reactive dye which required solvent for its preparation. David Lewis prepared p-chloro-aniline coupled to salicylic acid, which was used as the yellow but the range still lacked a bright blue.

After working for 12 months in Australia David Lewis returned to the UK. Keith Fincher followed shortly afterwards to continue the co-operative research. Larger quantities of the yellow, orange, red and navy dyes were synthesised and methods were developed to disperse the dyes in an aqueous media ready for print paste preparation. Successful paper printing trials were run with the cooperation of Stork in Holland and some limited lengths of fabric were successfully printed. Garments were manufactured and trialled with success

After a few months storage the red dye had diffused into the transfer paper and would not transfer. Another red structure was selected and the storage stability of the transfer papers was tested. The papers proved stable to accelerated storage. Problems were also encountered with the storage stability of the pre-treated wool which appeared to be of a biological nature. These were overcome by selecting an alternative surfactant.

Critically, the process still lacked a bright blue dye. A poorly sublimable disperse blue dye with acceptable fastness on wool was found but it could only be used to print pale blues and greens. A bright basic blue was also found but this dye was incompatible with the other dyes and due to its limited fastness could only be used to highlight prints.

The hunt continued for a bright chrome blue to complete the dye range. Coupling suitable diazotised amines to alpha napthol rather than beta napthol produced brighter blues but the synthesis always resulted in a mixture of the 2 and 4 coupled products but only the 2 coupled product formed a chrome complex. While old dye synthesis literature indicated the reaction of the 2 coupled product could be favoured when using solubilised alpha napthol these approached did not succeed with the synthesis of insoluble dyes. Eventually a commercial precursor of a neutral dyeing pre-metallised dye was found, which gave a bright blue with acceptable fastness.

Commercial quantities of the dyes were manufactured at Brighouse by a historic company Bottomley and Emerson which was then part of the Croda group. Azo dyes were manufactured in the old part of the plant, which was built on the side of a hill. Ice was manufactured at the top of the hill and on the next lower level the amines were diazotised in open wooden vats cooled by addition of ice. After diazotisation, coupling with the phenol occurred by draining the diazotised amine into a vat containing the phenol. A dispersing agent was added to the dye slurry to aid water removal during filtration. The mixture was finally drained into filter presses where the filtrate drained onto an open brick floor. The

wet filter cakes containing 40 to 50% dye were transported to Croda in Birmingham, where further dispersants were added and the concentration of dye was standardised. The mixture was ball milled for several days until a suitable particle size was obtained to produce a stable dye dispersion. These dye dispersions were marketed by Croda colours under the name of Sublichrome.

After working in the UK for about 18 months Keith Fincher returned to Australia. The technical feasibility of the process had been clearly demonstrated in a series of full scale industrial trials both for printing wool and for printing blends with polyester. By mixing conventional disperse dyes with the Sublichrome dyes excellent prints were obtained on wool polyester blends without the complex steaming and washing-off stages required for conventional blend printing. Surprisingly, during sublimation the disperse dye diffuses into the polyester while the Sublichrome dye attaches to the wool. Since there was no cross staining of the two component fibres during printing no washing-off was required and excellent fastness was obtained.

3 Conclusion

While the Keratrans process proved technically feasible and offered many advantages to the wool and wool polyester blend printer, controlling the conditions during steaming remained critical. Cooperation with IWS continued for a further 12 months looking at this issue and the detailed chemistry of the process. Two approaches to easing the steaming stage were successfully trialled. However, the Keratrans process never really gained a foothold probably because it didn't fit within one company's manufacturing processing line. The market was not large enough for one company to print Keratrans papers as Sublistatic did for polyester – so papers were printed in house. Wool printers didn't have transfer calendars, while transfer printers didn't have steaming equipment. There was also a fashion shift away from prints and commercial interest in printing processes declined.