II

REVIEW OF LITERATURE

The review has been divided in the following way:

1. Early textile printing and design.
2. Various techniques used for printing.
3. General properties of disperse dyes.
4. Research studies on transfer printing of polyester and polyester:cotton blends.

1. Early Textile Printing and Design.

Just as the beginning of the art of making cloth are lost into antiquity, so too are the origins of the first ornamentation of textile fabrics by printing (4).

Decoration is the first spiritual need of man, as Carlyle has pointed out. Pictorial representation was the earliest form of art and colour its most gratifying aspect. Primitive people used to decorate their garments with figures of animals, which they painted on with earth pigments. Such figured paintings were done with brushes and the colours did not last long, as they were not fixed.(4)

Some scholars hold the opinion that India was the original home of the earliest printed textiles and certainly many examples found in other parts of the world came from India as part of the great export trade, that India carried on from earliest times.

Evidence to the existence of printing in India has been obtained from the writing of the foreign travellers to India, from the accounts of the trading and export done by India and from the fragments of printed cloth discovered from various places.

Printing in India:

Blocks are said to have been used in India for printing from as early as 3000 B.C. although no such blocks have survived. (30) but a small stone block which has been dated as anterier to the 5th century A.D. has been found in the Bannu district of the North West frontier province.

The Roman and Greek travellers to India around 500 B.C. have described the printed fabrics worn by the people of India. Their writings say that the Hindus wore flowered garments made from fine muslin (4). Another evidence of printed fabrics being used in India around 300 B.C. is from the writings of the Greek, Magasthenes sent as an ambassador to the court of Chandragupta. He wrote that in contrast to the general simplicity of their lives, the Indians love finery and ornaments. They wore flowered garments made of finest muslin (6). Our knowledge of the printed cottons is substantiated by many accounts of the trading done by India.

Jayakar (18) has reported Gujarat as the heart of the cotton printing belt and as early as 1st century A.D. Gujarat was exporting Indian cotton prints, right through the middle ages, Gujarat continued to be the most important center of cotton printing. These printed cottons were from Ahmedabad and were printed in indigo blue and red colour. Purple black was produced by mingling the red and blue.

Indian printed fabrics were exported to Egypt, North Africa, Greece and ~~and~~ Europe from the earliest times, prior to even first century A.D. (30). The fabrics most commonly used were cotton, linen and silk. The printing was done by block. This involved only printing the resist or mordant after which the cloth was dipped in colour vats for development.

Further evidence to the printing in India is obtained from the fragments discovered at various places. Sir M. Aurel Stein found in the sand-buried ruins of Endere in Khotan on the borders of India, in a rubbish heap a printed fragment which he states must be accepted as dating somewhere between the 3rd and 8th centuries A.D. (3).

In Central Asia a printed fabric was discovered which can be dated to 8th century A.D. and having been printed in India. The printed fragments which have been discovered in an ancient tomb in Egypt dating back from 10th century A.D. show their origin according to authorities from India (12) and some printed fragments discovered by Sir Aurel Stein have been dated as 12th century A.D. and having been printed in Gujarat.

The first authority to make a concentrated study of the minor fragments was a Frenchman, R. Pfister in 1938. He isolated the Indian fabrics and traced their origin to Gujarat. He selected for the study those which he thought to be Indian an earlier than 17th century. The fragments were of two main type: (a) block printed, (b) resist dyed. The printed specimens had blue pattern on a white background. The pattern are reminescent of the pierced stone screen work that is a notable feature of the 15th century mosques and tombs in the region of Ahmedabad. Most of the fragments are probably of Ahmedabad origin.

India, the birthplace of the block printing industry has records of the printed fabrics of as far back as 400 B.C., but few actual fabrics of a date earlier than the 17th century have survived in India itself. This may be due to the depredations of the white ant, together with the excessively humid climate during the rainy season which has made it impossible to preserve cotton fabrics.

Printing in Egypt

According to the writings of Pliny the art of calico printing was known to the Egyptians during the first century and had been acquired from the Indians (3). The ancient Egyptians produced linen cloths of fine construction. The walls of the tomb of Beni Hassan (circa 2100 B.C.) depict figures, costumed with fabrics patterned in small conventional motifs in blue, amber and brown. Mummy cloths of later periods were decorated with printed borders in various colours. One of the earliest attempts at printing has been a fabric with a red and blue pattern, found near thebes and dated 1594 B.C. (4).

Printing with wooden blocks was practised from very early times. Small wooden blocks, no larger than a spool of thread found in Egypt from the 4th century A.D. Cottons unearthed at Akhmin on the lower Nile exhibit a blue dyeing resisted in a regularly repeated patterns by this method (4).

2. Various Techniques used for Printing.

Various techniques in order of their historical development used for printing are (a) block printing, (b) copper plate printing, (c) engraved roller printing, (d) screen printing, (e) transfer printing.

a. Block printing:

India is said to be the birth place of the block printing industry (30). Prior to the invention of wooden blocks for taking impression on textiles, textiles were decorated with the help of brush. Such painted fabrics were made in Masulipatam on the Coromandel Coast and were known as palampores and those made in Gujarat were known as 'chiddri'. The cloth used for 'chiddri' was coarse and used by the village people. The palampore fabric was used for wall hangings, floor spreads, coverlets and for men's gowns, waist-coats and women's dress as well as petticoats, these were the most beautiful painted fabrics ever made or likely to be ever made. Block printing is said to have been carried out in India as early as 400 B.C. Printing with wooden blocks is believed to have started in Gujarat. It is said that the idea of hand printing on cloth with engraved wooden blocks originated from beautiful wood carvings on buildings in Gujarat (6).

To make wooden blocks, best quality timber is required. 'Sag' or Indian Oak is used. The design to be obtained on the block is first drawn on paper and then transferred on to the block. After the design is transferred the engraving is done. The engraving is to a depth of 1/4 to 3/4 inch. These blocks are useful for line work and also for shapes that are not too big. Areas larger than 1/8-1/4 inch in width do not print well with these blocks.

When bigger areas of colour are to be printed a colour block is used. For making colour block along with wood, felt is used. The design is traced onto the block. Then the wood is cut into, to within 1/16-1/8 inch inside and then removed to a depth of 1/4 inch or so leaving a narrow wall of wood. Felt is soaked in gum and water and cut in the hollowed-out shape of the block and is then pressed into that shape. After this the wood outside is carved out leaving the felt shapes which can print evenly (29).

Intricate details of the design could be obtained in block prints by using brass or copper in form of strips. This was started in the 19th century. These were known as the coppered blocks. The copper strips were hammered into the blocks on the outline of the design. By this means, spots or lines of widths varying from 1/64 to 1/16 inch can be obtained (29).

The surface roller machine:

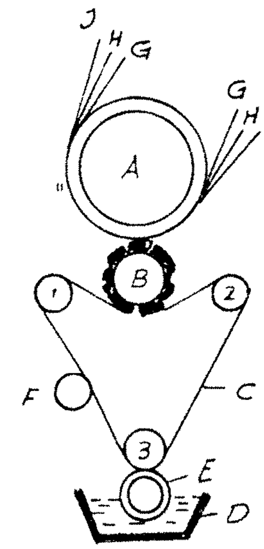
It was invented by a Frenchman Ebinger in 1800 and was the first development in the mechanization of block printing. This machine was not very workable as the wooden blocks in form of rollers warped and split very quickly and the prints were not very good.

Shortly afterwards a man named Burch, successfully experimented with surface roller printing. The colour was furnished from an endless blanket on which it had been evenly spread by two plain rollers- one rotating in the colour trough and the other distributing it. On leaving the furnishing roller the sieve was wiped by a steel 'doctor' blade (29).

The perrotine:

This was another attempt for the mechanization of block printing. In 1834 Perror of Rouen invented this machine. This performed all the actions of the block printer and printed the cloth successfully. Inspite of its success, it could not compete with the roller printing machine invented by Bell (29).

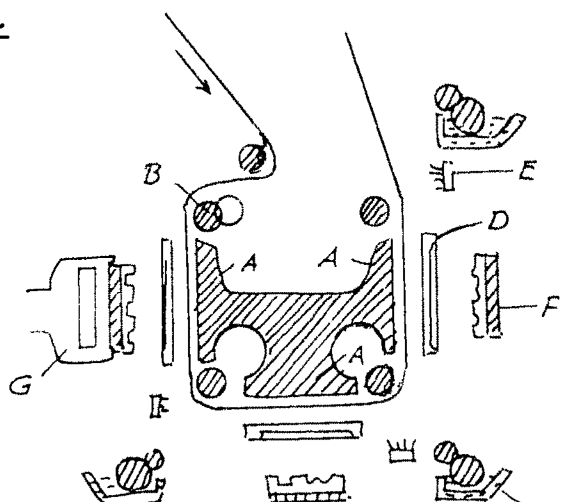
DIG. 1



A = PRESSURE BOWL, B = SURFACE ROLLER; C = FURNISHING BLANKET MOVING OVER ROLLERS 1, 2 AND 3, D = COLOUR TROUGH; E = PLAIN FURNISHING ROLLER ROTATING IN COLOUR, F = SECOND FURNISHING ROLLER SPREADING COLOUR EVENLY ON THE BLANKET, G = BLANKET FOR EXTRA RESILIENCE ROUND THE PRESSURE BOWL; H = BACK-GREY, I = CLOTH TO BE PRINTED J = PRINTED CLOTH.

DIAGRAM OF SURFACE ROLLER PRINTING MACHINE (29)

DIG. 2



A = CAST IRON TABLES

B = GUIDE ROLLERS

C = COLOUR BOXES AND FURNISHING ROLLER.

D = SIEVES

E = BRUSHES

F = PRINTING BLOCKS USUALLY 30 IN LONG BY 3 TO 5½ IN WIDE.

G = BLOCK CARRIERS.

DIAGRAMMATIC SECTION OF THE PERROTINE MACHINE (29)

The perrotine machine consisted by five main parts: cast-iron tables; sieves; mechanical tearers (comprising a brush and colour-box); a block carrier and finally, an arrangement for drawing the cloth forward after printing. The three wooden blocks about 76.0 cms long by 14.0 cms broad were fixed with the pattern sides at right angles to each other in a strong iron frame. They can each in turn be brought down on to the front, top and back of a four-sided 'table' covered with cloth and revolving on an axis. The cloth to be printed passes between the table and the blocks and gets its pattern in succession. The blocks are forced down upon the fabric by means of springs, and the fabric is printed.

<u>Copper Plate Printing</u>:

Towards the end of the 18th century there were the first attempts at printing from engraved copper plates. The printing was carried out by the 'intanglio' process. The copper plates were itched with the pattern to be printed. The colour was held in the incised lines and the pattern is transferred from them to the cloth by pressure applied by a wooden mallet. The pressure applied by a wooden mallet as in block printing did not suffice to produce a clear impression so a copper plate printing machine was constructed. This was a slow and difficult process and a continuous repeat could not be obtained, so this was converted into a cylinderical form, similar to the roller printing machines, of today (4).

Roller Printing Machines:

The earliest description of a roller printing machine dates back from 1743 in a patent issued to keen and Platt. The rollers were engraved plates bent around a mandril, the ends being joined by soldering, brazing, or riveting. Since no doctor blade was mentioned, the colour furnishing roller must have inked only the high portions of the engravings, so that it printed only in relief. In 1772 Atkin patented a single colour printing machine, also in relief. In 1780 Bonvalet, a cloth printer of Amiens constructed a machine which was turned by hand consisting of a wooden cylinder and a hollow iron roller with an engraved copper surface. Between 1790 and 1800 relief roller print m machines were set up, notably by Depouilly in France and Ebinger in England. Burch introduced the art of coppering the rollers and of a continuous colour furnishing blanket (4).

Engraved Roller Printing

Successful printing with engraved roller was done after the introduction of the 'doctor' blade by Thomas Bell, a Scotsman who patented it in 1783. The 'doctor' blade is useful in supplying the colour as well as to clean the colour from the unengraved portions thus the colour remains only in the incised surface of the roller and so prints are obtained in 'intaglio' (29).

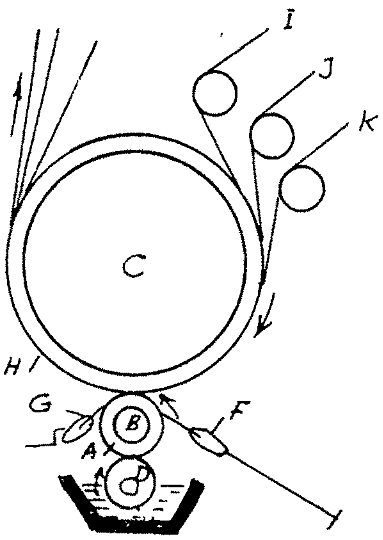
Screen Printing:

Screen printing as is known today is basically a stencil process used by the Japanese, probably around the end of the 8th century. The printing of cloth with stencils was first done by a Shinto priest called Yezen and so it is still called as the Yazen style. This was carried out by using stencils or screens made of especially prepared rice paper. Pattern containing free centers or holes were held together with human hair. In time the hairs were fixed across a wooden frame and later a silk gauze was used and so the silk screen as we know it came into use. The colour was gently pressed through the stencil with the help of a brush, the squeeze used today is a much later invention (29).

When screen printing was first developed it was done entirely by hand. A fabric known as the 'bolting silk' is stretched and fixed onto a wooden frame. A design is traced on a tracing paper and then transferred on the screen - this can be obtained by many a method the simple one of painting out the background with varnish to the most advanced photo-mechanical technique. For printing the screen is kept on the fabric, the dye paste is poured on the screen and forced through the screen on to the fabric with the help of a squeeze.

The entire process being done by hand was very slow, so attempts were made to mechanize the process. In 1954, the

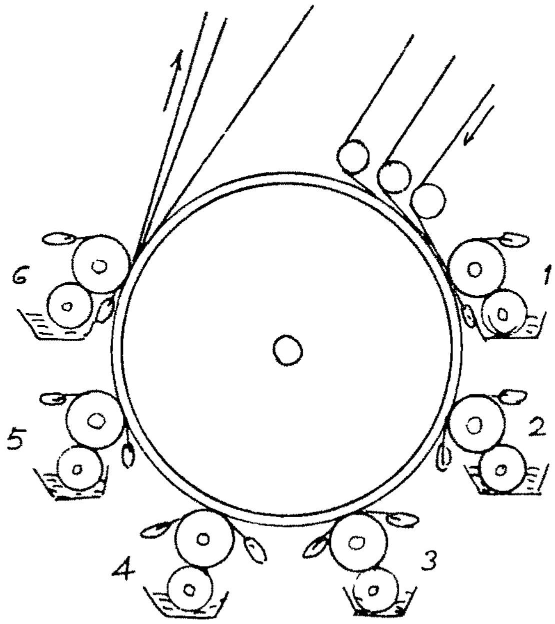
DIG.3



A - ENGRAVED COPPER ROLLER,
B - MANDREL; C - PRESSURE BOWL;
D - COLOUR - FURNISHING BRUSH OR ROLLER; E - COLOUR TROUGH,
G - LINT DOCTOR, H - LAPPING,
I - ENDLESS BLANKET; J - BACK-GREY; K - CLOTH TO BE PRINTED;
L - PRINTED CLOTH.

DIAGRAMMATIC SECTION OF A SINGLE-COLOUR MACHINE (29)

DIG.4



DIAGRAMMATIC SECTION OF A MULTI-COLOUR MACHINE (29)

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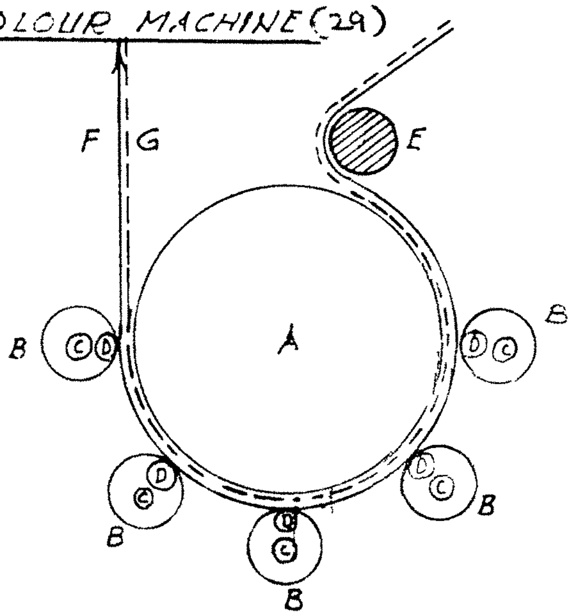


A - PRESSURE BOWL, B SCREEN,
C - AXLE (INCLUDING PRINT PASTE FEED)
D - ROLLER SQUEEGEE, E - GUIDE ROLLER; F FABRIC; G - BACK-GREY OR CONTINUOUS BLANKET.

TYPICAL ARRANGEMENT FOR SINGLE-FACE (SIMPLEX) PRINTING MACHINE (29) first fully automatic flat-bed machine came into operation. Basically all the operations of the flat-bed machine are the same as those of hand printing only that they are mechanized.

In the screen printing the latest development is the rotary screen printing. It is a combination of the roller printing and flat-bed machine.

The screen used is in the form of a roller. A two-ply screen, consisting of a metal mesh support screen and a nylon or terylene engraved screen is used. The support screen is used to give strength and maximum resistance to wear and tear. For printing the rotary screens are placed close together round a central pressure bowl, and the fabric is passed between with a firm support of a continuous blanket. The print paste is fed into the rotary screens through PVC tubing by means of an automatically controlled colour pump. A squeegee is used to press the colour through the mesh. Colour sequence is from dark to light to avoid smearing. The screens can be arranged in different ways for example above or below a fabric running horizontally, against a fabric running vertically, or round a central pressure cylinder (29).

<u>Transfer Printing in general</u>:

Transfer printing is a recent development for printing of textiles. It is a simple heat-transfer method of patterning fabrics. It involves the transfer of colour from one surface (paper) to another surface (cloth). The pattern is first printed on to a paper with special inks usually containing disperse dyestuffs which sublime at temperatures between 150° and 220°C. At this temperature the dyestuffs which are in their vapour phase, have little affinity for the paper but a high affinity for the fabric to be printed and thus the image is transferred from the paper to the fabric.

The technique of patterning fabric by heat transfer was first introduced in 1953 in Italy by Stampa Tessuti Artistic of Milan and was named the 'Star transfer printing process'. This was a direct and true fore runner of transfer printing as we know today. The big drawback to the star method was that a normal fixing process was also necessary after transfer and this made it costly and non-competitive. In 1952 ICI took out patents for a sublimation technique which they had evolve, but which subsequently they found was not commercially viable. In 1960 Noel Deplause started experimenting and in 1965 Filatures Provoust Masurel at Roubaix, northern France registered the name 'Sublistatic' and in about four years the company reached its full commercial peak (29).

The technique of transfer printing has been recently introduced in India. In 1977 a collaboration agreement was made between Strachan-Henshaw of U.K. and Hindustan Thermo Prints of India and the commercial production of transfer printing paper was started in December 1981 (31).

Paper used and its printing:

In principle any paper can be used as the carrier material but for economic reasons maximum dye should be released during transfer by the paper. The paper used must retain adequate strength after heating and have suitable surface properties for the printing method to be used. Machine glazed kraft; bond and cartridge are some of the suggested papers which can be used. The paper should be smooth and non-fibrous. For rotary screen absorbent paper has been suggested but to prevent high penetration which would cause poor transfer adjustment has to be made in the ink used (27).

Printing of transfer papers is done by gravure, flexography, lithography, letter press and screen printing.

Fabric Transfer Printing Machines:

1. Flat-bed presses.
2. Continuous blanket type machine.
3. Vaccum assisted machine.

1. Flat-bed presses: The press base is semi-rigid, padded with a blanket overlay. The fabric is placed on the press bed, the paper is placed on the fabric and the press head then lowered. Printing time and pressure are varied according to the fabric. This is mainly used for fully fashioned knitwear, cut and sew panels, dress lengths and motif printing.

2. <u>Continuous blanket type machine</u>: In this process the paper and the fabric are combined to pass face to face over the heated calenders, contact being maintained by an endless blanket. The cylinder is heated by electricity or hot oil. The output can be as high as 1420-1640 yard/hour.

3. <u>Vaccum assisted machines</u>: This is also a continuous calender type machine but the contact pressure is obtained by vaccum and not a blanket. It does not have a blanket or apron. It is heated with infra red radiators and the cylinder is perforated and covered with a light padding to which paper and fabric appear to adhere evenly and without tension. The flow of air through the paper and fabric assists transfer of the dye vapour. Deep penetration of dye in the fabric is obtained due to the vacuum created. Its printing speed is between 165 to 220 yards/hour. The advantage is that the 'handle' of the fabric is unimpaired owing to the low temperature required.

3. General Properties of Disperse Dyes.

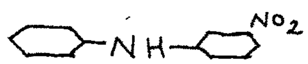
In 1921 the first hydrophobic manmade fiber came into market. This presented a new problem as it had no affinity for any of the existing dyestuffs. The first satisfactory method of coloration of cellulose acetate was found by Malland Ellis who observed that many simple insoluble azo dyes would be absorbed by cellulose acetate from an aqueous dispersion, stabilized with sulphated fatty alcohols or similar surface active compounds. A large number of dyes whose application depends on this principle made their appearance and are known as the disperse dyes. This class of dyes have been very useful and the demand has increased significantly with advent of the truly synthetic manmade fibers (32). The disperse dyes belong to one the following three classes (9):

a. Nitroarylamine disperse dyes.

b. Aminoazobenzene disperse dyes.

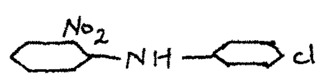
c. Aminoanthraquinone disperse dyes.

a. Nitroarylamine Disperse Dyes:

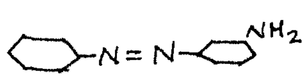


In the nitro dyes the chromophore is the NO_2 group and the auxochromes are the hydroxyl and aminogroups. The dyes exhibit benzenoid-quinonoid tautomerism and their colour is due to the presence of the quinonoid form.

e.g. C.I. Disperse yellow 22

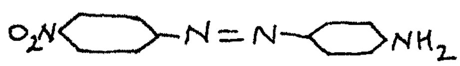


B. Aminoazobenzene Disperse Dyes:

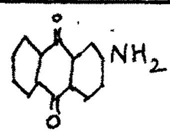


The characteristic feature of the azo colouring matter is the presence of the azo group - N = N- as chromophore usually associated with auxochromic hydroxyl or amino groups; the dyes exhibit benzenoid - quinonoid tautomerism with the corresponding quinone hydrozones.

e.g. C.I. Disperse orange - 3

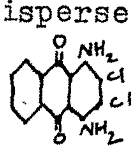


c. <u>Aminoanthraquinone Disperse Dyes:</u>



The characteristic chromophore of the anthraquinone and related colouring matters is the carbonyl groups and this may be present once or several times. Amino- and hydroxyl groups and their sybstituted forms NH_R, NR_2, NHCOR, OR are frequently present and act as auxochromes.

e.g. C.I. Disperse violet 28



The disperse dyes, used successfully for the synthetic fibers like polyester, came across some difficulty due to their sensitivity to heat; which made the dyes subolime on application of heat. Some non-ionic disperse dyes have been shown to sublime at temperatures as low as 140°-150°C under atmospheric conditions (8). This property of the disperse dyes to sublime was noticed, in the after-treatment of dyed polyester and polyester/cellulose mixtures at temperatures in the region of 190°-220°C, e.g. in pleating process, which lead to loss in colour value, staining of white grounds and the contamination of equipment. The disperse dyes differ in their sensitivity to heat; they sublime at different temperatures. When dyes having high sublimation fastness are used the tendency to sublime decreases.

This sublimation property of the disperse dye, which caused problems in the dyed fabrics was used advantageously to develop a new printing process namely transfer printing. In transfer printing the dye printed on paper is transferred on to the fabric by the application of heat. The dyes with good sublimation fastness are not useful as they would not transfer. The characteristics of dyes for heat transfer printing are given below:

1. The molecular weight of these dyes fall in the range 230 to 370. The range can further be narrowed to 250 to 340 (21).
2. The sublimation fastness of these dyes is generally not good. The dyes required must sublime at temperatures below 200°C.
3. Dyes should not have high polarity.
4. The vapour pressure of the dyes should be high (26).

The suitable dyes should exhibit excellent colour value, excellent heat transfer dyeability, excellent colour fastness (other than sublimation fastness and excellent printing ink suitability).

The technique of transfer printing of polyester has been well established. Successfully transfer printing on polyester-cotton blends is under constant research, as cotton is not receptive to the disperse dyes. Methods of imparting disperse dye affility to cellulose (7) are:

1. Chemical modification of cellulose.
2. Surface modification of cellulose.
3. Interfacial polymerization.
4. Grafting.
5. Resin treatment.
6. Use of high boiling swelling agents.
7. Use of metal salts.

4. Research Studies on Transfer Printing of Polyester and Polyester:Cotton Blends.

In the study of transfer printing on chemically modified cotton, Dr. Einsele et al. (14) have modified the cotton using by means of (1) Acetylation - a mixture of glacial acetic acid, acetic acid, anhydride and perchloric acid was used, (2) Benzoylation - Benzoyl thioglycolic acid and benzoyl salicic acid were used, (3) Reaction with monochloro-s-triazines-cotton was reacted with triazine derivatives by dissolving the triazine compounds in DMF, (4) Reaction with Isocyanates-Phenyl isocynate, cyclohexyl isocyanate and methyl isocyanate were used, (5) Other modification reactions- (a) sulfochlorides esp.p-toluene sulfochloride, (b) reactions with aromatic acid amide methylols, (c) grafting with stryrene, acrylonitrile and acrylia acid methyl ester. The best dye uptake was produced by benzoylation reaction with phenyl isocyanate and grafting with acrylonitrile. The dye fields averaged 70-80%. A comparison with PES showed suitably modified cotton to have the same or better dye affinity as PES. The brilliancy of the dyeings and prints on modified cotton was on par with PES.

It was found the substituents with hydrophlic groups produce smaller effects than those with hydrophobic character substituents with aromatic groups are superior to those with aliphatic groups in their effect.

In general the wash fastness was not good but satisfactory results were obtained with benzoylation and modification with phenol isocyanate.

EL-Kashouti et al. (15) in their study on transfer printing of chemically modified polyester/cotton blend had modified the cotton component of polyester/cotton blend by the introduction of cyanoethyl, carbamoylethyl, carboxymethyl and cyanoethyl together with carboxymethyl groups. The modified samples both before and after crosslinking with carbamate reactant were heat transfer printed and evaluated for colour strength. Cyanoethylation was the most effective modification, crosslinking impaired the printability.

Achwal and Deshmukh (1) in their study on modification of cellulose component in blends with polyester to impart transfer printability have evaluated the effectiveness of swelling agents treatment and cross linking agent treatment under different conditions with a view to compare the extent as well as fastness properties of disperse dye transferred to cellulosic component. Effect of pretreatments on the mechanical properties of the fabrics has also been evaluated. Polyester/cotton 67/33 and polyester/viscose 67/33 were the two fabric samples used. Transfer printing paper recommended for 100% polyester fabrics were obtained readymade and used. The cellulose was modified by pre-treatment with swelling agents, N-methylol cross-linking agents and a combination of dimethylol dihydroxy ethylene urea and swelling agents. The swelling agents used were (1) PEG-600, (2) PEG-1000, (3) Diethylene glycol monoethyl ether (DGEE), (4) Diethylene glycol monomethyl ether (DGME).

All the pre-treatments used gave higher transfer efficiency values than the untreated samples. N-methylel cross-linking agents used were melamine formaldehyde or dimethyel dihydroxy ethylene urea along with $Zn(NO_3)_2$, $6H_2O$ and dried at 80°C. Pre-treatment with these showed higher transfer on fabrics as compared to untreated samples. The combination of the two pre-treatments showed the transfer efficiency of the same order as shown by the swelling agent alone.

Wash fastness tested by ISI/4 test method showed that all the samples printed after pre-treatments showed good wash fastness. More than 88% dye retention was observed in case of samples pre-treated with polyglycols.

Heat transfer printing of cellulose has been studied by Padhye and Gupta (24). Treatment of cellulose with glycol ether swelling agents and polyepoxy condensates, prior to transfer printing has been done to increase the transfer printability. Polyester and its blends with viscose was used for the study. The dyestuff used was Navicet Blue FFR.

The results showed that the visual brillancy of the prints improved with the treatment by swelling agents. It was observed that after washing the dye content on PET part was not much changed and that the loss from the viscose part was within 5%. The percentage of dye transfer increased with the increase in the percentage of viscose in the blend showing that the swelling agent had principally affected the viscose part of the blend. The dye in the viscose part possessed good wash fastness as far as ISO III test was concerned.

Treatment with polyepoxy condensates gave similar results as treatment with swelling agents but the dye quantity taken up was less than that taken up by the swelling agent. Cotton fabrics which were treated with swelling agents showed less percentage of dye transfer as compared to similarly treated viscose fabrics. The reason given for this was the high swelling capacity of viscose than cotton.

According to the discussion in the study due to the presence of the swelling agent the structure of fiber opens and allows the dye to diffuse inside. During the time of transfer the swelling agent decomposes at the temperature of transfer printing and the structure collapses and the dye is entraped within the fiber thus the dye is retained even after washing.

Transfer printing of chemically modified cotton has been studied by Einsele (13). According to the author the substantivity of cellulose fibers for disperse dyes can be obtained by: (1) treatment with swelling agents such as polyglycols but the wash fastness of the prints are inadequate, (2) treatment with resins, mainly melamine resin precondesate (e.g. Heowaprint, transfer tex, lufixan and sublicotton process), disadvantages are high condensation temperature (220°C) with after results in a residual odour, and unsatisfactory fabric handle, (3) chemical modification e.g. treatment with benzoyl chloride, aliphatic and aromatic acid chlorides, acetic acid anhydride and polymers. The chemical modification of cotton by cyantholation was examined by pre-treatment with 2 percent NaOH, squeezing to 100 percent expression followed by treatment for several periods at 55°C in distilled acrylonitrile and the fabrics were examined for nitrogen content and DS Transfer printing was done with paper pre-printed with disperse dyes. The washing fastness obtained was inadequate. After treatment of the print with melamine resins or binders used in pigment printing or fiber reactive methylols gave some improvement although a wash fastness figure of 3-4 was not exceeded. Etherfication with acrylamide for amino-ethylsulphate takes place in a similar manner to cyantholation with alkali and results in much better dye absorption in transfer printing with disperse dyes; the resultant prints are much deeper and whilst the red and blue give prints of good wash fastness (4-5) the yellow was unsatisfactory.

Tsuji et al (33) have studied the printing of chemically modified cotton fabrics. Cotton fabrics were chemically modified to allow transfer printing with disperse dye and cationic dyes. Acetylated cyanoethylated and styrene grafted cotton fabrics could be printed with disperse dye. Light fastness was excellent but durability to laundering was poor, cationic dyes were less successful.

Nishida et al. (23) in their vapor-phase transfer printing of polyester/cellulose blends by surface treating have studied various methods of surface treatment. Fabrics used were Polyester/cotton 65/35, polyester/rayon 65/35 and polyester/ramie 65/35 commercially available transfer printing paper was used. Acetic acid, propionic acid and Butyric acid treatment were used separately for all the fabrics. The results showed that these treatments helped to obtain very bright printing of fabrics. The fabrics had good fastness to washing dry-cleaning and sublimation, but a loss in strength of the fibers was observed after the treatment.

Blanchard et al. (5) in their study on transfer printing cotton and cotton blends have given several chemical treatments to modify cotton and cotton blends and make them suitable for transfer printing with disperse dyes. The fabrics used were 100 percent cotton and blends of 50/50 and 70/30 cotton-polyester. The fabrics were printed with commercial transfer printing papers. Ethylene and propylene glycols used to increase the affinity of cellulose for disperse dyes were permanently attached to cellulose through the use of DMDHEU crosslinking agent. The results though promising, showed that in most cases, good print durability to laundering was difficult to obtain on cotton and cotton blend fabrics that contained only glycol, crosslinking agent and catalyst. The print ratings of 100% cotton and 50/50 polyester/cotton were the same before washing but after five washings the print appearance in terms of color saturation and design sharpness was superior on the blend fabrics. Melamine formaldehyde resins along with blycols have been reported in the study to be useful for modifying cellulosic fabric for transfer printing with disperse dyestuff, polymer-treated fabrics have also been reported to be receptive for the disperse dyestuff. In the study cotton and cotton blends were modified with thermo-plastic polymers. Polyacrylate along with polypropylene glycol and DMDHEU was used for modification. The print ratings were poorer than those of glycol-treated fabrics. Another chemical treatment was the in-situ polymerization. Interfacial polymerization techniques were used to form polymers on the fiber surface. Reactions between an acid chloride and a bisphenol to form a polyester or an acid chloride and a diamine to form a polyamide were carried out. The results showed that before washing the transfer prints were very good and print durability to laundering was fair to good depending on the fabric. The best results were obtained on 50/50 cotton-polyester print fabric.

Chemical treatment of partial acetylation of fabric has been observed to be one of the most effective methods for modification of cellulose containing fabrics. Prechloric acid in glacial acetic acid was used. Transfer print ratings before and after five washings were very good.

It was summarized that before washing the print quality of modified fabrics is outstanding but durability to washing is less satisfactory than similarly printed polyester. It was suggested that further research on improving print durability was needed for cellulosic fabrics.

Deshpande and Chavan (11) in their study on In-Situ polymerization - a technique for improving printability and soil release properties of polyester-cellulose blends have suggested aneconomical method which improves the transfer printability of polyester-cellulose blends. The method used is in-situ polymerization of acrylic acid, acrylamide and their mixtures onto polyester-viscose blend fabrics and evaluating the transfer printability with disperse dyes. Commercial grade finish KVS containing built-in catalyst and polyethylene glycol 600 were also used. A solution containing finish KVS, acrylic monomer and other ingradients was applied by padding (80% expression) to polyester-viscose blend fabrics while the monomer was in process of free-radical polymerization. Five different padding formulations for sample treatment along with untreated samples were used. The samples were transfer printed using commercial as well as laboratory printed papers under identical conditions. The results showed that the cloth treated with acrylamide and acrylic acid gave more or less equal results. The prints obtained on modified fabrics were superior than those on untreated or only resin treated fabrics. The polymer deposited fabrics showed better fastness to washing as compared to untreated or only resin treated fabrics.

Weiland and Robin (34) conducted a study on the transfer printing of cellulosics. They have developed a method for modifying cellulose to make it receptive for disperse dyestuffs. This study was based on the study done by Blauchard and co-workers using reactive resins. Fabric used was cotton sheeting. One inch square transfer papers, coloured with all available dispersed dyes were prepared. N-methylol carbomates plus polyethylene glycol and a cross-linking latex was used for the treatment. The treated samples when washed, some have fairly good durability while some dispersed dyes were completely washed out. It was concluded that selection of disperse dyes was very important to get durability. It was also concluded that it was essential that the curing of the finish on the fabric be done simultaneously with the transfer of colour to the fabric. The dye receptivity was optimized by adding water-soluble monomers to the resins. The colour loss after washing five times for treated cotton was 40%. On 50/50 polyester/ cotton colour loss was 10 to 20%. A colour loss of 40% is unsatisfactory but 10% to 20% is acceptable.