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PRINCIPLES OF TEXTILE PRINTING

ASIM KUMAR ROY CHOUDHURY



Principles of Textile Printing

Principles of Textile Printing discusses technical aspects of textile printing, covering almost all topics related to textile printing, including the types and quality of printing important for user satisfaction. It offers historical and introductory aspects of textile printing, styles and methods of printing, and printing and ancillary machines.

- Describes a variety of existing technologies and a wide range of designs created by applying colors in restricted portions using printing tools.
- Identifies technical, as opposed to artistic, aspects of textile printing.
- Covers a wide range of diverse and economical designs created by applying colors in restricted portions using printing tools.
- Discusses theoretical as well as practical aspects of textile printing.
- Explores a broad variety of printing types.

The book aims to educate those readers from large printing houses as well as from cottage and smaller boutique printers so that their products meet fastness standards.

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Asim Kumar Roy Choudhury



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Preface

My dreams are finally accomplished! My first two authored books, *Modern Concept* of Color and Appearance and Textile Preparation and Dyeing, were published jointly by Science Publishers, USA and Oxford & IBH Publishing Co. Pvt. Ltd. India in the years 2000 and 2006, respectively. The two volumes of Principles of Colour and Appearance Measurement written by me were published by Woodhead (UK) and Textile Institute in the year 2014. Subsequently, the Textile Institute books Principles of Textile Finishing and Flame Retardants for Textile Materials were published by Elsevier (2017) and CRC Press (2020), respectively. With the publication of this printing book, I am glad to state that I have covered all aspects of textile chemistry – dyeing, printing and finishing (including flame retardants) in books authored by me.

Textile printing is the most important, most interesting and most critical sector of textile coloration. The vast worldwide market of textile materials is largely due to changing fashion trends based on newer and newer printing designs along with changing color combinations. Despite the topic's immense importance, the number of books based on technical aspects of textile printing is limited. The printing books available in the market are very superficially written by designers and professionals lacking detailed technical aspects.

This book consists of eight chapters. In the introductory chapter, historical aspects of textile materials and printing methods from primitive to the present state of art are discussed in brief. From ancient times, people were fascinated by color and used to dye or print textile materials with coloring matters available in nature – in plants, in animals and in minerals. While dyeing involves overall uniform coloration, printing regards localized application in selected areas as per design in single color (in uniform or varied depths) or in multiple colors. Fresh designs are regularly being created by artists to keep up with changing fashion trends. Two aspects of textile printing, namely methods (i.e., machines, tools) and styles (i.e., chemical aspects), are explained. Blocks, stencils, engraved rollers and screens (flatbed – manual, mechanized, rotary screen) are used to apply colors in printing. Water-soluble dyes and water-insoluble pigments can be applied directly in the design portions (direct style); the color of the dyed fabric in the design portions destroyed (discharge style); or design portions prevented from absorbing colors (resist style).

Textile materials contain inherent, added and accidental impurities which may hamper uniform coloration. Dyeing and printing have similar preparatory steps. The methods of removal of impurities are discussed in the second chapter, namely singeing (i.e., removal of projected fibers), shearing and cropping (i.e., removal of projected yarns), desizing (i.e., removal of starch and similar materials applied to prevent breakage of yarn in weaving), scouring (i.e., removal of oils, fatty matter and other bulk impurities), bleaching (i.e., removal of coloring matters) and heat-setting (i.e., heat treatment of synthetic fabric for better dimensional stability).

The chemistry of coloring matters, namely water-soluble dyes and water-insoluble pigments, are discussed in the third chapter. The dyes are classified into several classes depending on their method of applications, type and quantities of chemicals required, pH, temperature, and so on, such as direct dyes, acid dyes, basic or cationic dyes, metal complex dyes, vat dyes, reactive dyes, mordant dyes and disperse dyes. After dyeing or printing, it is important to check whether the applied colors can withstand the effects of external agents such as washing, light, rubbing and dry heat. The methods of testing those fastness properties are discussed in this chapter.

Various means of printing textile materials are discussed in Chapter Four. Dyes and pigment can be applied directly to the fabric as per design (direct style), resisting penetration of color in the design portions (resist style) or destroying color in the design portions (discharge style). In transfer printing instead of printing fabrics directly, papers are printed and subsequently colors or designs are transferred to the fabric from paper by heat or other means. Spray printing, flock printing, crepe, emboss and burn out styles provide special effects. The segment-wise dyeing (space dyeing) of yarn can also provide an abstract type of localized dyeing resembling printing. In digital printing, the design is digitally finalized on a computer and is printed on the fabric using printers, as in paper printing. Due to several advantages, digital printing is becoming universally popular.

The fifth chapter deals with the chemistry (recipe) and the sequence of operations in various textile printing processes based on direct, discharge and resist styles of printing. The recipes and sequence of operations in printing of cotton, wool, silk, nylon, polyester and acrylic fabrics are discussed in detail. The colorants used are acid, metal-complex, vat, solubilized vat, reactive, azoic, cationic and disperse dyes.

Chapter Six deals with manual methods of printing, namely block printing, stencil and manual screen printing methods. Block printing and stencil printing have been popular since the beginning of civilization for the beatification of textile materials. Block printing is tedious in terms of block making and the slow speed of the printing process. Stencil printing is obsolete now, but it has given birth to another method: screen printing. Screen printing may be manual or mechanized. In spite of the increase in the demand of rotary screen printed and digitally printed textile materials, a small section of users always demand block-printed and manual screenprinted materials in small lots, especially with changing fashion.

The seventh chapter discusses mechanized means of textile printing, namely the roller printing machine, flatbed printing machine and rotary screen printing machine. The copper roller printing machine, patented in 1783, was the dominant printing machine for about 150 years. The screen printing was mechanized in two ways – flatbed screen printing machines and rotary screen printing machines. The rotary screen printing machine dominated the textile printing market before the arrival of digital printing.

The introduction of the computer has changed every sphere of human life. Inkjet printers, originally developed for paper printing, slowly entered into textile printing market and clearly showed advantages on short runs with excellent resolution (photo quality printing). Inkjet printing of textile is becoming popular day by day globally. In addition to conventional two-dimensional printing, inkjet printers are capable of printing in three dimensions. 3D printing concepts and technologies are slowly being adopted in textile printing. The eighth and last chapter discusses 2D and 3D inkjet printing of textile materials.

I would like to thank all those who helped to make this book possible. My special thanks to Prof. Richard Murray, Chairman, Textile Institute Publications and Helen D Rowe, Vice President, the Textile Institute. Both of them always inspired me to write textbooks. I also wish to thank the reviewers who gracefully gave so much of their time to review the book proposal, as well as those at CRC Press for making this project successful.

Asim Kumar Roy Choudhury

Author Biography



Dr. Asim Kumar Roy Choudhury is presently working as Director (Academic), KPS Institute of Polytechnic, Hooghly (W.B.), India. Earlier he worked as principal of the same institute for about six years. He was a faculty member of Government College of Engineering and Textile Technology, Serampore (W.B.), India, for 33 years and retired from the post of professor in the year 2014. He has over 45 years' working experience in textile coloration in academia and industry, has written numerous research papers, acted as

reviewer for several reputed international journals, and presented papers in several international conferences. He is a fellow and Silver Medalist of the Society of Dyers and Colourists, UK. He is a member of the editorial board of the Textile Institute book series.

His first book, *Modern Concept of Color and Appearance*, was published in the year 2000 and his second book, *Textile Preparation and Dyeing*, was published in the year 2006 jointly by Science Publishers, USA and Oxford & IBH Publishing Co. Pvt. Ltd., New Delhi. He wrote a textile progress entitled "Green chemistry and the textile industry" in 2013. He authored four Textile Institute books, namely

- 1) Principles of Colour and Appearance Measurement
 - (a) Volume 1: Object Appearance, Colour Perception and Instrumental Measurement (Woodhead, 2014)
 - (b) Volume 2: Visual Measurement of Colour, Colour Comparison and Management (Woodhead, 2014)
- 2) Principles of Textile Finishing (Elsevier, 2017)
- 3) Flame Retardants for Textile Materials (CRC, 2020)

So far, he has contributed several chapters in 18 edited books published by reputed publishers including CRC Press, Woodhead, Elsevier, Springer, Pan Stanford and Apple Academic.

1 Introduction to Textile Printing

1.1 TEXTILES – HISTORICAL PERSPECTIVE

At the very beginning of human civilization, humans felt the need to cover their bodies for protection from heat and cold. They began with animal skin and plant material. Gradually they learned to make cloths from naturally available textile fibers. Later they learned to beautify those cloths by coloring with natural colorant obtained from vegetables, animals, insects and so on. Many centuries then passed when people learned various complicated methods of application of colorants to make bright and color-fast shades.

Clothing and textiles are important in human history. They reflect the materials available to a civilization as well as the technologies humans have mastered through the ages. It is not known when humans began wearing clothes. Anthropologists believe that the animal skins and vegetation were adapted into coverings to protect human bodies from cold, heat and rain, especially as humans used to migrate to new places of different climates; alternatively, covering may have been invented first for other purposes, such as magic, decoration, cult rituals or prestige, and later found to be useful for protecting the body. Evidence suggests that human beings may have begun wearing clothing as far back as 100,000 to 500,000 years ago.

Where this style of printing originated – whether in India, Egypt, China or elsewhere – is not clear. Brunello states that an early variety of cotton dyed with madder around 3000 BC was found in jars in the Indus valley (Brunello, 1973). Taylor (1986) gives evidence of madder on flax found in Egypt and dated at 1400 BC. In China the dyeing of silk was developed very early, and China is credited with the invention of paper printing and therefore may well have seen the birth of fabric printing.

Textiles have a long and distinguished history in the Indian sub-continent. In the second millennium BC, Indian textile workers were aware of the method of dyeing in fast and intense color using mordant (a substance with attraction or affinity for both the fiber and colorant).

Mughal emperors in India were great lovers of plants and flowers; they built many beautiful gardens. Artists painted nature-like flowers, which evolved into a widely used decorative motif. Many 18th century chintz palampores (a type of hand-painted and mordant-dyed bed cover) feature a central flowering tree growing from a rocky mount or arising from water surrounded by sacred lotuses and marine creatures. The tree is bordered by vases, animals or birds and a series of narrow and broad borders of undulating patterns based on flowers and leaves. Figure 1.1 shows an Indian (Coromondal coast) palampore for the Sri Lankan market during the 18th century Chintz trade, from an open-access collection of The Metropolitan Museum of Art, USA (www.metmuseum.org/).



FIGURE 1.1 Palampores, the 18th-century chintz, trace to Europe, where they were prized as wall hangings and bed and table coverings. They typically show a central flower-and-fruit-bearing serpentine tree emerging from a hillock with stylized peaks or rocks.

Indian textiles were traded in ancient times with China and Indonesia, as well as with the Roman world. Later the Roman merchant navy was eventually replaced by Arab traders, and they in their turn by the Portuguese, after Vasco Da Gama arrived in India at the end of the 15th century.

There are many Indian words still in English usage which reflect this period of massive trade in textiles, such as calico, dungarees, gingham, khaki, pajama, sash, seersucker and shawl. "Chintz", related to a Sanskrit word meaning colored or spotted, now means cotton or linen furnishing fabric of floral pattern stained with fast colors and made anywhere, but it originally referred only to light, color-fast, cotton fabrics made in India for the English market. Chintz production was a very complex process involving painting, mordanting (fixing a dye), resisting and dyeing depending on the color being used. The original chintz designs were hand-painted and resist-dyed, but block-printed designs were incorporated later. Goods were listed by importers as painted, regardless of whether they were painted or printed. The considerable interactions between trading companies, exporting manufacturers and the buying public developed. Manufacturers and makers in Europe copied Indian designs liberally, taking over their European markets (Victoria and Albert Museum, 2013).

The Industrial Revolution played a major role in transforming the production and consumption of textiles in 19th-century Europe. Many of the major inventions of this period applied directly or indirectly to the textile industries.

1.2 PRIMITIVE COLORANTS

From ancient times, people were fascinated by color and used to dye textile materials with coloring matters available in nature. Natural dyes can be sorted into three categories:

- Natural dyes obtained from plants (e.g., indigo),
- Those obtained from animals (e.g., cochineal) and
- Those obtained from minerals (e.g., ochre).

Although some fabrics such as silk and wool can be colored simply by being dipped in the dye, others such as cotton require a mordant. Natural dyes can therefore be classified into two categories:

- · Substantive and
- Adjective.

Substantive dyes become chemically fixed to the fiber without the aid of any other chemicals or mordant, namely indigo or certain lichens. Adjective dyes, or mordant dyes, require some sort of substance (usually a metal salt) to prevent fading of color during washing.

Most natural dyes are adjective dyes, and do require the application of a mordant (the metal salt) solution to the fibers at some point in the dyeing or printing process. A mordant is an element which aids the chemical reaction that takes place between the dye and the fiber so that the dye is absorbed. Aluminum and iron salts are the most common traditional mordant, while copper, tin and chrome came into use much later. In rural areas where these metal salts were not easily available, plants were also used as mordant, especially those that have a natural ability to extract such minerals from the earth, such as club moss. Most ancient and medieval dyers mordanted yarns and fabrics before dyeing. Alum and iron were used as mordant in Egypt, India and Assyria from early times, as there are many alum deposits in the Mediterranean region. Medieval dyers used alum, copper and iron as mordant, and cream of tartar and common salt were used as to assist in the dyeing process.

Nature is colorful. The desire to create garments and other artifacts that reflect the beauty of the nature around us and provide for the expression of our artistic nature has been evident from early days in human history. The decoration of the body presumably predates the production of clothing. Since prehistoric times, man has been conscious of his colorful surroundings, and has tried to extract colors from nature in order to produce colored materials to cover himself. In prehistoric times, man wore colored and even patterned skins to protect his body. The materials which he used later – linen, wool and cotton – were practically colorless, and tempted him to color those materials. He soon discovered that colors produced from earth and minerals - usually yellow, brown-red or black - are not very suitable for this purpose, because their affinity to the fiber was low. Hence he tried coloring extracts obtained from the vegetable and animal kingdoms. The success achieved by him in this field was indeed impressive. Most of these ancient natural dyes not only possessed good color strength, but they also possessed fastness properties to a degree which has only been surpassed by the most recent synthetic dyes. These natural dyes were applied by dyeing methods which remained practically unchanged for several millennia.

At the beginning of the 19th century, natural dyes dominated the world market whilst synthetic dyes were almost unknown. The only synthetic dye that was known at that time was picric acid, discovered in 1771, which too made up a very little share of the total dye used.

Until the end of the 19th century, the coloring materials were all obtained from natural sources. The majority were of vegetable origin – plants, lichen and trees – though a few were obtained from insects and mollusks. Over thousands of years a large number of natural dyes had been used, but only a dozen or so proved to be practically useful, as most of these natural coloring matters are very unstable. The extraction of dyes from natural sources was a slow, inefficient, wasteful and very labor-intensive process. Sources of supply were unreliable and standardization was non-existent. The resulting dyes were rarely pure compounds and since the proportions in the mixture were variable, the reproducibility of the color shades was a serious problem. Many of these dyes did not have strong affinity for the fiber, and pre-treatment with metallic salts was essential.

The 19th century saw a dramatic reversal of this situation. The 1856 discovery of aniline dyes, the first completely synthetic dyes, by Englishman W.H. Perkin, changed textile dyeing technology dramatically. Prior to Perkin's discovery, all textile dyes were derived from natural sources, namely plants, insects and minerals. Perkin was not intentionally working towards preparing synthetic dyestuffs but towards quinine, the anti-malarial drug. He attempted the preparation of quinine by the oxidation of allyltoluidine with potassium dichromate in sulfuric acid. He failed and turned his attention to the simplest aromatic amine: aniline. Again he obtained a very unpromising mixture, a black sludge, but on boiling his mixture with ethanol,

he obtained a striking purple solution, which deposited purple crystals on cooling. Perkin recognized that this new compound might serve as a dye, later to be called Mauveine or mauve. Perkin was very fortunate. Not only did his discovery arise from testing an erroneous theory, but it also required the presence of substantial toluidine impurities in starting aniline.

Within 50 years after Perkin's discovery of Mauveine in 1856, synthetic dyes accounted for over 90% of the dyes used. These spectacular changes were initiated by a relatively new science: organic chemistry.

By 1850, the empirical formula of an organic compound could be easily established, but the structure of these organic molecules remained a perplexing problem for organic chemists. Kekule's most remarkable single contribution to organic chemistry was his paper, published in 1865, on the structure of benzene. The solution of the structure of benzene made an enormous impact on both organic chemistry and the dyestuff industry. The immediate impact of unrevealing chemical structures was the manufacture of two important natural dyes – alizarin and indigo – by chemical synthesis. Simultaneously, new classes of synthetic dyes were developed such as xanthenes, phenolthiazines and sulfur dyes. Meanwhile, significant progress had been made in azo dyes. Caro in 1875 discovered Chrysoidine, a dye used for many years, by diazotizing aniline and coupling the diazonium compound with m-phenylenediamine, the first azo dye for wool. Congo Red, made in 1884, was the first dye which had direct affinity for cellulose, and could be applied directly on cotton without using any mordant, while the natural coloring matters used in those days invariably required a mordant (Roy Choudhury, 2006).

The raw materials are first converted into dye precursors called dye intermediates by unit processes such as nitration, sulphonation, halogenation, reduction, oxidation, amination and so on. The manufacture of dyes from these intermediates is a multistage batch process and various chemical reactions such as diazotization are carried out. Commercial products must be standardized to give acceptably consistent shades, depths of shade and other physical properties, and they often contain as little as 10–20% of actual colorant.

The second half of the 19th century saw the introduction of many new classes of dyes by British chemists. Since then, very few new chromogens have been added to the range of available dyestuffs.

Chromogen is the term used to describe that complete arrangement of atoms which gives rise to the observed color. The term chromophore describes the various chemical units (building blocks) from which the chromogen is built.

In the 40 years after 1875 (Caro's discovery), the Germans progressively built up their dyestuff industry and produced up to 90% of the world's dyes, whilst the British remained stagnant. The period since the First World War saw a big expansion in the dyestuffs industry, during which time the United States, Japan, Britain, Germany and Switzerland became major manufacturers (Gordon and Gregory, 1987).

Two remarkable developments in the post-war period made by Scottish Dyes Ltd. (later ICI) are copper phthalocyanine in 1927 and fiber-reactive chlorotriazinyl dyes in 1954. With the introduction of hydrophobic fibers like polyester and polyacrylonitrile, new classes of dyes were developed. But they are merely modifications of dyes that were already available. In fact, a high percentage of the present organic chemical industry (such as pharmaceutical, agrochemical, etc.) is an offshoot of the dyestuff industry. Hence, just as Perkin is rightly acclaimed the father of the dyestuff industry, so the dyestuff industry itself could be called the mother of the modern organic chemical industry.

Traditionally, synthetic dyes were known as coal tar dyes because the aromatic organic raw materials containing six-member ring structures of carbon atoms used for dye manufacture were originally obtained from coal tar. Major raw materials are benzene, toluene, xylene, naphthalene and anthracene; these are later largely supplied by the petrochemical industries. The raw materials are first converted into dye precursors called dye intermediates by unit processes such as nitration, sulfonation, halogenation, reduction, oxidation and amination. The manufacture of dyes from these intermediates is a multistage batch process and various chemical reactions such as diazotization are carried out.

1.3 TEXTILE COLORATION

Textile coloration can be broadly classified into two distinct categories as follows:

- 1) dyeing overall uniform coloration of textile materials;
- printing colors (single or multiple) applied in selected portions of textile material as per design.

To know the art and history of dyeing, one must first understand the process of dyeing itself. According to Webster's dictionary, dyeing is "the process of coloring fibers, yarns or fabrics by using a liquid containing coloring matter for imparting a particular hue to a substance".

Textiles may be colored by the following methods:

- Textiles may be temporarily stained by rubbing or soaking in a colored solution using some chemical fixative to preserve the color.
- The other means is the pigmentation of the textile surface by an adhesive material.
- The pigments may also be added into the solution or melt of polymers during polymerization.
- A true dyeing is the deposition of color inside textile material in an insoluble or chemically bonded form from a solution containing the colorant.

1.4 TEXTILE DYEING AND PRINTING

The word "printing" implies a process that uses pressure, being derived from a Latin word meaning pressing. Textile printing is one very important operation in textile manufacture. It is normally carried out at the fabric stage and sometimes at the garment stage. In dyeing, colorants are applied uniformly on the textile materials, while in printing they are applied in selected portions as per design using printing tools (block, screen, roller or inkjet printer). In both dyed and printed fabrics, the colorant should be physically or chemically bonded with the textile fiber, so that the colorants can withstand washing and rubbing. If colorant comes out during washing, the dyed fabric will lose color from all or certain portions of the fabric, making those portions lighter in color. If color fades uniformly from the whole fabric, the fading of color may not be noticed quickly unless it is compared with the original fabric. But in the case of printed material, the loss of color will cause loss of prominence of the printed design, often with simultaneous staining of the ground or non-design portion of the printed fabric, resulting in quick rejection by the consumer/customer.

The mechanism of coloration by textile printing is similar to dyeing, but in dyeing the target is uniform penetration or spreading of a single color in all directions of the fabric, whereas in printing one or more colors are applied in selected parts of the fabric as per sharply defined patterns. The flow of coloring liquids is restricted in selected portions by increasing its viscosity with the help of thickeners like gums or emulsions.

In printing, wooden blocks, stencils, engraved plates, rollers, or silk screens and metal screens are used to restrict the flow of color paste as per printing designs. More or less similar colorants are used in dyeing and printing. However, dyeing is carried out by dipping textile materials in a large volume of dilute colorant solution, while in printing, low volumes of concentrated and thickened colorant solutions are applied with the help of a printing machine or tool. Thickening agents prevent the color from spreading by capillary attraction beyond the limits of the pattern or design.

1.5 TEXTILE PRINTING IN HISTORICAL PERSPECTIVE

The knowledge of textile printing was known in Europe, via the Islamic world, from about the 12th century, and was widely used. Fairly large and ambitious designs were painted for decorative purposes such as wall-hangings and lectern-cloths. (A lectern is a reading desk with a slanted top.) It is derived from the Latin word *lectus*. Low fastness of painting was less of a problem for the above materials as they did not need washing. When washing became common, the technology rapidly changed to wood block prints. Superior cloth was also imported from Islamic countries, but this was much more expensive.

The Incas of Peru and Chile and the Aztecs of Mexico also practiced textile printing previous to the Spanish Invasion in 1519; but owing to the lack of records before that date, it is impossible to say whether they discovered the art for themselves, or, in some way, learned its principles from Asiatic cultures.

As early as the 1630s, the East India Company was importing printed and plain cotton fabrics for the English market. By the 1660s British printers and dyers were making their own printed cotton to sell at home, printing single colors on plain backgrounds; less colorful than the imported prints, but more to the taste of the British. Designs were also sent to India for their craftspeople to copy for export back to England. There were many dye houses in England in the latter half of the 17th century, Lancaster being one area and on the River Lea near London another. Plain cloth was put through a prolonged bleaching process which prepared the material to receive and to hold applied color; this process vastly improved the color durability of English calico (a plain-woven cotton textile) and required a great deal of water from nearby rivers.

The competition between French and English textile manufacturers and designers was fueled by international exhibitions. France responded to the success of the 1851 exhibition by organizing its own in 1855. It remained the leader in costume and interior fashions, while the English sought to capture a larger share of the luxury goods market. French textile designers were traditionally better trained and earned more money than their counterparts elsewhere in Europe; French studios existed which specialized in designs for export. The Victoria and Albert Museum was founded in 1852 as a repository for art objects intended to serve as an inspiration to the design community in addition to serving the public at large. Three French museums, the Musée Historique des Tissus in Lyon, Musée des Arts Décoratifs in Paris, and Musée de l'Impression sur Étoffes in Mulhouse (in the cotton-printing center of Alsace), were all founded between 1856 and 1863 with goals similar to those of the Victoria and Albert Museum (Watt, 2003).

Printing was the technique favored by late 19th-century textile artists due to the ease of translating a concept to a finished product. As mechanical printing techniques continued to improve, the range of fabrics that could be successfully printed increased, and textured fabrics such as cotton velveteen became popular furnishing fabric in the later decades of the century.

India was rich in various embroidery techniques and printing techniques. Indian tradition was also rich in paintings, as can be seen from the paintings of Ajanta murals and miniature paintings. In ancient times, the art of weaving and dyeing on cotton was well developed; it developed on silk later. In the fifth century, floral and geometric designs were popular in India, as we can find from the trade between India and Egypt.

Printing on plain fabric developed in Europe in response to the popularity of "chintz" textiles imported to Europe from India in the early 17th century. These fine cotton fabrics were patterned with richly colored painted and dyed designs of exotic flora and fauna. Equally important, the colors resisted fading or running when washed in water. Imported cotton printed fabrics rapidly gained popularity throughout Europe and were seen to pose a threat to the powerful silk-weaving industry. For this reason, textile printing on a large scale was not successful in Europe until the 18th century, despite the fact that a method for color-fast printing was developed in Europe by 1670. Additionally, legislation was passed in France (1686) and England (1700) prohibiting the import and domestic production of printed textiles. In England, however, printed textiles could be made for export only, so technology continued to develop legally. The American colonies were a major market for these textiles. The Dutch, who had no such prohibitions, developed a textile printing industry during the late 17th century as well, but the French and English led the industry in the 18th century, despite legislation curbing production. A method of printing with engraved copper plates was developed in Ireland in 1752 and then brought to England. Prints from copperplates produced designs with even finer details, almost equal to the quality of a print on paper, but they were limited to one color. However, woodblocks and hand-painting could be used to add colors to copperplate prints. The English held a virtual monopoly on the production of fine copperplate printed cotton until the French ban was lifted in 1759. In the following year, Swiss-born Christophe Oberkampf (1738-1815) established a factory at Jouy-en-Josas near Paris. The factory at Jouy was extremely successful, due in part to the skill of one of its chief designers, Jean-Baptiste Huet (1745–1811), and to this day, pictorially printed cotton fabrics are commonly referred to as "toile de Jouy" (Watt, 2003).

The steps in conventional textile printing process are:

- 1) Fabric preparation
- 2) Design selection
 - (a) Artworks as per design
 - (b) Color separation
 - (c) Design transfer to blocks, rollers or screens manually or by exposure of light-sensitive coating
- 3) Preparation of printing paste
- 4) Printing by blocks, roller or screen
- 5) Drying followed by steam/hot air fixation
- 6) Washing off
- 7) Drying and finishing

1.6 PREPARATION OF MATERIALS

The cloth is prepared by washing and bleaching. For a colored ground it is then dyed. The preparation processes for dyeing and printing are more or less the same. For dyeing, the treatments should be very thorough, so that the penetration is uniform in all three dimensions. For printing, the penetration requirement is not very critical, as after printing the penetration of color should be limited to the extent so that the color fastness is satisfactory. High penetration of color may reduce color yield at the fiber surface – printing is mostly done for bright and strong surface colors.

Some fabrics require very careful stretching and straightening on a stenter before they are wound around hollow wooden or iron centers into rolls of convenient size for mounting on the printing machines.

1.7 METHODS AND STYLES OF PRINTING

Textile printing has two broad aspects:

- · Methods of printing
- Styles of printing

The methods of printing deal with mechanical aspects of printing machines while the styles of printing deal with the chemistry of printing paste and ancillary postprinting processes. The latter depend largely on the chemical and physical properties of the textile material to be printed.

1.7.1 METHODS OF PRINTING

Wood-block printing was the earliest form of textile printing and continued well into the 19th century. Roller printing was first developed in England in the 1780s and was in general use by the first decade of the 19th century. Roller printing was based on copperplate

printing technology, and employed a revolving engraved metal cylinder to print cloth continuously, greatly speeding production capacity. One roller printing machine could print as much yardage as 20 hand block printers. The early machines could print only one color. By 1860, the roller printing machines could print up to eight colors simultaneously and towards the end of the 19th century more than 20 colors were printed. Block printing was not completely replaced by the roller until the second half of the 19th century.

Textile printing is labor-intensive and a skillful job. It is mostly a continuous process. Due to high production, the operation needs very careful attention and prompt action. Unlike other textile production operations, textile printing demands long experience and high skill of the operators. In spite of careful attention, a good amount of production is rejected due to various printing faults. A rejection percentage of around 10% is usual, and it may be as high as 20–25%. While the faulty dyed material can be corrected by redyeing, the rejected printed material cannot be rectified as it cannot be reprinted. Printing faults are various and often occur in large quantities; due to high production, a large quantity is wrongly printed before the fault is rectified.

There are several methods for producing colored patterns on cloth. Among the commercially most important methods are:

- 1) Hand block printing
- 2) Engraved roller printing
- 3) Flat or table screen printing
- 4) Rotary screen printing
- 5) Transfer printing
- 6) Digital textile printing

The characteristics of printing paste are:

- · Highly concentrated dye solution
- · Thickened to prevent excessive strike-through and bleeding
- · Fixation and other auxiliary chemicals added
- Dyestuff must be chosen as per suitability for the fiber type in the fabric to be printed

1.7.1.1 Hand Block Printing

Woodblock printing is a technique for printing text, images or patterns. Used as a method of printing on textiles and later paper widely throughout East Asia, it probably originated in China in antiquity. In this process, a design is drawn on, or transferred to, a prepared wooden block. A separate block is required for each distinct color in the design.

The most primitive textile-printing technique was that using blocks with raised printing surfaces, which were inked and then pressed on to the fabric. By repeated impression of the block along the length and width of the fabric, the image from a single block builds up into a complete design over the fabric area. Some early blocks were made of clay or terracotta, others of carved wood. Wooden blocks carrying design motifs were found in tombs near the ancient town of Panopolis in Upper Egypt. In the same area a child's tomb contained a tunic made of fabric printed with a design of white rectangles, each enclosing floral motifs on a blue background. Pliny (born in AD 23) described in his book *Historia naturalis* how in Egypt they applied colorless substances to a fabric that was later immersed in a dyebath that quickly produced several colors. As Pliny also records that the best-quality alum was obtained from Egypt, it seems likely that alum was one of the mordants used and that the dye was madder.

By the 14th century, the use of wooden blocks for printing was certainly established in France, Italy and Germany, but the craft was practiced by "painters", using mineral pigments rather than dyes. One of the early European uses of blocks was to produce church hangings that imitated the more expensive brocades and tapestries. Cennini, writing in 1437, described in some detail the production and use of bricksized wooden blocks to print a black outline on brightly colored cloth, which was then hand painted with other bright colors (Brunello, 1973).

1.7.1.2 Roller Printing

Roller printing, also called cylinder printing or machine printing, is a textile printing process patented by Thomas Bell of Scotland in 1783 in an attempt to reduce the cost of the earlier copperplate printing. This method was used in Lancashire fabric mills to produce cotton dress fabrics from the 1790s, most often reproducing small monochrome patterns characterized by striped motifs and tiny dotted patterns called "machine grounds" (Tozer and Levitt, 1983).

The printing of textiles from engraved copperplates was first practiced by Bell in 1770. It was entirely obsolete as an industry in England by the end of the 19th century. The presses first used were of the ordinary letterpress type, the engraved plate being fixed in the place. In later improvements, the well-known cylinder press was employed; the plate was inked mechanically and cleaned off by passing under a sharp blade of steel; and the cloth, instead of being laid on the plate, was passed round the pressure cylinder. The plate was raised into frictional contact with the cylinder and in passing under it transferred its ink to the cloth.

The great difficulty in plate printing was to make the various impressions join up exactly; and, as this could never be done with any certainty, the process was eventually confined to patterns complete in one repeat, such as handkerchiefs, or those made up of widely separated objects in which no repeat is visible, like, for instance, patterns composed of little sprays, spots and so on.

In its simplest form, the roller-printing machine consists of a strong cast iron cylinder mounted in adjustable bearings capable of sliding up and down slots in the sides of the rigid iron framework. Beneath this cylinder, the engraved copper roller rests in stationary bearings and is supplied with color from a wooden roller that revolves in a color-box below it. The copper roller is mounted on a stout steel axle, at one end of which a cogwheel is fixed to gear with the driving wheel of the machine, and at the other end a smaller cogwheel to drive the color-furnishing roller. The cast iron pressure cylinder is wrapped with several layers of a special material made of wool and cotton lapping, the object of which is to provide the elasticity necessary to enable it to properly force the cloth to be printed into the lines of engraving.

A most important appliance is the color doctor, a thin sharp blade of steel that rests on the engraved roller and serves to scrape off every vestige (trace amount) of superfluous color from its surface, leaving only that which rests in the engraving. In order to prevent it from wearing irregularly, it is given a to-and-fro motion. A steel or cleaning doctor, known technically as the lint doctor, is placed opposite of the color doctor for the purpose of cleaning off loose filaments or lint, which the roller picks off the cloth during the printing operation.

Larger machines printing from two to 16 colors are precisely similar in principle to the above, but differ somewhat in detail and are naturally more complex and difficult to operate. In a 12-color machine, for example, 12 copper rollers, each carrying one portion of the design (of a single color), are arranged around a central pressure cylinder or bowl, and each roller is driven by a common driving wheel, called the crown wheel.

With all these delicate components at their command, a machine printer is enabled to fit all the various parts of the most complicated patterns with ease and precision, which is remarkable considering the complexity and size of the machine.

The engraving of copper printing roller is performed by three different methods, namely:

- 1) By hand with a graver, which cuts the metal away;
- 2) By etching, in which the pattern portion is dissolved out in nitric acid;
- 3) By machine, in which the pattern is simply indented.

1.7.1.3 Stencil Printing

Stenciling is a method of transferring a pattern by brushing, spraying, or squeezing ink or paint through the open areas of a stencil. In stenciling the pattern is cut out of a sheet of stout paper or thin metal with a sharp-pointed knife, the uncut portions representing the part that is to be reserved or left uncolored. The sheet is now laid on the material to be decorated and the color is brushed through its interstices.

Stencil printing is a less expensive, cleaner, and simpler alternative to screen printing. It is an easy way to print an image, or several images, repeatedly on a surface, like a poster or a t-shirt.

The first findings of stencils (hand stencils) were found in Asia and Europe and date back to over 35,000 years ago. Images were created on the walls of caves by blowing pigment over a hand against the wall. Since then, hand stenciling and classic stenciling are used on all different kinds of surfaces and materials to create images and texts. Stencils are also used for cloth coloring, especially in Japan. This type of cloth coloring using stencils is called Katazome, and it was used during the Edo period in feudal Japan. Stencils are also used in Europe to color old master prints from 1450.

1.7.1.4 Screen Printing

Screen printing is a form of stenciling that first appeared in a recognizable form in China during the Song Dynasty (960–1279 AD). It was then adapted by other Asian countries like Japan, and was furthered by creating newer methods. Screen printing was largely introduced to Western Europe from Asia sometime in the late 18th century, but did not gain large acceptance or use in Europe until silk mesh was more available for trade from the east and a profitable outlet for the medium discovered.

The main benefit of screen printing is that it is cost-effective and large-scale production is possible with it.

The development of screen printing began in Japan in the middle of the 17th century. Early development involved the use of design stencils held together by fine silk threads or even human hair. The designs were laid onto textile fabrics and color was applied only to the areas outside of the designs. Since the silk threads were so fine, they were not apparent in the final fabric design.

The Japanese technique was taken to France where modern flat screen printing was developed, initially using silk fabric stretched over a wooden frame.

Screen printing is a method of printing in which a design is imposed on a screen of polyester or other fine mesh on a rigid wooden or metal frame; nondesign areas are coated with an impermeable substance – generally with photosensitive lacquers which harden when exposed to light, especially ultraviolet light. The screen containing open mesh in the design area is pressed against the substrate. A fill blade or squeegee is moved across the screen stencil, forcing or pumping ink into the mesh openings for transfer by capillary action during the squeegee stroke. The open areas of mesh transfer ink or other printable materials which can be pressed through the mesh as a sharp-edged image onto a substrate. Basically, it is the process of using a stencil to apply ink onto another material whether it is open width fabric, t-shirts, posters, stickers, vinyl, wood, or any material that can keep the image on its surface. It is also known as silkscreen, serigraphy and serigraph printing. A number of screens can be used to produce a multicolored image or design.

Screen printing is further divided into three types:

- 1) Manual
- 2) Flatbed screen printing machine
- 3) Rotary screen printing machine

1.7.2 MANUAL OR HAND SCREEN PRINTING

Hand screen printing is very much useful for small scale production of garments and fabric pieces of limited length such as sari (an unstitched garment traditionally worn by women from South Asia of about 5 meters length).

Hand screen printing is carried out on a flat, solid table covered with a layer of resilient felt and a washable blanket (usually coated with neoprene rubber). Sometimes the table is slightly inclined (about 6^o) from back to front to facilitate easy lifting of the screen after printing. The heat for drying the printed fabric may be provided either under the blanket or by hot air fans above the table. The table size should be such that it can accommodate the minimum length and width of the fabric to be printed. For small garments, a good number of garments are printed at a time in each table. The tables are generally made longer in multiple of 5 meters so that the printed materials get enough scope for drying.

Fabric movement or shrinkage must be avoided during printing in order to maintain registration of the pattern. The fabric to be printed is laid on the table and stuck to the blanket directly, using either a water-soluble adhesive or a semi-permanent adhesive; alternatively, it is "combined" with a back-grey. In the latter instance, an absorbent fabric is stuck to the blanket and the fabric to be printed is pinned down on top of it.

Sometimes fabric and back-grey are combined before fixing to the table using an adhesive and a specially adapted pad mangle. Combining is most suitable for printing lightweight fabrics, where there is a danger of smudging or loss of adhesion caused by the presence of excessive print paste. For very fine fabric such as that of silk, the blanket and back-grey are replaced by coating the printing table with wax. Before printing the fabric to be printed is stuck to the wax layer on the printing table by hot blades and after printing the printed fabric is taken out by hot blades.

Before a design can be printed, it must be reproduced on the screens in a suitable form. One screen is required for every color in the design, except when the fabric is dyed to the background color (known as the ground color) before or after printing, or when a third color is produced by one color falling on another. When printing is carried out on dyed background color, it is termed the "blotch".

Before printing begins, the screens must be carefully positioned on the fabric. The area printed by a screen (screen repeat) must fit exactly alongside the adjacent one, a slight overlap being preferable instead of a gap. With flatbed screen printing, this is not automatically achieved (as is the case with rotary printing). The differently colored areas must be in register and, again, a small overlap is usually allowed. To achieve accurate registration, it is common practice to attach to the screen frame a bracket which locates against fittings, known as "stops", on a guide rail along one edge of the table.

The stops are spaced exactly one (lengthways) screen repeat apart along the whole length of the table. Two adjustable screws set the distance of the frame from the rail. As a further aid, repeat crosses known as "pitch marks" may be incorporated at one or both sides of the screen and the positions of the following screens checked against the first pitch mark.

After printing, the fabric is dried by hot steam pipe fitted under the printing table or by hanging over table for air (fan) drying. This is followed by a fixation process by steam or hot air and a final wash.

1.7.3 FLATBED MACHINE

Flatbed screen printing machines are mechanized screen printing machines. Large sized screens are placed horizontally along a rubber blanket, keeping defined distances between them. Under stationary condition, the screens hang above the blanket. During printing, all screens are brought down on the fabric lying above the blanket. In semi-automatic machines, the squeezes are moved widthwise manually, while in fully automatic machines the squeezes are moved mechanically.

All the screens for the design (one screen for each color) are positioned accurately along the top of a long endless belt, known as a blanket. A machine intended to print traditional furnishing designs might have space for 15 or more screens. The width of the gap between the areas printed by any two adjacent screens must be a whole number of lengthways design repeats. The lengthways design repeat need not necessarily

be the same as the lengthways screen repeat. There may be several design repeats per screen repeat; for example, where there are three design repeats per screen repeat, the gap between adjacent screens need only be one third of a screen repeat.

The fabric is gummed to the blanket at the entry end and moves along with the blanket in an intermittent fashion, one screen-repeat distance at a time. All the colors in the design are printed simultaneously while the fabric is stationary. The screen is brought down on the fabric for the squeeze movement. Then the screens are lifted and the fabric and blanket move on. When the fabric approaches the turning point of the blanket, it is pulled off and passes into a dryer. The soiled blanket is washed and dried during its return passage on the underside of the machine. Hot melt adhesive is used for temporarily attaching the fabric to the rubber blanket. Hot blades are used for attaching and detaching the fabric from the rubber blanket before and after printing respectively. Long tables, typically 20–60 meters long, are used, and some drying unit is attached at the end of printing table for drying the printed fabric.

The flat-screen printing machines are still very popular where the scale of production is not large, or where capital investment is limited. Moreover, printing of very large design repeats for bedcovers and bed sheets are convenient to print in flatbed machines.

1.7.4 ROTARY SCREEN PRINTING MACHINE

Due to the semi-continuous process, low productivity, and non-continuous patterns of flatbed screen printing, inventive machine makers developed rotary screen printing. Rotary screen printing is so named because it uses cylindrical screens that rotate in fixed positions while the flat screens are raised and lowered over the same print location. Rotary screens press the squeegee within the screen. Each color requires a separate rotary screen. Those are placed horizontally on the top of an endless rubber blanket and they rotate providing horizontal movement of the printed fabric lying between rollers and blanket. The idea was first proposed in 1947 in Portugal, but the initial commercial machine was first introduced by Stork (Holland) at the ITMA show in Germany in 1963. In concept, the idea is to take a flat screen and simply shape it into a roll by sealing the ends of the flat screen together. The simple modification converts a semi-continuous process to a continuous one. However, initially there were many technical hurdles to overcome (such as making seamless screens) before rotary screen machines became practical.

For rotary screens, the size of the design repeat is dependent upon the circumference of the screens. This was initially seen as a disadvantage, because the first rotary screens were small in diameter. However, with today's equipment, rotary screens are available in a range of sizes and are no longer considered design-limited. Today's rotary screen machines are highly productive, allow for the quick changeover of patterns, have few design limitations and can be used for both continuous and discontinuous patterns.

Estimates indicate that this technique controls approximately 65% of the printed fabric market worldwide. The principal disadvantage of rotary screen printing is the high fixed cost of the equipment. The machines are generally not profitable for short

yardages of widely varying patterns, because of the lengthy clean-up and longer machine down time while changing the design. Flat screen printing is much more suitable for high pile fabrics, because only one squeegee pass is available with rotary screens. Rotary machines are used for carpet and other types of pile fabrics. Most knit fabric is printed by the rotary screen method because it does not stress (pull or stretch) the fabric during printing.

1.7.4.1 Transfer Printing

In transfer printing, the design is first printed on to a flexible non-textile substrate (such as paper) and later transferred by a separate process to a textile material. Designs may be printed and stored on a relatively cheap and non-bulky substrate such as paper, and printed on the more expensive textile in proper time with rapid response to sales demand. The production of short-run repeat orders is much easier by transfer processes than it is by direct printing. The design may be applied to the textile with relatively low skill input and low reject rates.

Certain designs and effects can be produced only by the use of transfers (particularly on garments or garment panels). Many complex designs can be produced more easily and accurately on paper than on textiles.

Most transfer-printing processes enable textile printing to be carried out using simple, relatively inexpensive equipment with modest space requirements, without effluent generation and elimination of washing-off the printed fabric.

1.7.4.2 Digital Printing

Direct digital fabric printing is a process where rolls of fabric are printed using large format inkjet printing machines. In a similar process to a desktop computer printer, printer heads containing many fine nozzles squirt tiny droplets of inks onto pre-treated fabric. Direct digital printing has been developed particularly for the natural and nylon market. Fabrics are pre-treated with chemicals to help in the bonding of the print by the fibers. The digitally printed fabric is then post treated to fix the dye into the fabric.

Direct digital fabric printing method is a quick and relatively easy process with files loaded into specific print software and then sent to printer. However, the image definition is not always as sharp or clear as other fabric printing methods such as sublimation transfer printing. Types of inks, texture of the natural fabric, fabric pre-treating agent, temperature and humidity can all play a role in final printed image quality.

The practical approach of digital textile printing has encouraged many designers and manufacturers to choose it over other forms of printing. Though digital printing has experienced sluggish growth in comparison to traditional printing, it is gradually catching up with the changing dimensions of the textile industry.

As many as 650 million square meters of fabric were digitally printed until the second quarter of 2014. The current global output of digitally printed textile is growing at a steady annual rate of 25%, according to Textiles Intelligence. A market study shows that digital printing is to grow at 20.1% annually through 2019. The global digital textile printing market size was valued at \$2.0 billion in 2020 and expected to reach \$7.9 billion by 2030, at a CAGR of 14.8% from 2021 to 2030 (Allied Market Research, 2021).

The reasons for a steady growth of digital textile printing are numerous, such as:

- Digital printing is not only a higher creative form of textile printing, but it also provides greater design flexibility, compared to screen printing.
- Designers prefer digital printing for small print lots, as it is more cost efficient.
- It is eco-friendly, with lesser physical inventory levels leaving smaller carbon footprints.

Digital printing involves direct printing on fabrics with printers, thereby saving almost 95% of water, 75% energy usage and generating minimal textile waste.

The manufacturers that rely on digital textile printing easily adapt to swift changes in global trends in comparison to people involved in other forms of printing. Nevertheless, the future growth of digital textile printing widely depends on deeper penetration of digital printing into commercial print production. The machine manufacturers also need to develop technologically advanced production printers in order to survive competition from conventional forms of textile printing machinery.

Other than the competition from traditional printing methods, another technical hitch was the print speed of digital printing, something which has been taken care of. From adding more heads in a row to increase the firing frequency or increasing the number of nozzles, modern digital textile printing machines are advanced and offer great printing speed (Digital printing: Set to transform the global textile market, 2018).

From carpets to clothing, from home textiles to banners: many modern designs would simply be impossible to realize without sophisticated textile printing techniques. Although rotary screen printing and flat screen printing have long been the dominant technologies in the market for printed textiles, there is a quiet but ever louder voice calling for a sustainable, high-quality alternative suitable for large format textiles – digital textile printing. Yet many companies are still unwilling to invest substantial sums in the installation of new digital printing machines – a mistake.

(Stephan, 2014)

When the technology was launched 15 years ago, digital printing machines were capable of producing only 10 square meters (m^2) per hour. Today, their capacity far exceeds 3,000 m² per hour. By way of comparison, conventional textile printing machines can print up to 8,000 m² per hour – but with far greater consumption of energy and water (Stephan, 2014).

1.7.4.3 Market Share

The demand of printed fabrics in various textile sectors as reported by Raymond (2015) is as follows:

Apparel textile: 54% Interior textile: 38% Industrial textile: 8% A large number of market studies about textile printing are available at premium prices, which may be useful for future planning of printing industries such as:

- www.prnewswire.com/: Global Digital Textile Printing Market 2018 Forecast to 2023 – A \$2.31 Billion Opportunity Driven by Growing Demand for Sustainable Printing, Apr 2018.
- www.zionmarketresearch.com/: Textile Printing Market: Industry Perspective, Comprehensive Analysis and Forecast, 2015–2021, Report Code: ZMR-362.
- www.smitherspira.com/: The Future of Digital Textile Printing to 2021, 31 Oct 2016.
- www.alliedmarketresearch.com/: Textile Printing Machine Market Overview, Sep 2017.

Production (%) by various printing methods are listed here (Provost, 2014):

- Rotary screen printing machine: 65%
- Flat screen printing: 25%
- Transfer printing: 4%
- Hand printing: 3%
- Digital printing: 2%
- Others: 1%

The textile printing industry is one of the largest consumers of water in the textile industry and there is increasing legislation to reduce pollution, greenhouse gases and water usage in the major textile printing countries, for example, India and China – the world's largest textile screen printing market, which recently began formally implementing an updated Environmental Protection Code on January 1, 2015. The adoption of digital textile printing is seen by many traditional textile printing countries as a real answer to many of their environmental issues, which are now being addressed by enforcement of local legislation.

Digital textile print production reached over 1.2 billion square meters in 2015 (in the region of 3.6% market penetration) and with current growth rates of the order of 20% per year, the traditional screen printing market should achieve 6.25% market penetration by 2019.

Estimates for total Indian digital textile printing are in the region of 85 million square meters, approximately 7% of the current digital market – still very small, considering India is the second largest textile printing market, which currently prints 17.5% of the global 31 billion square meters of the traditional textile prints. The real unknown factor, which could significantly increase digital-textile print production penetration, is the possible future market penetration of the fixed-printhead-array digital textile machines (so-called single-pass types), which have the capability to match the millions of square meters printed per year by rotary screen machines.

The digital textile printing market is expected to be worth USD \$2.31 billion by 2023 from USD \$1.76 billion in 2018, at a CAGR of 5.59% between 2018 and 2023.

However, the growing popularity of digital advertising media is one of the factors restraining the digital textile printing market growth (Provost, 2016).

1.8 STYLES OF PRINTING

Traditional textile printing techniques may be broadly categorized into four styles:

- Direct style of printing, in which colorants containing dyes, thickeners and the mordants or substances necessary for fixing the color on the cloth are mixed to make printing paste and printed on the fabric in the desired pattern.
- 2) Mordant style of printing, in which the fabric is printed with one or more mordants in the desired pattern prior to dyeing of cloth; the color adheres only in portions where the mordant was printed.
- 3) Resist style of printing, in which a wax or other resisting substance which prevents penetration of color into the fabric is used. The fabric is printed with the resisting agent followed by quick dyeing or padding. The resisted areas do not accept the dye, leaving uncolored patterns against a colored ground. Some colorants may be mixed with resisting agent, which get fixed in the resisted portion resulting in multi-color printing.
- 4) Discharge printing, in which a reducing agent is printed onto previously dyed fabrics to destroy some or the entire colors in the printed portion.

Resist and discharge techniques were particularly fashionable in the 19th century, as were combination techniques in which indigo resist was used to create blue backgrounds prior to block-printing of other colors. Modern industrial printing mainly uses direct printing techniques.

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2 Preparatory Processes Before Printing

2.1 INTRODUCTION

The fabric obtained after weaving is known as grey fabric. It contains both natural as well as added impurities. In order to make the fabric suitable for dyeing and printing, it is essential to remove the impurities present in grey fabric. The processes involved in the removal of these impurities are known as preparatory processes or fabric pre-treatment.

For perfect coloration of a substrate, it is necessary that all the impurities be removed from the surface so that the colorants can perfectly sit on the surface or penetrate inside the substrate as required by the particular system. The colorants should also be clearly visible without interference by the color of the impurities.

Textile materials possess a variety of impurities, namely:

- 1) Natural or inherited impurities;
- Impurities added purposefully for better spinning (in yarn manufacture) or weaving (in fabric manufacture) – e.g., antistatic agents or lubricants;
- 3) Accidental impurities such as oils and greases acquired while handling of the materials.

All such impurities are to be removed before actual dyeing or printing processes. The steps by which the impurities are removed are called preparatory processes. As the impurities present vary from fiber to fiber, the preparatory processes will differ and the conditions of treatments are to be decided by considering fiber properties too.

Preparatory processes may be broadly classified into two groups, namely:

- 1) Cleaning processes, where bulk of the foreign matters or impurities are removed by physical or chemical means.
- 2) Whitening processes, in which trace coloring matters are destroyed chemically or the whiteness of the materials is improved optically.

Among all textile fibers, cotton is most widely used for production of apparel textile fabrics. The composition of natural cotton fiber is as follows:

Cellulose: 88–97% Protein: 1–2% Pectin: 0.4–1.5% Oil, fat and wax: 0.4–1.5% Mineral matters (ash): 0.7–1.6% Others: 0.5–8%

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Pectin acts as adhesive binding wax to the fiber. When it is removed, wax can be subsequently emulsified. Among all non-cellulosic materials, only part of the calcium pectate/wax complex must be removed in order to obtain fibers of satisfactory wettability and dyeability. The natural waxes bestow a soft touch on the fiber but are undesirable for the subsequent dyeing and finishing operations. These products provide lubrication during spinning but are to be removed subsequently to impart water absorbency to the fibers.

The scouring (or alkali boil) process imparts the hydrophilic character and permeability necessary for the subsequent processes (bleaching, mercerizing, dyeing or printing). Good scouring is the foundation of successful finishing (Trotman, 1968).

In scouring, the removal of wax is not the only factor to be considered. In other words, there is no correlation between the water absorbency and its natural wax content. Absorbency, as indicated by the time required for wetting to take place when the fabric is immersed in water, varies with the scouring treatment and may have markedly different values even when the wax contents of samples are similar. An explanation for these results is that the distribution of the wax within fiber structure decides its absorbency. This has been confirmed by the fact that the complete extraction of wax by solvent may be unable to make cotton absorbent, while a mild scouring may yield absorbent cotton still retaining much of its inherent wax. Lack of absorbency may be observed even if the wax content is low - there is sufficient area still covered with wax to present a hydrophobic surface. A fiber immersed in boiling water for some time, followed by air-drying, may possess improved absorbency as the molten wax forms droplets inside the fibers and remain as such after drying. By contrast, when drying at high temperature, the molten wax may spread back over the fiber and form a hydrophobic layer. The main barrier to the penetration of water is the primary wall of cotton. The study with an electron microscope shows that the scouring process causes numerous pits in the primary wall. The primary wall is modified when boiled with 1.5% caustic soda and is destroyed completely when boiled with 3% caustic soda at 40 psi pressure.

Mineral salts constitute another impurity, which must be removed during pretreatment. These may not affect exhaustion in batch dyeing, but in continuous dyeing with low material to liquor ratio (< 1:1), may render some dyes to precipitate on the material. They also catalytically decompose bleaching chemicals thereby damaging the fabric during bleaching. Heavily colored lignified substances like residues of seeds, husks and leaves are also objectionable in the finished material.

2.2 AIMS OF PREPARATORY PROCESSES

The aim of preparatory wet processing is to treat the goods by standard procedures so that they are brought to a state in which they can be dyed, printed or finished without showing any fault or damage on the material. During chemical preparation of textile materials, the following conditions should be looked into:

- Uniform power of absorption for dyes and chemicals of the prepared material during subsequent processing.
- 2) An even water imbibition value of the prepared materials.

- 3) Complete removal of all types of impurities including broken seeds, etc.
- 4) Minimum damage of the prepared materials.
- 5) Absence of creases and wrinkles in the prepared materials.
- 6) High whiteness value of the prepared materials.

The preparation, however, is a non-value-added stage of the coloration process and therefore, the preparation stage of the process is often not optimized. Preparatory processing is frequently done excessively, and high quantities of chemicals, auxiliaries and utilities (water, steam, electricity and time) are unnecessarily used. This can result in a high carry-over of preparation residues (cotton impurities, preparation chemicals and auxiliaries) that will have negative influence on both dyeability and the dyeing system, or will require long multi-stage intermediate wash-off procedures. The pretreatment processes must balance the requirements of the dyeing and finishing stages and the intended end use of the textile material.

2.3 PREPARATORY PROCESSES

Different textile materials possess different types and quantities of inherent impurities. The preparatory processes, therefore, vary significantly for different textile substrates. However, they can be generalized into a few types.

- 1) Removal of loose fibers or yarns projecting on the surface; in the "Singeing" process, the removal is done by burning, while in the "Shearing and cropping" process, projected threads (which hamper uniform printing) are cut with the help of an extruder type of blade.
- 2) In "Desizing" starch or other sizing materials, which are applied on yarn before weaving are removed.
- 3) The most important preparatory step is known as "Scouring", by which most of the water-soluble and water-insoluble impurities are removed. For cotton, prolonged scouring under strong alkaline condition (with caustic soda) is required to achieve desired absorbency. Wool and silk require mild alkaline treatments, while synthetic fibers require much milder treatments.
- 4) "Bleaching" is the last preparatory step in which coloring matters present in the textile materials are removed. The material becomes whiter in appearance; consequently, the dyed or printed materials become brighter and purer in color. If the final product is to be sold as white, the bleached material may be subsequently treated with a blue pigment or an optical whitening agent to make the appearance dazzling white. In earlier days, bleaching powder, sodium hypochlorite, sodium chlorite and hydrogen peroxide were used for bleaching of textile materials. However, chlorine compounds are banned now on ecological grounds and hydrogen peroxide is universally used for bleaching.

Wool and silk are very sensitive to alkali. Hence, scouring is done under mild alkaline conditions with soap with or without soda ash for a short period. Whiteness demanded for these fibers are not very high. Hence, mild bleaching is done. Bleaching may not be essential in many cases. For synthetic textile materials, mild hot wash may suffice instead of scouring. Sometimes light scouring with non-ionic detergent may also be a preferred option. Bleaching may not be necessary unless a high degree of whiteness is demanded. For these fibers, an additional preparatory process called "Heat-setting" is carried out before or after wet treatment, to achieve dimensional stability of the material during subsequent treatments at high temperature.

2.4 PREPARATION OF COTTON MATERIALS

Cotton is mostly processed in fabric form and rarely in fiber form. Some quantities of cotton material are prepared and dyed in yarn form. The different stages for processing of cotton fabrics are shown in Figure 2.1.

2.4.1 INSPECTION AND MENDING

Grey fabrics are first inspected to check whether they are in conformity with the standard. They are sorted into lots. Fabrics in each lot should be of same width and similar weight per unit length so that they can be processed in the same manner. All the pieces of a lot are sewn end to end with loops, which can be easily removed after finishing. The seams should be 10 mm wide, and for certain processing – such as chain mercerizing and continuous drying – the seams should be wider (15 mm) and stronger. In some textile units, gluing or bonding of fabric is used instead of sewing in order to reduce the amount of rags. A polymer coat is applied to the ends of the fabrics to be bonded, which are then placed between heated metal surfaces. The polymer melts and binds the ends of the pieces.

The fabric, after sewing end to end, is passed slowly over an inspection table with inclined glass top. The table is illuminated with a fluorescent lamp fitted below. The illuminated fabric is visually inspected for various weaving faults and damages, which are suitably marked with colored pencils. The marked fabric is then repaired for missing end (warp) or pick (weft) by mending, or the damaged portion is cut off, as it may otherwise be entangled with machine parts causing excessive damage.

Earlier this important step was considered to be a routine one. However, with the enforcement of stringent quality control regulations, scientific practices and electronic devices soon overcame bad practices such as nominal checking or no checking.

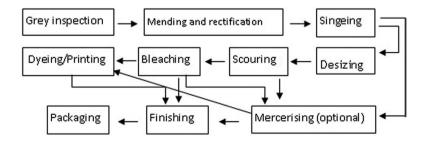


FIGURE 2.1 Sequence of operations in cotton fabric processing.

The use of electronic instruments has enabled precise inspection of a piece, leaving no scope for unnecessary cutting. Stains, holes, thick and thin places and warp/weft thread breaks can now be detected by laser beams as in the Sick-scan-system Ko-Re-Tra of E. Sick, GmbH (Karmakar, 1999). The apparatus operates on three different principles: coaxial (emitter and receiver at the same place), remission (receiver at a freely adjustable angle) and transmission (receiver on the opposite side of the fabric). The light source is helium-neon laser or a xenon high-pressure lamp.

An unmended hole or an oily stain can give rise to either tearing or hole-formation in bleaching or to patchy dyeing/printing. If a physical damage is already present, that portion is best cut off and the pieces are re-stitched. This is also the case for intensively oil-stained portions.

In addition to the naturally occurring impurities, a number of impurities are embedded on the textile materials accidentally. The most common accidental impurities are stains caused by various agents, which are easily visible in the embedded portions. Most of the stains should be removed by local spotting with an efficient stain remover followed by thorough rinsing and soaping.

The stain removers are generally a solvent (e.g., acetone, methylated spirit, petrol), solubilizing agent (e.g., acetic or oxalic acid), oxidizing agent (e.g., sodium hypochlorite solution, potassium permanganate and oxalic acid or hydrogen peroxide) or reducing agent (e.g., sodium hydrosulfite) for the material present in the stain. Some stain removers are available in the market, which are capable of removing varieties of stains.

Non-scourable oils are difficult to remove from cotton, giving rise to uneven dyeing. The oil, grease and tar stains are generally removed by spotting on the stained portion with a stain remover comprising emulsified solvents in liquid forms. The solvents may be isopropyl alcohol. The emulsifier may be anionic (such as sulfated oils or alkyl aryl sulfonates) or nonionic (ethylene oxide condensates). The stains are spotted with the stain remover, rubbed, left for a short time and then washed. The treated area should not be dried before washing.

2.4.2 SHEARING AND CROPPING

After inspection and mending, small projected yarns may remain on the surface of the fabric, which obstruct penetration of dyes during dyeing and printing processes. They may also be entangled with machine parts causing damage of the materials. These projected yarns are removed by a process called "shearing and cropping", during which the projected fibers or yarns are cut from the fabric surface.

In shearing operation, dry or occasionally slightly dampened fabric is drawn between a shearing bed or table and the shearing device, which consists of a shearing cylinder and a ledger blade. The action is similar to that of a lawn mower.

Figure 2.2 shows a simplified diagram of a shearing machine (Rouette, 2001). The shearing cylinder (1) generally consists of a thick-walled hollow cylinder with a bearing journal firmly inserted at both ends. The cylinder should not be unbalanced or eccentric in running. The speed of the cylinder during shearing is between 500–2000 rpm depending on the fabric to be sheared. Depending on the particular design, the cylinder has 10–24 or, in the case of a carpet shearing machine, 40 spiral

blades (2) mounted securely around its circumference. In a conventional shearing cylinder, the shearing spirals are fitted onto the cylinder in equal distances regardless of the number of spirals used. In modern shearing machines, as in Multicut MC-5, the spirals are arranged asymmetrically to avoid periodic variation of pile length. The angled foots or support limbs of spirals are bent in such a way that it matches the curvature of the cylinder and always point in the opposite direction to the rotation of the cylinder in order to absorb pressure developed during shearing. To prevent heating up during running, felt saturated with oil is placed against the shearing cylinder.

The spirals are made with different profiles with names like knee, concave, cleaning, breaking, mortise and so on. They have different cutting or wedge angles. Cutting edges running parallel to the cylinder axle have obtuse (>90°) cutting angles, while those running in a straight line diagonally to the cylinder axle have acute (<90°) cutting angles. Most of them have sizes around 1.1–2.0 mm, except for mortice spirals (4 mm) used for shearing of carpets.

The ledger blade (3) is a 10–12 cm-wide knife blade, 3–6 mm thick, corresponding in length to the width of the shearing machine. The blade was ground on its underside for approximately 3 cm towards the cutting edge. An absolutely uniform contact surface between the cutting edge of the ledger blade and the fabric (4) is ensured. The opposite side of the blade is screwed or clamped to the support beam. The cutting angle of the blade should be small in order to obtain the cleanest possible shear. The cutting edge of the ledger blade generally has lower hardness than that of the spirals. Consequently, the wear of ledger blade is greater. This is advantageous, as grinding of the ledger blade is less expensive than that of shearing cylinder.

The shearing table (5) may be hollow (Figure 2.2a) or pointed (Figure 2.2b). Seams must not be allowed to pass under the shearing device; otherwise they will be cut open. Seam joint sensors (6) lift the shearing rolls away from the fabric surface or the shearing bed is lowered, whenever a seam-joint reaches the shearing point.

Rotating brushes are installed both in front of, as well as behind, the shearing device to align the fibers correctly for shearing and to remove cut ends after shearing respectively. Modern shearing machines can operate at a speed of 100–150 m/min.

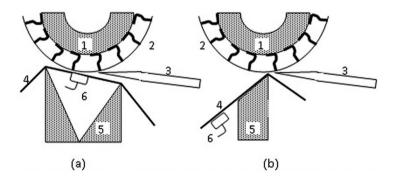


FIGURE 2.2 Shearing machines with (a) hollow table and (b) pointed table.

Modern shearing machines are generally computer-controlled and have the following features:

- 1) Fabric feeding device ensuring the entry of crease free fabric (electronically controlled).
- 2) Pair of two or more revolving shearing or cutter rolls with left- and righthand spiral blades. A four-cutter machine has four cutting points: two for face and two for reverse side of the fabric.
- 3) Shearing machine fitted with serrated blades, found satisfactory for the cutting of polyester materials.
- 4) Spiral revolving brush.
- 5) Fiber fluff collection by vacuum suction devices.
- 6) Fluff exhaust.
- 7) Ferrous and nonferrous metal detectors (electronic).
- 8) Seam joint sensors, which lift the shearing rolls away from the fabric surface whenever a seam-joint comes in contact.
- 9) Width and thickness sensing devices. The thickness (of fabric) measuring device provides automatic shear height (the distance between the shearing device and the shearing bed) adjustment.
- 10) Length measurement.

Shearing has assumed great importance recently, in view of its potential for improving fabric quality. In the case of polyester blended fabrics, in particular, shearing has proved to be of great value in reducing the incidence of micro beads for dyed fabrics. In the case of cotton fabrics, care should be taken to see that the shearing blades do not scratch the surface of the fabric, which otherwise may cause dyeing defects during subsequent dyeing.

2.4.3 SINGEING PROCESS

When yarn is made from short staple fibers, both ends of the fiber may not be embedded inside the yarn and are projected due to the twist imparted during spinning. For multi-filament yarns, some filaments may break or cut in places and are projected from the yarn surface. Singeing is a very effective method for removal of such projected fibers. Singeing of textile fabrics is necessary for the following reasons:

- a) Many cotton materials are valued for their smooth appearance, such as lustrous sateen and satin weaves, poplins for shirting, handkerchief fabric and so on. When yarn or fabric is made, the surface appears fuzzy or hairy due to the presence of projected fibers or yarns. The smooth lustrous appearance of fabric is thus affected. Similarly, sewing and embroidery threads should have a smooth surface devoid of projected fibers.
- b) Such fabrics are also soiled easily.
- c) The protruding fibers obstruct subsequent dyeing and printing process in an uncertain manner. It is almost essential with goods intended for printing.

- d) The goods to be mercerized are singed to develop maximum luster in the fabric.
- e) In case of polyester/cellulosic blended fabrics, singeing is the best method for controlling pilling. Pills or beads are formed on the surface of these fabrics during use. Sometimes double singeing is done to minimize pilling.

However, singeing is not essential for all types of fabrics.

The object of singeing is to burn off projecting hairs without scorching or otherwise damaging the body of the fabric. Improper singeing may cause irreparable faults. Some singeing faults and recommended precautions are:

- a) Before singeing, the fabric should be perfectly dry, as wet fabric scorches much more readily than dry fabric. The fabric may be dried by passing over a heated cylinder.
- b) Uneven singeing can cause streaks when the fabric is dyed, or bubbles when the fabric is finished.
- c) Improper singeing may lead to as much as 75% loss of tensile strength in warp direction.
- d) The fabric to be singed should not contain any acid-releasing salt (e.g., zinc chloride, which is normally used as anti-mildew agent), which may liberate acid on heating and thus tender the fabric.
- e) Stopping of singeing machine may cause heat bars on fabric.
- f) Creases produce streaks on singeing, which are magnified when dyed.
- g) Singeing may cause hardening of size and can lead to difficulties in desizing.
- h) There is a possibility of thermal damage to temperature sensitive fabrics.
- i) During singeing of synthetic fabrics, the protruding fibers melt and recede from the flame and form beads. The beads are disoriented in morphological structure and they absorb more dyes during dyeing, causing specky dyeing. In order to avoid this problem, these fabrics are singed after dyeing. However, when dyeing is carried out by thermosol method (dye fixing by hot air), singeing before dyeing does not create any problem.

Traditionally, singeing machines are of three types, namely:

- 1) Plate singeing machine
- 2) Rotary cylinder or roller singeing machine
- 3) Gas singeing machine

The fabric is passed at a very high speed over internally heated (750°C) red-hot curved copper plates (2.5–5.0 cm thick) and a red-hot rotating copper cylinder in plate and roller singeing machines, respectively. Special traversing arrangements for the fabric are provided to prevent local cooling and wear and tear of the metallic parts. Plate and roller singeing are obsolete nowadays, because of insufficient singeing and for producing typical hardness on the fabric. Although gas plants have long been used, the type and size did not suit the processing houses. With the advent of suitable gas units, the above contact singeing methods soon became outdated and the

gas-fired singeing machines achieved universal approval. Contact singeing (roller singeing) is still used to singe velvets.

In a gas singeing machine, the fiber ends should be loosened from the body of the sized yarn by pre-brushing and subsequently by the flame. When the flame with a temperature of about 1,300 °C touches the cold and moist material, an air/steam buffer zone is created between the flame and fabric. This may hinder singeing operation. The flame should have sufficient and controlled thermal and mechanical energy to reach to the base of material. The situation is further complicated by the fact that the pyrolysis of cotton is an exothermic process while that of polyester is endothermic. Polyester ignites at 480–500 °C, while it melts at much lower temperature (250–270 °C). In order to avoid melting of polyester before burning, the energy is to be supplied in a shock form and pyrolysis should be like an explosion igniting the whole length of the projected fiber instantly (Karmakar, 1999).

In a gas singeing machine (Figure 2.3), first the fabric in open-width is passed at a speed of 160–180 m/min through a pair of hot metallic drying cylinders (2) to dry as well to warm up the fabric to be singed with the help of a guide roller (1). The fabric is then passed through a number of weft straighteners or curved rollers (3) to remove weftwise creases from the fabric. The fabric, after passing through a braking device (4), is subjected to cleaning by means of brushes, which rotate in a direction opposite to fabric motion. The brushes are placed inside a chamber (5) and an exhaust fan removes the fluff and dust collected by the brushes. Then the fabric passes over gas burners with ceramic nozzles (6) where singeing is carried out. Two or more gas burners are used and the passage of the fabric is so arranged with the help of a large number of guide rollers that the singeing of both sides of the fabric can be done in a single passage. Two different sets of burners may also be used for singeing both sides of the fabric. The burnt gas is removed from the chamber through a chimney (7). After singling, the fabric is still hot and may carry some sparks along with it. It is, therefore, drawn by mangles through a trough of water called quench box (8), and thereby sparks are extinguished. To avoid wetting of the fabric, quenching by passage through steam is also possible. Additionally, a desizing compartment may be attached to impregnate with the desizing solution followed by squeezing.

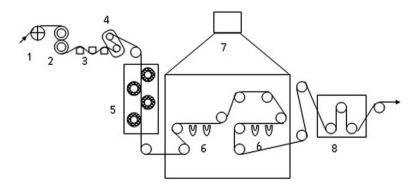


FIGURE 2.3 Schematic diagram of a gas singeing machine.

During the singeing process, a possible further action useful for having a wider range of workable products and for a better managing of the system is the regulation of flame intensity. Generally, in thermodynamics, the intensity is defined as the heat quantity that passes through a geometrical section in a specific time; so for changing the intensity it is necessary to act at least on one of these two considered elements (the heat quantity in a specific time or the geometrical section).

Usually, it is easier to manage the quantity of the fuel that feeds the burner in a mixing station by mixing with air. Of course, there are some physical limitations in order to keep the flame stable and powered on (functioning burner field), but in general it is possible to change the heating flow in a range of tens of kW per geometrical section units.

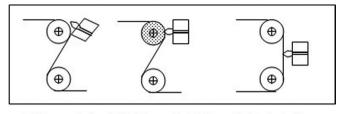
It is important to avoid an oxidizing flame that may lead to undesired carbon and sooty residuals. In any case, it is necessary to remove these eventual residuals with proper washing cycles to be made after the singeing process. The singeing process typically is made on grey fabric just because all the combustion residuals should be removed by washing cycles (Cibitex, 2021).

In gas singeing machines, automatic feeding of a suitable mixture of gas and air under pressure is provided to the burners in order to ensure complete combustion of gas. Coal gas, petrol gas or butane gas may be utilized. In recent years, there is a trend to use fully combustible fuel instead of gas-air mixture. It is possible to adjust the width of the burner to suit that of the fabric. It is also possible to adjust the flame height and consequently the heat intensity by altering the pressure of the gas or airgas mixture; pressure is measured via a manometer in terms of the air-gas mixture's height in centimeters.

In modern singeing machines, the gas/air mixture must be thoroughly mixed and metered at constant pressure and in the stoichiometric ratio for burning. Osthoff-80 singeing machine utilizes a patented double burner flame system with a Singmatic card control, which automatically controls flame height, width and temperature. The singeing effect is maintained by controlling the fabric temperature after singeing to a preset value. On the compact Parex 5000 Series Mark VI singer of Ernest Turner, there is pneumatic control of the angle of the flame to the fabric, while ultraviolet flame scanners, rapid start-up and automatic cleaning of the burners, combined with rapid shutdown, are valuable features of the machine.

The burners, together with the combustible mixture of air and gas, are the heart of the singeing machine. A good machine design ensures that the flame does not flutter. It is intense and uniform and singes even the difficult fibers. The two burners ensure a uniform flame along its whole length. The flame can be adjusted without undermining the quality. The two burners have been purposely designed to supply enough heat and kinetic energy to ensure singeing even though a cushion of air and steam builds up owing to the reaction between the cold, wet fabric and the flame, which makes the treatment difficult.

The speed for protein fiber combustion is much lower than that of cellulosic fibers; hence, woolen fabrics (90–150 m/min depending on the machine design) are singed at a speed of about 45–70 m/min. A couple of felt-covered rollers or another spark extinguisher is used instead of a quenching device.



(a) Tangential (b) Water-cooled Roller (c) Onto Fabric

FIGURE 2.4 Different burner positions in a modern gas singeing machine.

A modern singeing machine should be versatile and should be capable of singeing all types of fabrics, including blends, synthetic filament and spun fabrics. Depending on the type of fabric, singeing positions may vary (Figure 2.4), such as (Bhagawat, 1991):

- a) Tangential singeing;
- b) Singeing on water-cooled rollers or with counter-acting cool air;
- c) Singeing onto free-moving fabric.

In tangential singeing (Figure 2.4a), the flame impinges on the fabric at an angle. Consequently, only protruding fibers are burnt and the fabric surface is not directly affected. This is ideally suited for lightweight and sensitive fabrics. This is also suitable for synthetic filament fabrics, as they require mild singeing just to remove tiny broken filament-ends only.

In a water-cooled roller (Figure 2.4b), the flame impinges directly on the fabric and it is reflected back to the surface by the water-cooled roller situated at the back of the fabric. An elastic steam-air cushion formed inside the fabric resists deeper penetration of the flame and singeing occurs only at the surface. The fabric also remains cooler and heat-sensitive fabrics are protected from singeing heat. Thus, this singeing position is most suitable for synthetic, blended and open-structured fabrics.

In the "onto fabric" system (Figure 2.4c), the flame passes through the fabric and both sides are accessible to the flame. The flame enters the interstices of the fabric and, therefore, imparts good singeing. This position is very suitable for fabrics made from natural and man-made cellulosic fibers, and for heavy industrial and technical fabrics.

For proper singeing, the burner is kept very near to the fabric in tangential singeing, while the flame should meet the fabric at right angle position in the other two cases.

The functions expected from a good singeing machine are:

- 1) It should be capable of burning out all the fiber-ends protruding from the fabric surface.
- 2) The singeing effect should be uniform throughout the fabric width and on both side of the fabrics.

- 3) In order to ensure safe singeing, the burners should operate only when the fabric speed attains desired minimum value.
- 4) To minimize the unsinged length of fabric at the start, the drive should be so designed that the minimum speed is attained very quickly.
- 5) The burning of the fiber ends should not be only from the surface, but also from the interior of the fabric weave. Hence, optimum fabric speed will be decided by the fabric structure for a particular fabric sort.
- 6) The singeing process should not affect fabric properties like tear-strength, resilience, etc.
- 7) The machine should be provided with an effective and easy control over flame height.
- 8) The burners should be capable of individual swiveling to and from the fabric (or inactivating device), and correspondingly the burners are to be automatically ignited or extinguished. This will be necessary when the machine attains the desired speed and when it stops or slows down (due to several reasons), respectively.
- 9) A set of brush rollers, one each for the front and back of the fabric, should be provided in order to clean the fabric of any possible residue of soot.
- 10) An efficient static eliminator is necessary at the delivery end to conduct away any static electricity generated during fabric run.

A warning noise or fire alarm should operate in case of a fire. As an added precaution, wet sprinklers and unburned gas detectors have become necessary due to stringent safety regulations. The flame should never be yellow, smoky or sooty. This may cause permanent damage to polyester blended material.

In mills, the singeing room is always separated from the other departments. Frequent occurrences of fire in the singeing room may be due to the following reasons:

- 1) Careless threading in the machine at the start.
- 2) A momentary slowing down of the speed of the machine.
- 3) Sudden stoppage of the machine due to machine faults.

One recurring problem with the singeing process is that most of the unwanted short fibers on non-desized weft fabrics do not protrude from the yarn; they are stuck to the fabric owing to the size present on the fabric.

2.4.4 DESIZING PROCESS

The yarns, particularly the warps running lengthways throughout the fabric, are subjected to a high degree of abrasion during weaving. To prevent breakage or damage of warp yarns due to abrasion, "size" is imparted to the warp yarn. The presence of size on the fabric makes it stiff and renders its treatment with different liquors used in dyeing and finishing difficult. Therefore, one of the initial steps in wet processing is the elimination of size and water-soluble admixtures, the operation being called "desizing".

About 75% of the sizing agents used throughout the world consist of starch and its derivatives because of low cost and high effectiveness as a sizing material on cellulosic textiles. Starch is difficult to remove, as it is not soluble in water or in normal scouring liquor.

The desizing process is, therefore, carried out with lower concentrations of desizing agents at lower temperatures. The destruction of cellulose is thus minimized, but the time required to complete desizing is appreciably high.

The major components of the size are starch, wax and tallow. These, along with a number of secondary components, are baked to a cake on the sized yarn as it dries at a high temperature. This cake sometimes proves extremely difficult to clear from the yarn. Occasionally, emulsifying agents are added in the size to facilitate their removal. The term desizing is restricted to the removal of starch, while wax and tallow are loosened during desizing and are removed by the subsequent scouring process.

The purpose of desizing is not a complete elimination of all the sizes on the fabric. Rather, the process must be carried out in such a way that the subsequent processes can be carried out in the best possible manner and without difficulty.

Starch desizing methods of grey cotton fabric can be classified as follows:

- 1) Hydrolytic methods
 - a) Rot steeping storing water soaked and padded fabric for 24 hours at room temperature
 - b) Acid steeping storing acid (2 g/l hydrochloric or sulphuric acid) soaked fabric for 2–6 hours
 - c) Enzyme steeping storing amylase enzyme treated fabric for 2-3 hours
- 2) Oxidative methods
 - a) Chlorine desizing
 - b) Chlorite desizing
 - c) Bromite desizing
 - d) Peroxy compounds

Hydrolytic methods consist of degradation of starch into different intermediate compounds and finally into its monomer glucose. Hydrolysis is mostly carried out by enzymes, either those inherently present in water or added externally or by mineral acids. Generally, hydrolysis processes are slow and require significant time; hence they are mostly batch processes. However, they are comparatively safer than oxidation processes.

Rot and acid desizing methods are obsolete now. Chlorine and bromine compounds are not eco-friendly and their use is discontinued.

Desizing by enzymes is the safest method. Ease of handling, storage and disposal makes enzymes a choice catalyst for any processing industry. The enzymes have now been largely used for pre-treatment processes of textile materials, namely desizing and scouring of cellulosic materials and degumming of silk.

Enzymes are biological catalysts. They are naturally occurring proteins capable of catalyzing specific chemical reactions, and, being catalysts, facilitate the reaction without being consumed. The advantages are (Cavaco-Paulo and Gübitz, 2003):

- 1) Enzyme-catalyzed reactions are at least several orders of magnitude faster than chemically-catalyzed reactions.
- 2) Enzymes have far greater reaction specificity than chemically-catalyzed reactions and they rarely form by-products.
- 3) Enzymes act as catalysts for reactions under comparatively lower temperature (below 100 °C), lower pressure (atmospheric) and around neutral pH.
- 4) Enzymatic treatments offer savings in chemicals and energy and have less or no impact on the environment. The enzyme itself is fully biodegradable.

Time required for desizing depends on the method of application, kind of fabric (tightness of weaving, weight, etc.) and the temperature and concentration of the enzyme. The incubation times in various methods are reported (Cavaco-Paulo and Gübitz, 2003) to be as follows:

Jigger: 2–4 ends (60–100°C) Winch: 30 minutes (90–100°C) Cold pad-batch: 6–24 hours (15–40°C) Hot pad-batch: 3–8 hours (60–70°C) Pad-steam: 15–120 seconds (90–110°C)

The amounts used depend on the activity of the product and there are at least two systems for measuring that activity. The recommendations for Aquazyme 120 L from Novo Nordisk (120 refer to the strength of the enzyme) for various machines are as follows:

Quench box: 10–25 g/l Winch: 2–10 g/l Jigger: 2–10 g/l J-box: 20–50 g/l Combi-steamer: 20–50 g/l

However, enzymes suffer from the disadvantage that their desizing action is destroyed if the conditions of temperature and pH are not favorable. There are very few enzymes not inactivated or destroyed by temperatures over 75°C. Once destroyed, they cannot be revived or reactivated. Currently thermo-stable enzymes (e.g., α -Bacillus subtilis, α -Bacillus licheniformis, etc.) are available, which can withstand temperature up to 90°C. Certain enzymes require some specific bivalent metallic ions (e.g., Ca²⁺, Mg²⁺, Fe²⁺, Mn²⁺, etc.) as activators which act probably by stabilizing enzyme-substrate complex or sensitizing substrate to the attack of enzymes. Certain chemicals like alkalis, antiseptics and acid liberating agents tend to inhibit enzyme activity.

Oxidizing agents such as chlorine, chlorite, and bromite attack the glucose ring or the ether linkage, forming carboxyl or aldehyde groups. Both reactions ultimately result in depolymerization of starch into water-soluble products. However, cellulose being of similar structure as that of starch is not spared, and some degradation of cellulose into oxycellulose is inevitable. The oxidative desizing processes are therefore to be carried out carefully to minimize such degradation. Ammonium perdisulfate $(NH_4)_2S_2O_2$ and acid hydrogen permonosulfates have been shown to be efficient desizing agents, especially when polyvinyl alcohol (PVA) is used. PVA is water soluble, but after heat-setting of the fabric, the PVA size, present on the fabric, gets polymerized and is difficult to wash off unless a desizing agent is used (Roy Choudhury, 1996).

2.4.5 SCOURING OF COTTON

TABLE 2.1

Scouring is the most important wet process applied to textile materials before dyeing or printing. It is mostly a cleaning process in which the foreign matters or impurities are removed. The impurities may be natural, added or accidental, as discussed earlier. When the impurities are removed, the cotton becomes absorbent. In fact, the success of a scouring process is judged by the improvement in wettability of the scoured material.

More specifically, scouring is done in order to remove unwanted oils, fats, waxes, soluble impurities and any particulate or solid dirt adhering to the fibers, which otherwise hamper dyeing, printing and finishing processes. The process essentially consists of treatment with soap or detergent with or without addition of alkali. Depending on the fiber type, alkali may be weak (e.g., soda ash) or strong (caustic soda).

Typical formulations and conditions for batchwise and continuous scouring processes reported elsewhere (Lewin and Sello, 1983) are shown in Table 2.1.

For polyester-cotton fabrics, the concentration of sodium hydroxide is to be reduced to avoid the risk of hydrolysis of polyester.

Conditions for Batchwise and Continuous Scouring Methods				
Batchwise machines \rightarrow	Kier	Winch/ je	t Jigger	Package or beam
Caustic soda solid, g/l	5-10	5-10	5-15	15-20
Wetting agent, g/l	0.5-1	0.102	0.5-1	0.5-1
Detergent, g/l	0.5-1	2	4	2-4
M:L ratio	1: 3-5	1: 15-30	1: 2-4	1: 5-8
Temp, °C	130	95-98	95-98	100-130
Time, hours	4-6	1-2	2-4	3-5
Continuous machines \rightarrow	J-box, conveyor pad-roll		Open-width, ospheric steamer	Pressure steamer
Caustic soda, % o.w.m.	3-6		4-10	6-10
Wetting agent, % o.w.m.	0.1-0.5		0.1-0.5	0.1-05
Detergent, % o.w.m.	0.5-1		0.5-1	0.5-1
Temp, °C	100		95-98	130-140
Time, minutes	30-120		10-30	1-2

1 4 4

2.4.6 SCOURING OF WOOL

The methods employed for scouring cotton would rapidly destroy wool due to high alkalinity (especially caustic alkalinity) and high temperature. In addition, mechanical pressure applied in wet state should be low in order to avoid felting of the material. As a result of considerable experimental work to reduce felting, several new scouring machines have been developed in the industrial stage.

Wool may have to be scoured at various stages during its manufacture: as raw wool fiber, in sliver or yarn form, or in the form of woven or knitted fabric. Unlike raw cotton, containing wax, raw wool is greasy, difficult to spin, and it must be scoured before spinning.

Emulsion scouring with soap is the most common method of cleaning loose wool. Scouring, most popularly known as wool washing, is done with 2-4% soap and 2% sodium carbonate, calculated on the weight of the wool. At present, wool scouring is most economically done with nonionic detergents.

2.4.7 SCOURING OF SILK

Although sericin and fibroin, the two components of raw silk, are both protein, they differ considerably in their relative compositions of various amino acids and accessibility. The process for removal of water-soluble sericin is known as degumming, boiling off, and, less commonly, scouring.

The main degumming agent is soap. Boiling off or degumming of silk is carried out just below boil (90–95°C) in soap solution (5–10 g/l) with (1 g/l) or without alkali, according to the quality of the fiber. The removal is based on the water solubility and higher alkali sensitivity of the sericin as compared with the fibroin at pH values from 9 to around 11.5. Stronger alkalis may attack fibroin. Degumming of silk can also be done with a proteolytic enzyme (e.g., 1–2% on the weight of material, Trypsin) at about 40°C for 1–4 hours.

2.4.8 SCOURING OF SYNTHETIC FIBERS

Polyamide and polyester fibers are generally adequately scoured using an alkyl polyoxyethylene sulfate and sodium carbonate. With polyamides or nylons, nonionic synthetic detergents (1.5-2 g/l) with the addition of an alkali (0.5-1.5 g/l sodium)carbonate or trisodium phosphate) are suitable.

The scouring procedures for synthetic fibers are relatively simple since the fibers contain fewer impurities, most of which have at least some degree of water solubility – the most important being sizes and lubricants. The major sizes used are polyvinyl alcohol, carboxymethylcellulose and polyacrylic acid, all of which are completely or partially water soluble. It is not always necessary to scour polyester fiber materials before dyeing.

For acrylic fibers, anionic surfactants should be avoided, because they may restrain the uptake of basic dyes. These fibers are scoured with an ethoxylated alcohol, either alone or with a mild alkali such as sodium carbonate or phosphate.

2.4.9 MERCERIZATION

Mercerization is a process in which fabrics (typically cotton) are treated with caustic soda (NaOH) solution to cause swelling of the fibers. This improves properties such as fiber strength, shrinkage resistance, luster and dye affinity. The caustic actually rearranges the cellulose molecules in the fiber to produce these changes.

Traditionally, a cold solution of 25–26% by mass of sodium hydroxide is used, although better penetration and more even treatment is obtained with the more recent hot mercerizing technique.

2.4.10 HEAT-SETTING

Unlike natural and regenerated fibers, the yarns and fabrics manufactured from synthetic fibers require a special preparatory operation called heat-setting. During this operation, the material is subjected to thermal treatment in tensioned condition in hot air, steam or hot water medium. Unless this treatment is done, these materials will shrink when treated with aqueous solution in loose condition, and as a result the linear dimensions and the shape of ready-articles change.

The main techniques of setting are (Rao and Gandhi, 1991):

- a) Dry-heat-setting (or simply, heat-setting/thermo-setting)
- b) Steam-setting
- c) Hydro-setting

The optimal conditions for setting various textile fibers in water, steam and dry-air are shown in Table 2.2 (Peters, 1967).

2.5 BLEACHING

TABLE 2.2

After the desizing and scouring processes, the textile materials are in very absorbent form and can be dyed without much problem. But the materials are still yellowish or brownish in color, which may affect the tone and brightness of the shade obtained by dyeing and printing, particularly for light shades.

Optimum Temperature and Time for Setting of Textile Fibers						
	In	water	ter In steam		In hot air	
	°C	Minutes	°C	Minutes	°C	Minutes
Triacetate	-	_	_	_	190-220	0.5-2
Nylon 6	100	120-180	108-121	10-30	175-190	0.25-0.5
Nylon 6,6	100	120-180	115-130	10-30	190-215	0.25-0.5
Polyester	100	120-180	140	10-30	180-220	0.33-0.66

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Whiteness of scoured goods is far below satisfactory because none of the above preparatory processes can remove the coloring matters. The textile substrates possess these substances naturally, or these are added to facilitate processing or dropped accidentally. The quantities of such materials are normally very negligible but they are firmly embedded into the textile materials. Their removal requires a special step of preparatory process called "bleaching".

The main object of bleaching is the removal and/or destruction of natural and adventitious coloring matters with the production of pure white materials. The natural coloring matters present in various textile materials are different. But a method of bleaching may be suitable for a number of textile fibers, though the conditions and the extent of bleaching required may be different in different cases. For example, Egyptian cotton is darker in color and more difficult to bleach as compared to American varieties. One must be careful while choosing the bleaching agent as the textile material may be damaged in the presence of a particular bleaching agent, particularly under certain pH range and temperature.

In a broader sense, the term bleaching encompasses a series of operations designed to produce a clean, white material including three distinct processing stages, namely, desizing, scouring and whitening.

Cotton contains portions of the husks of the cotton ball, called motes, which are trapped between the cotton fibers during picking. During ginning, these motes are further reduced in size and entangled with the fibers. Caustic scouring softens, decolorizes and erodes these particles, allowing their removal during the washing operation following scouring and bleaching; other particles simply get bleached and remain in place.

Bleaching agents convert colored impurities into colorless particles. Color is imparted by a chromophore – a moiety usually involving alternating carbon-carbon single and double bonds. Bleaching destroys these double bonds by addition (saturation) or rupture. Once the free electrons of a double bond are tied by substitution or by rupturing the double bond, electromagnetic radiation is not absorbed and is reflected in the visible region of the spectrum and color ceases to exist (Mock, 1985). Sun bleaching was the main form of whitening until the Romans used the fumes of burning sulfur to bleach wool. Until the mid-18th century, the Dutch had a virtual monopoly on bleaching in Europe. The Dutch method of bleaching linen consisted of steeping for several days in liquor made alkaline with the extract of burnt seaweed. The cloth was then well rinsed until clean, and spread on grass fields for sunlight and air exposure for several weeks. These operations are called bucking and crofting, respectively.

Many colored compounds, when acted upon by reducing agents, become colorless due to structural modification. The oldest such substance used for bleaching wool, and to a lesser extent for silk, is sulfur dioxide. The Romans used to stretch cloth on a cage-like frame followed by burning sulfur underneath the frame. The degree of whiteness was adequate, but lacked permanence. Moreover, this was not useful for cellulosic materials.

The discovery of chlorine by Scheele in 1774 and the observation of its bleaching action revolutionized the methods of treating linen and cotton. In 1799, Tenant commercially manufactured bleaching powder by the use of dry hydrated lime and chlorine gas in Glasgow. Since around 1830, bleaching powder has been the chief agent for the bleaching of vegetable fibers.

In the late 1890s, a firm later known as DuPont first produced peroxide bleached materials. Their sodium peroxide process was mainly for wool and silk. The electrolytic process for manufacture of hydrogen peroxide was developed in the 1920s, and by 1930, several mills were experimenting with peroxide bleaching.

Bleaching with peroxides seems to have passed through three phases in its history, the first being the early use of barium peroxide and the solutions of hydrogen peroxide which could be made from it. This came to an end around 1912, when sodium peroxide became available in commercial quantities. Since about 1927, concentrated solutions of hydrogen peroxide have been manufactured from various routes. It is, in fact, the only oxidative bleaching agent for wool and silk, but is also safe for all textile fibers – hence the name "universal bleacher".

Since its introduction as a commercial product in 1939, sodium chlorite has achieved an ever-increasing place amongst the bleaching agents for cellulosic fibers, especially linen. Sodium chlorite is active under acidic condition. Hence, this is useful for white cotton goods where the natural softness can be preserved by eliminating alkaline scouring process. With the invention of synthetic fibers, especially polyester, sodium chlorite gained popularity as a bleaching agent. These fibers are unstable under alkaline conditions under which other bleaching agents are normally applied. However, chlorine compounds are not eco-friendly and their use is now discontinued. Peracetic acid, made available in 1948 by BECCO, is widely adopted for bleaching polyamides and acetate rayon.

Even after bleaching, the whiteness may fall short for white goods. Whiteness can be further enhanced by treating with a blue pigment or dye, which suppresses the yellowish tinge of the materials, or with an optical brightening agent, which allows more light reflection from the textile surface by converting ultra-violet light of the illuminating source into visible light.

2.5.1 REDUCTIVE BLEACHING AGENTS

Many coloring matters can be reduced to colorless compound by reducing agents. However, on exposure to air and sunlight, the reduced colorless components get oxidized and the yellowish tint reappears. Before the invention of hydrogen peroxide, sulfur dioxide was the only bleaching agent for wool. But whiteness achieved by reductive bleaching agents is not permanent. Hence, they are not popular.

2.5.2 OXIDATIVE BLEACHING AGENTS

Oxidative bleaching agents are used much more than reductive bleaching agents. Earlier, atmospheric oxygen was utilized in "*dew bleaching*" process. The medial process of bleaching was to lay the material out in a field for exposure to air and sunlight. In ancient days, this slow process was the only method for bleaching cotton and linen goods.

Slow atmospheric oxidation is not commercially viable. Hence, a number of chemical oxidation processes are being utilized for bleaching of various textile fibers. The most important oxidative bleaching processes are:

- 1) Hypochlorite bleaching
- 2) Hydrogen peroxide bleaching
- 3) Sodium chlorite bleaching

Hypochlorite and chlorite bleaching are no longer used due to their harmful effects on our health.

2.5.2.1 Peroxide Bleaching

Although hydrogen peroxide is costlier than hypochlorites, the former has several advantages, which have contributed to its greatly increased use during recent years. The advantages are:

- 1) It is a universal bleaching agent and can bleach most of the textile fibers without damaging the materials.
- It is eco-friendly. As the decomposition products of hydrogen peroxide are oxygen and water, bleaching can be safely carried out in an open vessel. No AOX is generated even in the presence of salts.
- 3) Hydrogen peroxide does not react with proteins. Hence, a permanent whiteness can be achieved without preliminary alkali treatment.
- 4) As peroxide bleaching is done under alkaline conditions at or near boil, both scouring and bleaching can be combined. In fact, it is the only bleaching agent that can be used for the combined process. As desizing is also possible with hydrogen peroxide, it is possible to combine all the three processes. The presence of natural impurities during peroxide bleaching is advantageous as they exert a stabilizing effect upon hydrogen peroxide, preventing excessive loss of oxygen. Earlier it was thought that prolonged alkali boil is necessary for removal of wax so that the cotton materials become absorbent. However, recent studies show that for imparting absorbency it is not necessary that the wax be completely removed. The rupture of primary cell walls of cotton fiber where wax is situated may be sufficient to impart absorbency. The presence of hydrogen peroxide in combined processes accelerates rupture of cell walls. Hence, the absorbency is attained much quicker than separate scouring and bleaching processes.
- 5) Peroxide bleaching has also led to the introduction of continuous processes, as it can be completed within an hour or so. It allows versatile processing such as batch or continuous, hot or cold, rapid or long dwell.
- 6) As peroxide bleaching is done at or near boil, the broken seed or other vegetable matters are removed during the treatment and consequently the cloth appearance after bleaching is much better and fuller than hypochlorite bleached material.
- 7) There is little risk of tendering due to over-bleaching.

- 8) Colored goods dyed with vat dyes can be safely bleached with hydrogen peroxide.
- 9) No souring or any other after-treatment is necessary after peroxide bleaching.
- 10) It is compatible with most dyes and FWAs.

The difficulties of peroxide bleaching are:

- 1) Instability of hydrogen peroxide solution at high alkalinity and in the presence of metallic impurities.
- 2) The use of a stabilizing agent is indispensable for the reason that peroxide ensures whitening in conditions where it is rather unstable. These substances regulate the release of oxygen, which does not have any bleaching action and may cause fiber damage. Sodium silicate, though a most widely used stabilizer, is liable to deposit on the fabric and on the equipment.
- 3) The use of multiple chemicals needs careful control.
- 4) The process is comparatively expensive.

2.5.2.2 Strength of Hydrogen Peroxide

Hydrogen peroxide is available in liquor form. The strength of its solution may vary widely and is expressed in terms of the volume of available oxygen liberated from one unit volume of the liquor. Thus, if 1 ml of solution liberates 1 ml of oxygen at S.T.P., the solution is equivalent to 1 volume peroxide solution. The relationship between volume strength and percentage composition of hydrogen peroxide is shown in Table 2.3.

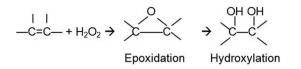
At present, it is more common to express strength by percentage weight of hydrogen peroxide. Textile bleaching grade hydrogen peroxide is mostly of 27.5% and 35% strength.

2.5.2.3 Bleaching Action

In peroxide bleaching, the carbon-carbon double bond is destroyed by epoxidation and hydroxylation (Equation 2.1) (Mock, 1985):

TABLE 2.3 Relationship Between Volume Strength and Percent Strength of Hydrogen Peroxide

Volume Strength	% Strength
1	0.3
10	3.0
100	27.5
131	35
197	50



Earlier bleaching action of hydrogen peroxide was thought to be due to the liberation of nascent oxygen, but this explanation is no longer valid. Under certain conditions, particularly with regard to pH, hydrogen peroxide decomposes into hydrogen and perhydroxyl ion (HO₂⁻), which is thought to be responsible for bleaching action. More recent work (Dannacher and Schlenker, 1990) has strongly implicated the superoxide radical anion (\bullet O₂⁻). Hydrogen peroxide solutions normally require the addition of an activator to bring about bleaching. The most common activator is alkali, which presumably encourages the formation of the perhydroxyl anion; this then reacts further with hydrogen peroxide to give the superoxide ion (Equation 2.2).

$$H_{2}O_{2} \rightleftharpoons H^{+} + HO_{2}^{-}$$

$$H^{+}$$

$$HO_{2}^{-} + H_{2}O_{2} \rightarrow \bullet OH + \bullet O_{2}^{-} + H_{2}O_{2}$$

Alkalinity favors the liberation of perhydroxyl ions; the rate of forward reaction is increased due to neutralization of H⁺ ion released forming water (H⁺ + OH \rightarrow H₂O). However, excessive alkalinity causes the peroxide to become unstable.

In the presence of catalysts, the alternate reaction takes place evolving oxygen.

$$2H_2O_2 \rightarrow 2H_2O + O_2$$
 [Equation 2.3]

The liberated oxygen has no bleaching power, and the catalysts, therefore, cause wastage of hydrogen peroxide.

With increase in temperature, the stability of hydrogen peroxide decreases. For natural and man-made fibers, the time of bleaching will be too long unless the temperature is higher than 80°C. In practice, the treatment is done at 90–100°C for $1-1\frac{1}{2}$ hours, but in a pressurized vessel the temperature may also be raised to 120 to 130°C, with reduction in treatment time as short as 20 minutes. However, the evolved oxygen accumulates at the top of the enclosed vessel, which can cause tendering of the material due to oxycellulose formation at high temperature.

Hydrogen peroxide is decomposed catalytically by traces of many metals such as copper, iron, manganese, chromium and their oxides. This is accompanied by increased degradation of cellulose.

The oxidation of the cellulose by hydrogen peroxide takes place simultaneously with its decomposition. Bleached cotton appears to have a catalytic effect on the decomposition. The rates of decomposition and oxidation increase with the pH, but at higher pH values the decomposition rate increases faster. Very little oxidation occurs at pH 7 and with HCl-extracted cotton, indicating that traces of a catalyst is required for the oxidation reaction. The main functional groups formed on the cellulose by oxidation appear to be ketones, while very few aldehyde and carboxyl groups were also

found. The ketone groups, thus formed, are inactive and do not bring about yellowing and color reversion. The attack on cellulose is not directed at random to all carbons of the anhydroglucose units of the chains, it is directed mainly to the C_3 hydroxyl groups.

The catalytic effect of metal ions is not limited to the decomposition of hydrogen peroxide. Simultaneously the fibers are attacked, degree of polymerization (DP) and the tensile strength decrease considerably. Localized concentration of the catalyst accelerates the oxidation of the fabric to such an extent that *pinholes* or *razor cuts* are formed in the fabric. These are due to local dissolution of the cellulose of very low DP values (Lewin and Sello, 1983). Stabilizers are necessary to slow down the decomposition of both hydrogen peroxide (Equation 2.5) and the active bleaching agency. The most common stabilizing agents have been colloidal sodium silicates. The formulae of silicates are best represented in terms of the ratio of sodium oxide to silica, as in sodium metasilicate (Na₂O:SiO₂) and orthosilicate (2Na₂O:SiO₂). These silicates, however, are in crystalline form in which the ratio is 1 or greater. In the colloidal forms originally preferred for peroxide bleaching, the ratio is less than 1. For example, in the so-called *alkaline glass* form, the ratio is 1:2; whilst in the so-called water glass form, it varies from 1:1.6 to 1:1.38. The colloidal silicates are efficient and economical stabilizers, but care is needed to ensure efficient washingoff in order to avoid deposits of silica on the fabric and equipment. Although such colloidal forms have been preferred, the crystalline meta- and ortho-silicates can also be used and may provide easier wash-off. The mechanism by which these stabilizers work is complex, although the elements of buffering action and sequestering of transition-metal ions, such as those of iron (III) and copper (II), which otherwise catalytically degrade hydrogen peroxide, undoubtedly contribute. Magnesium ions also play an essential part in the mechanism and must be added (as the sulfate) if they are not already present in the system sufficiently. A small quantity of magnesium salt must be present if sodium silicate is to act as a stabilizer. Hard water containing at least 2° hardness will usually supply the need. Hardness between 2° and 7° would give satisfactory results. If soft water is used, 0.1 to 0.2 g/l magnesium sulphate is to be added. Sodium silicate may impart harshness to the material due to the deposition of insoluble silicon compounds. This may create a problem in circulation in the package dyeing machine. To avoid such precipitation, additional alkali may be added to bring the ratio of Na₂O: SiO₂ around 2.25: 2.75. To avoid a risk of degradation of cellulose, a mixture of sodium hydroxide and sodium carbonate is used as alkali. The major disadvantage of silicate stabilizers is that they form hard scales on equipment. They also have a tendency to deposit on fabric causing poor handle.

Water-soluble impurities in raw cotton can have a considerable stabilizing effect on hydrogen peroxide solution. It is, therefore, preferable to bleach unscoured cotton, unless the material is heavily soiled.

Theoretically, sequestering agents should be the best stabilizers – stabilization may be affected by elimination of heavy metal ions responsible for free-radical formation. The various types of sequestering agents used in textile processing are:

- 1) Polyphosphates
- 2) Polyhydroxy-carboxylic acids

- 3) Aminopolycarboxylic acids
- 4) Phosphonic acids
- 5) Polyacrylic acids

It is important to recognize that whilst transition-metal ions catalyze the destruction of stabilized peroxide, the alkaline-earth element stabilizes peroxide. In the absence of calcium and magnesium, even silicates cannot act as bleach stabilizers (Shore, 1990). Proteins also exert a stabilizing influence and can inactivate slight traces of copper in the bleaching liquor. Other stabilizers include magnesium silicate or hydroxide, trisodium phosphate, sodium pyrophosphate, tetrasodium pyrophosphate and commercial non-silicate stabilizers (e.g., a mixture of sodium oxalate and sodium pyrophosphate). Nowadays, organic chelating agents are also used as stabilizers. A very important function of stabilizer is to maintain the internal pH of the fiber, irrespective of the pH of the liquor, between 8.0 and 8.5. So far as the buffering is concerned, sodium silicate and non-silicate mixed stabilizers mentioned earlier are most effective.

The recent peroxide stabilizers are blends of several materials, mainly of the following chemical types or their mixtures:

- 1) Alkali (e.g., silicate, caustic soda or sodium carbonate)
- 2) Organic sequestering agents (e.g., EDTA, DTPA, heptonate or phosphonate)
- 3) Inorganic salts (e.g., magnesium salts)
- 4) Dispersants (e.g., acrylates or phosphonates)
- 5) Protein degradation products
- 6) Certain surfactants
- 7) Polymeric materials or colloids (e.g., acrylic polymers)

Magnesium and calcium salts are more stable at high temperature as compared to free aminocarboxylic acid. Polycarboxylic acid mainly acts as a dispersing ion-exchanger. Phosphonates are good complex formers with good dispersing properties. Nevertheless, due to pollution problems, they are now substituted by acrylates.

DTPA as sodium or magnesium salt and its hydroxy derivatives have good sequestering properties as well as stability to oxidation. However, EDTA and DTPA have now been replaced by heptonates and gluconates (Karmakar, 1999).

Hydrogen peroxide is not an active bleaching agent for cellulosic fibers under neutral and acidic conditions. On the other hand, excessive alkalinity will cause instability and decomposition of hydrogen peroxide with liberation of oxygen. Compounds, which increase pH values such as sodium hydroxide, sodium carbonate and ammonia, are activators. In order for bleaching to be completed within a reasonable time, it is necessary to adjust the pH of the bleaching liquor between 10 and 10.5 for cotton, while for wool it is between 8 and 9. For cotton, a mixed alkali of sodium hydroxide and sodium carbonate is used. But for wool, these may be harmful – sodium pyrophosphate, tetrasodium pyrophosphate or sodium silicate may be used. However, if sodium silicate is used, the material should be thoroughly rinsed after bleaching in order to prevent harsh feeling.

Bleach activators are added to promote the oxidation potential of alkaline hydrogen peroxide. These generate peracids, which allow bleaching to be conducted at lower temperatures for a reduced time, resulting in energy.

A trace amount of residual hydrogen peroxide (several ppm) can cause dyeing problems, such as unevenness and batch-to-batch variation of dyed shades and poor dyeing, depending on the stability of the dyes. The reactive groups and/or chromophore of many reactive dyes get oxidized.

Currently, many cellulosic dyeing and finishing plants are using three or four rinses to remove peroxide or are using reducing agents such as sodium bisulfite, the excess of which may adversely affect the shade.

$$H_2O_2 + Na_2SO_3 \rightarrow Na_2SO_4 + H_2O$$
 [Equation 2.4]

The advantage of catalase enzyme (Niels, 2000) is that it attacks only hydrogen peroxide and nothing else. The reaction is as follows:

$$H_2O_2$$
 + catalase \rightarrow 2 H_2O + O_2 + catalase [Equation 2.5]

The reaction rate is extremely fast and under optimum conditions 1 mole of catalase is able to decompose 500 million moles of hydrogen peroxide in one minute. The catalase is free to decompose more hydrogen peroxide as long as the desired pH and temperature are maintained. The need to neutralize before adding the dye is beneficial since catalase is most active in the pH range of 6–8.

Normally, when using catalase, the number of rinses can be reduced drastically. The catalase is applied in the dyebath prior to adding chemicals and dyes. This is acceptable because catalase acts on hydrogen peroxide only and no other chemicals. The steps to be followed are:

- After bleaching, the bath is cooled to 70–80°C and if needed, the machine is drained.
- It is then refilled and pH is neutralized with acetic acid, the amount of which is decided by the residual caustic soda.
- After running for 10–15 min, the pH is checked and adjusted to 6.5–7.5 before draining.
- The bath is refilled, catalase is added (amount depending on the concentration of the product) and run for 10 minutes.
- The dyes, electrolytes, chemicals and alkali can be added to the machine without draining the liquor.

2.5.2.4 Continuous Process

Continuous processes were developed with the advent of hydrogen peroxide as a cost-effective alternative to hypochlorite in the late 1930s. Peroxide can be used

continuously after a shorter alkali boil-off. In order to allow time for the chemicals to work, a first-in/first-out system, called a J-box, was developed to replace storage pits based on first-in/last-out systems, which used to give uneven results.

In a semi-continuous pad-batch process, the fabric is impregnated in open width in the bleaching liquor typically containing 0.5-0.8% caustic soda, 2-3% sodium silicate, 0.8-1.2% hydrogen peroxide – all on the basis of o.w.m. It is then preheated by passing through a steam or infrared chamber and made into a circular batch consisting of about 2,000 meters of fabric on a rotating roller. It is then held in a steamheated reaction chamber for a given time prior to washing off (Lewin and Sello, 1984).

Open-width continuous equipment include J-boxes, roller steamers and conveyor steamers. The open-width bleaching processes have been developed in recent years at a rapid pace. These processes are of particular importance for polyester-cotton blends, which are very sensitive to creasing. The quality of processed goods may suffer in these machines due to uneven heating, and the energy consumption is high. But these machines have revolutionized bleaching processes as treatment time has been brought down significantly. Roller steamers with 50–200 meters capacity allow very short reaction time because of rapid and uniform heating. In roller steamer systems, the impregnated cloth is passed through a closed steamer over a number of rollers. The machine is ideally suited for highly crease-prone fabrics. They suffer, however, from high chemical costs and the high cost of frequent replacements of various machine parts. The conveyor steamers with 200-500 meters capacity permit the processing of more relaxed fabrics by plaiting them without tension on the conveyor; longer dwell time results in more efficient use of chemicals. The scouring and bleaching recipes for cotton fabrics in three continuous steamers with varying dwell periods are shown in Table 2.4 (Mahapatro and others, 1985).

Most of the recent installations are a combination of roller-conveyor steamers (Figure 2.5) [Mock, 1985]. The enlarged roller preheater and conveyor sections, needed to prevent packing creases, can be used separately or in tandem. The fabric path may be changed without rethreading. Thus, there will be maximum flexibility with regard to retention time. The fabric passes over a number of rollers on entry to the heated chamber to ensure level heating and to start the reaction in a flat, crease-less condition. After prestabilizing in this way, the fabric is rippled onto a conveyor consisting of a large number of driven rollers, all of which are close together. Such a conveyor, also called a roller bed, keeps the fabric pile continuously moving so that the folds in the fabric are never long enough in one position for a permanent crease to form. The contact time of the bottom of the fabric pile with each roller is also not long enough for drying to occur. Such types of steamers are also known as roller bed steamers.

2.5.2.5 Enzymatic Processes

Oxidoreductases – enzymes that catalyze oxidation or reduction reactions – may find use in enzymatic bleaching process. Although some degree of color removal is possible through the use of selected enzymes, seed coatings remain a severe problem.

	Dwell Time in the Steamer (minutes)			
Chemicals (g/l)	20–30	10–15	2–3	
Scouring				
Caustic soda	20-30	30–40	80-100	
Scouring aid	3–8	5-10	10-15	
Wetting agent	2–3	2–3	2–3	
Bleaching				
Hydrogen peroxide (35%)	20-30	30–40	40-60	
Sodium silicate	5-10	12-15	15-20	
Caustic soda	4–6	5–7	6–8	
Wetting agent	0.5	0.5	0.5	

TABLE 2.4Scouring and Bleaching Recipe for Three Continuous Steamers with VaryingDwell Periods

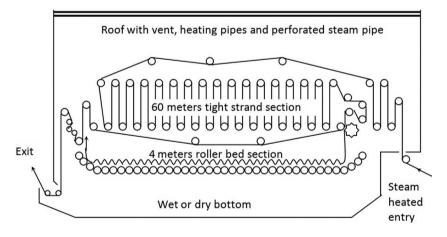


FIGURE 2.5 Combination roller-conveyor steamer

2.6 COMBINED SCOURING AND BLEACHING OF COTTON

The advantages of this process are increased production with reduction in labor cost and reduced treatment time and lower consumption of water, steam and electricity. The loss in weight and strength of material is less. The disadvantage is increased chemical cost as a higher dose of hydrogen peroxide is required. The declining pricerates of peroxide with increasing cost of utilities may make the process more economical. In the presence of hydrogen peroxide, the scouring process is accelerated and less time is generally required to achieve good absorbency of the material. The process may be carried out in conventional machinery by treating grey, desized or mercerized fabric directly with caustic soda, soda ash, scouring aid, hydrogen peroxide, sodium silicate or other peroxide stabilizers at or above 80°C for 4–6 hours, depending on the type of fabric and machinery used for the process. To adopt the process, the scouring-aids play an important role. Many solvent-based compositions are available in the market. The solvents remove wax and grease and the emulsifier incorporated removes the impurities and keeps them in suspension. A major portion of such composition is nonylphenol ethylene oxide condensate. However, objections are being raised against these products due to water pollution problem by solvents. Eco-friendly solvent-free products are composed of high HLB anionic surfactants, anti-redeposition agents and very powerful hydrotope.

2.7 COMBINED PREPARATORY PROCESSES

The modern approach to integrated chemical pretreatment involves combined desizing-scour-bleach operation using a continuous open-width pad, steam, washoff, dewater and dry sequence. Alternately, enzyme desizing may be carried out by amylases, separately followed by alkaline oxidation using caustic soda, hydrogen peroxide and a wetting agent. A one-step process for desizing, scouring, bleaching and slack mercerizing process is described next (Huang and Yen, 1997):

The cotton fabric is impregnated in a mixed solution containing sodium hydroxide (10–30%), hydrogen peroxide (20 g/l) and trichloroethylene (50 g/l) for 3 minutes, followed by curing for 30 seconds at 120°C. The physical properties of the treated material are similar to those obtained using a conventional two-step approach. Potassium or sodium peroxydisulphate may be incorporated in the recipe while carrying out integrated processing. However, oxidative treatment gives rise to oxidative damage and complete removal of the primary wall of cotton. Careful monitoring is essential to minimize fabric damage.

2.8 EFFECTS OF PRETREATMENT ON PRINTING

Tarakçioglu et al. (2004) investigated the effects of various pretreatment parameters on printing viscose fabrics with reactive dyes. Among the pretreatment processes for common viscose fabrics, the most important step that affects printing properties directly is caustisizing or semi-mercerizing. There is no need for bleaching and a reductive clearing after-treatment.

2.9 PREPARATION OF PROTEIN FIBERS

Animal or protein fibers are very irregular in composition. They contain a significant amount of non-fibrous impurities – about 50% in case of wool and about 15–30% in case of silk. These fibers are very sensitive to alkali and are damaged quickly on alkaline wet treatment at high temperature (especially wool). Hence, these fibers are scoured with large amount of soap or detergent, with little or without alkali at low temperature. The time of treatment is also much shorter as compared to that in case of cotton.

Raw wool contains about 40-50% impurities. Hence, wool must be scoured in fiber stage, but the fiber scouring process is quite troublesome as the fiber is very alkali-sensitive and gets easily entangled (i.e., felted). Complete removal of wool wax is not desirable at this stage. The fiber should retain a small portion (between 0.4% and 0.6%) of the wool wax in order to avoid brittleness causing fiber breakage during the subsequent spinning process. Sometimes spinners of woolen yarns prefer a residue as high as 3%. The feedback parameters of scouring are residual grease content of the wool and the subjective assessment of quality – color, brightness, felting, loftiness, and so on.

Wool fiber scouring machines are of three types:

- Swing rake machine
- · Harrow machine
- Paddle machine

Saponification of wool wax requires higher alkaline conditions, which would damage the wool fibers. However, it may be readily emulsified, particularly at a temperature slightly higher than its melting point (40–45°C). Emulsion scouring with soap is the most common method of cleaning loose wool. Scouring, most popularly known as *wool washing*, is done with 2–4% soap and 2% sodium carbonate, calculated on the weight of the wool. At present, wool scouring is most economically done with non-ionic detergents. Wool needs further scouring after spinning or weaving to remove remaining wool grease.

Raw silk does not possess the luster and softness for which this fiber is known. The gummy substance called *sericin* covering the fibrous material, *fibroin*, imparts a harsh handle and must be removed in order to bring out the supple and lustrous qualities. Although sericin and fibroin, the two components of raw silk, are both proteins, they differ considerably in their relative compositions of various amino acids and accessibility. The process for removal of sericin is known as degumming, boiling off and, less commonly, scouring.

The traditional method of degumming with soap is still the one mostly used, especially in China and India. However, slowly the processes using synthetic detergents or enzymes are becoming popular. The advantage of soap degumming is that an especially soft handle is produced. However, the treatment time is very long (2–6 hours).

The best soaps for degumming silk are made from olive oil commercially sold as *Marseilles soap*, which is now somewhat expensive; as a result, the less effective oleic acid soaps are being widely used. Tallow soaps are difficult to remove after degumming. Soap from cottonseed or coconut oil has been suggested, but they leave an unpleasant odor in the material.

When neutral olive soap is used with a small amount of alkaline reagents such as sodium carbonate, phosphate or silicate, the pH of the liquor should not fall outside the range of 9.2 to 10.5. The concentration of soap is generally not less than 20-30% of the weight of the material, which works out at 5–7 g/l for a liquor ratio 30-40:1.

The temperature of the degumming bath generally lies between 90 and 95°C; higher temperatures up to boil are apt to bring about some yellowing of the silk and

inferior handle. The addition of alkali to soap solution increases the rate of degumming and makes the process economical since the quantity of soap and time required are reduced. High-grade olive oil soap liquor gives a starting pH of 9.2–9.5, which rapidly falls to 8.5.

Silk has an inherent slightly yellowish color. This natural color is desired by some fashion designers as a *soft white* or natural shade. The desired degree of whiteness can be relatively easily achieved with mulberry silk, but with tussah silks, depending on their origin, a light to pronounced yellow-brown tint is unavoidable and pale dyeing and printing may be affected by this color. Bleaching is therefore especially important for tussah silk. Most varieties of silk are bleached by steeping, but winch machines may be used for fabrics. The treatment is carried out with 0.55% w/w hydrogen peroxide solution made alkaline with sodium silicate and ammonia to give a pH of 10, or with addition of tetrasodium pyrophosphate and EDTA at 60–75°C for 2-4 hours.

For wool and other protein fibres, the control of alkalinity is most important as high alkalinity may cause breakdown of polypeptide chains with consequent loss in strength. The minimum alkalinity required to activate hydrogen peroxide is sufficient to damage the fibre if the temperature exceeds 60° C. The recommended pH is 8–8.5, which is much lower than that maintained during cotton bleaching. Iron or copper causes catalytic decomposition of hydrogen peroxide. If the woollen material contains traces of such metals, there will be immediate tendering of the material. However, the defect can be noticed during use only. Adding sequestering agents in the bleaching bath can eliminate the action of metallic catalysts. 2 g/l tetra-sodium pyrophosphate – 1 g/l EDTA (30 %) are added in the bleaching bath.

(Brady, 2017)

2.10 PREPARATION OF SYNTHETIC MATERIALS

Unlike natural and regenerated fibers, the yarns and fabrics manufactured from synthetic fibers require a special preparatory operation called *heat-setting*. During this operation, the material is subjected to thermal treatment while in tensioned condition in hot air, steam or a hot water medium. Unless this treatment is done, these materials will shrink when treated with aqueous solution in loose condition, and as a result the linear dimensions and the shape of ready-articles change. The amount of shrinkage is dependent upon structural parameters such as orientation and crystallinity of the fibers, previous history of treatments and tensions applied, and external variables like temperature, time and tension applied during shrinking. The amount of thermal shrinkage exhibited by any particular fiber product reflects its history: the draw-ratio, the tension developed during other processes and any heat-treatment that has been applied.

Setting process releases the strains imposed during drawing, knitting or weaving processes, minimizes creasing during wet processing, and imparts a high dimensional stability. The main techniques of setting are:

- Dry heat-setting (or simply, heat-setting/thermo-setting)
- Steam-setting
- Hydro-setting

Dry heat-setting is generally carried out on synthetic fabrics in pin or clip stenter machines equipped with one or more heat-setting sections in which a temperature of approximately 170–230°C, and can be performed under the following conditions:

Fiber	Temperature (°C)	Time (seconds)
Nylon 6	175-190	15-30
Nylon 6,6	190-215	15-30
Polyester	180-220	20-40
and its blends w	ith cotton	

Synthetic fibers are produced in factories under strict controls. These fibers, therefore, possess no or negligible inherent impurities. Some additives, however, are added to facilitate yarn and fabric production. These additives, as well as accidental impurities, if any, are to be removed by mild scouring. Polyamide and polyester fibers are generally adequately scoured using an alkyl polyoxyethylene sulfate and sodium carbonate.

With polyamides or nylons, nonionic synthetic detergents (1.5-2 g/l) with the addition of an alkali (0.5-1.5 g/l sodium carbonate or trisodium phosphate) are suitable. Anionic detergents like fatty alcohol sulfonates behave like acid dyes and are adsorbed by the fiber. Their presence on the fiber will slow down dyeing and may reduce the exhaustion of the dyebath. If the material is to be dyed with acid dyes, a nonionic detergent is to be used.

Synthetic fibers are mostly free from impurities and normally those can be dyed or printed without bleaching. Sodium chlorite has some bleaching effect on polyester and nylons – other bleaching agents are ineffective. It does not cause damage to the fiber and indeed, there is a slight increase in the degree of crystallization. The bleaching may be carried out with 1-5 g/l sodium chlorite for about 1 hour, best at $98-100^{\circ}$ C and practically at $90-95^{\circ}$ C, to minimize the evolution of intolerable chlorine dioxide.

2.11 FUTURE TRENDS

Chemical preparatory processes have no direct impact on the selling cost of the material. But the quality of final printed products largely depends on uniform, consistent and satisfactory preparation of the material before printing. The preparatory processes may be conducted batch-wise or in continuous manner. Batchwise processing is liable to variation of quality in respect to absorbency and other properties affecting dyeing and printing. Hence, more emphasis is given on continuous processing which assures consistent quality and very high production. However, continuous processes require strict control and vigilance. The chemical consumptions are also very high resulting in higher costs and higher pollution loads.

Textile pre-treatment involves desizing, scouring and bleaching processes. Each process requires a plethora of chemicals along with water, out of which the unexhausted chemicals are drained in the effluent stream. This makes preparatory processes largely unsustainable.

Sustainability of textile processing can be improved in several ways (Roy Choudhury, 2017) such as:

- 1) Substitution of unsustainable textile materials and chemicals by greener organic and biodegradable materials
- 2) Elimination or minimization of the use of toxic chemicals in production and packing
- 3) Minimization of the use of water and chemicals and recycling them
- 4) Minimization of the consumption of energy and fuel in production and transport
- 5) Minimization of waste and easy waste disposal
- 6) Strict maintenance of environmental management systems

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3 Dyes and Auxiliaries for Textile Printing

3.1 INTRODUCTION

A dye is a natural or synthetic coloring substance which is used for dyeing or printing of textile, paper, leather and other materials so that the color of the dyed or printed materials is not faded by washing, heat, light, or in other external conditions to which the material is commonly exposed. The dyes are generally applied from aqueous solution. The dyes can adhere to compatible surfaces by forming solution, covalent bond or in situ complexes with salts or metals, by physical adsorption or by mechanical retention (Zollinger, 1987).

The coloring matters used for coloration of textiles, plastics, paints, printing ink and other colorant preparations may be broadly classified into two categories: dyes and pigments. The dyes are soluble in water or made soluble during application and have affinity for one or more textile fibers under precise conditions of temperature and under the presence of specific auxiliaries. Dyes are largely used for dyeing of textile materials. They have limited use for coloration of plastic and similar materials in the form of additives in their solution or melts. The pigments are water insoluble. They are mostly used for textile printing, paints, printing inks and plastics. They can also be added in polymer melt or solution, or by applying on fiber surface with the help of an adhesive type substance called binder.

The pigments may be classified as follows:

- a) Inorganic pigments, such as various metallic oxides, hydroxides, chromates or other salts, which are mostly used for paints and similar color preparations.
- b) Organic pigments, such as insoluble azo or polycyclic keto compounds, which are mostly applied on textiles.
- c) Toners, sparingly water-soluble azo compounds precipitated as barium, calcium or magnesium salts.
- d) Lakes, precipitates of water-soluble dyes as metallic salts.
- e) Complex of basic dyes with selected inorganic acids such as phosphomolybdic acid, phosphotungstic acid and phosphomolybtungstic acid resulting in fluorescent pigments, which are used for printing of textiles and for making poster or signal colors.
- f) Metallic co-ordination complexes of organic compounds (e.g., copper phthalocyanine).

Many thousands of dyes are developed for coloration of a great number of textiles and other materials, and the color of such materials must withstand extremely varied external conditions. The manufacturers produce newer dyes as well as discard older dyes frequently. The dyes are, therefore, to be classified into different groups for systematic application and recording. The classification may be on the basis of the chemical groups present in them or most popularly on the basis of their methods of application, such as direct, acid, basic, vat, disperse and so on. A particular dye class may be suitable for one or more fiber type.

Dyes used for textile materials must possess the following four principal properties (Giles, 1974):

- 1) Intense color.
- 2) Solubility in water, either permanently or temporarily during dyeing.
- 3) Affinity or substantivity towards textile fibers so that they are absorbed and retained by them. Reactivity of certain dyes with fibers assures firm retention.
- 4) Adequate fastness ability to withstand the treatments which the textile materials undergo in manufacturing processes and in normal use.

3.2 CHEMICAL CLASSIFICATION OF COLORANTS

The organic colorants may be broadly classified into three groups (Nassau, 1983). Benzenoids are the most important group among synthetic colorants. These include various aromatic compounds – in textiles, the most important chromophores are:

- 1) Azobenzene (Figure 3.1(a))
- 2) Triphenylmethane (Figure 3.1(b)) and
- 3) Anthraquinone (Figure 3.1(c))

Benzenoids are also occasionally accompanied by thio (>C=S), nitroso (-N=O) and many other groups.

Versatile azo groups (-N=N-) are not available in nature. Azo groups incorporated in benzenoids form the basis of majority of synthetic dyes. Approximately 70% of all dyes (belonging to various dye-classes) used in textile industries are azo dyes.

Magenta and other triphenylmethane dyes were among the earliest synthetic coloring matters and they still remain a large and important group. Dyes of the triarylmethane class are usually red, violet, blue or green dyes. These are characterized by high tectorial power and brilliant hue but generally possess only light to moderate fastness.

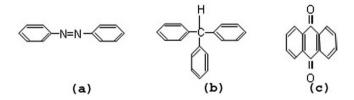


FIGURE 3.1 Three classes of organic colorants: (a) azobenzene, (b) triphenylmethane and (c) anthraquinone.

Anthraquinone dyes have important properties of chemical stability, light fastness and brightness, which are difficult to attain with other structures. However, anthraquinone dyes are at present on the decline, not due to any shortcoming of these compounds as dyes, but chiefly because their chemical synthesis is expensive. The process of anthraquinone production is costly from a waste disposal point of view; the waste products include strong acid, chromium, vanadium and mercuric salts, plus a variety of ill-defined organic and inorganic impurities, all of which have to be safely disposed of without contaminating the environment.

Dyes are classified in two ways based on:

- 1) Chemical constitution
- 2) Dyeing properties

There is little correlation between the two methods. The members constitutionally classified as azo dyes are found amongst several of the classes based on application. The practical dyer will be concerned only with the classification according to methods of application. The chemical classes are more important for dye makers and researchers.

3.2.1 CLASSIFICATION ACCORDING TO THE CHEMICAL CONSTITUTION

Globally, thousands of dyes are being produced by various dyestuff manufacturers. The industry is never static; new products are continually being introduced and established ones are occasionally withdrawn. The situation becomes complicated with frequent changes of the names of the products. These difficulties were felt long back, and the need for a systematic classification and recording resulted in a system called the color index developed by the Society of Dyers and Colorists, UK in 1924, and supplemented in 1928. In 1945, the American Association of Textile Chemists and Colorists (AATCC) collaborated and the publication is now being jointly published in eight volumes (SDC and AATCC, 1982). The first four are original volumes, while the others are revisions and supplements.

Volumes 1 and 2 contain detailed classification of dyes and pigments according to usage, while volume 3 shows classification according to chemical constitution. Volume 4 contains, among other things, commercial names of dyes and pigments and their respective C.I. (Color Index) designations. Two numbers, namely C.I. generic number and C.I. constitution number, are allotted for each dye. For example, the C.I. designations of two dyes may be C.I. Basic Violet 7 (48020) and C.I. Disperse Blue 3 (61505). While the first portion is the generic number, the bracketed portion is the constitution number. The generic name consists of dye class according to usage (e.g., Direct, Acid, Basic, etc.), hue name (whether yellow, orange, red, violet, blue, green, brown or black shade imparted by the dye on the substrate, additionally white colored pigment), and unique number for each dye of a particular chemical structure. The dyes with different chemical structures of a particular usage class of a particular hue are allotted consecutive numbers. C.I. constitution number is based on chemical structure of the colorant. A range of numbers is reserved for each chemical class (e.g., for monoazo dyes C.I. constitution number 11,000–19,999 and for disazo dyes

20,000–29,999) and a number is allotted for the dyes of a particular chemical constitution. A dye may belong to a number of usage class; a vat dye may also be used as disperse dye and may be included in both usage classes.

Volume 1 of the Color Index shows details of dyes under usage dye classes, namely acid, mordant, basic, disperse, natural dyes and pigments, food and leather; while volume 2 shows details of dyes under other usage dye classes, namely direct, sulfur, vat (including solubilized), ingrain dyes, azoic diazo and coupling components, oxidation bases, pigment, solvent dyes, fluorescent brightening agents and developers. The supplement volumes include revision, extension of above usage dye classes as well as details of reactive dyes.

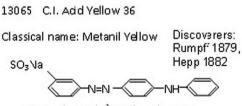
Volumes 1 and 2 provide the following information on dyes of each C.I. generic number:

- · Names of the manufacturers and commercial names
- Application methods on various textile fibers or other substrates and after-treatments
- · Fastness properties
- Dischargeability
- Solubility
- · Effect of metals
- Textile usage
- Non-textile usage

Volume 3 shows chemical aspects of dyes of each C.I. constitution number, namely chemical structure, name of the discoverers, brief manufacturing process and so on. For example, the details under C.I. Constitution Number 13065 are shown below in Figure 3.2.

3.2.2 CLASSIFICATION ACCORDING TO THE METHOD OF APPLICATION

The dyers and printers are not much aware of the chemical constitution of dyes. They are more concerned about the application method(s) in dyeing and printing and the resistance of applied dyes to various external agents like washing, rubbing, light and so on. Some dyes are suitable for application in both dyeing and printing, while others may not be suitable for application in dyeing or printing.



Metanilic acid → Diphenylamine

FIGURE 3.2 An extract from the Color Index (SDC & AATCC).

The dyes may be classified according to the methods of application or dyers' point of view as follows (Roy Choudhury, 1996).

3.2.2.1 Direct Dyes

Direct dyes or substantive dyes have direct substantivity to cellulosic materials. These are sodium sulfonate derivatives of organic aromatic compounds, and invariably contain one or more azo groups. These dyes can also be applied on protein fibers, namely wool and silk, but are not commonly used because the rate of dye exhaustion is very slow. These dyes are not suitable for printing because of poor wash fastness and severe staining on ground (non-printed) portions of the fabric.

3.2.2.2 Acid Dyes (Including Metal-Complex Acid Dyes)

Acid dyes are mainly used for protein and polyamide fibers. These dyes have no affinity for cellulosic fibers. The term acid dye indicates that they are derived from organic acids and not because they are acidic in nature. These are sodium salts of sulfonic acid derivatives – occasionally carboxylic derivatives of organic aromatic compounds. They mostly contain one or more azo groups. Chemically they are very similar to direct dyes. While the direct dyes are coplaner and bigger in molecular size, the acid dyes may or may not be coplaner and some of them are of low molecular size and consequently provide lower wash-fastness. They have more solubilizing groups than the direct dyes (Roy Choudhury, 1996).

Acid dyes are typically used to dye natural protein (wool and silk), synthetic polyamide (nylon) and to a small extent acrylics and blends of these fibers. The generic term "acid dyes" includes several individual dye classes. As per the Color Index definition, metal complex dyes are also included in the category of acid dyes. Chrome dyes are also considered acid dyes.

If these dyes have two hydroxyl groups or one hydroxyl and one carboxylic group in o-o' position with respect to azo group, then dyes can form complexes with multivalent metal atoms like chromium, thereby improving wash-fastness (Roy Choudhury, 1996).

On the basis of chemical composition, acid dyes are of three types, namely:

- 1) Simple non-metal complex acid dyes
- 2) Chrome dyes, natural and synthetic, which can form metal complex with chromium and other metal salts applied before, during or after dyeing. They had limited use in wool dyeing in the past and now obsolete.
- 3) Pre-metallized or metal-complex dyes

The complex may be formed during dye manufacture, commonly known as pre-metallized dyes. These dyes may be of two types: 1:1 or 1:2, representing the type of complex, having one and two dye molecules per metal atom respectively. The complex may also be formed during dyeing. These dyes are suitable for both dyeing and printing.

On the basis of dyeing properties, acid dyes used for wool dyeing are arbitrarily classified into four groups, namely:

- 1) Level-dyeing or equalizing acid dyes
- 2) Fast acid, half-milling or perspiration-fast dyes

- 3) Acid milling dyes
- 4) Super-milling dyes.

This list is in order of increasing fastness and decreasing levelness, although there may be overlap between adjacent categories.

The leveling acid dyes are most often used for pale to medium-depth shades, where a high degree of fastness is not required. There are two broad subdivisions of equalizing acid dyes: monosulfonated and disulfonated. There are also a few tri- and tetra-sulfonated equalizing acid dyes. The monosulfonated dyes have relative molecular mass (r.m.m.) in the range of 300–500. These dyes migrate well and give good coverage of dyeability differences within the fiber. Disulphonated dyes have slightly higher r.m.m. (400–600) values. They are less capable of covering differences in dyeability than monosulfonated. The chemical structures of a monosulfonated (C.I. Acid Blue 40) and a disulfonated equalizing acid dye (C.I. Acid Blue 45) are shown in Figure 3.3(a) and (b), respectively.

Acid milling dyes are so named because they have some degree of fastness to milling processes, which indicates a higher level of wet fastness than other acid dyes. Even within the class, there is a further subdivision, the so-called supermilling acid dyes. These dyes have still higher wet fastness properties attributed to longer alkyl side chains. This group comprises dyes of high anion affinity requiring minimum amount of acid. They are commonly known as neutral dyeing acid dyes.

The milling acid dyes are sold under various trade names, such as Supranol (DyStar), Polar and Irganol (Ciba), Sandolan N/Milling N and Lanasyn Brilliant (Clariant) dyes. Some important milling acid dyes are:

C.I. Acid Yellow 79, Reds 111 and 134, Violet 48, Blues 80 and 138, Green 25.C.I. Acid Red 86 (Figure 3.4) is a disulphonated milling acid dye having alkaline milling fastness of 3–4.

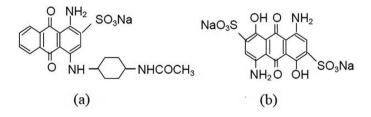


FIGURE 3.3 (a) C.I. Acid Blue 40; (b) C.I. Acid Blue 45.

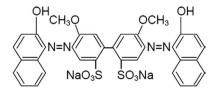


FIGURE 3.4 C.I. Acid Red 86.

As the name implies, in metal-complex dyes one metal atom, commonly chromium, is complexed with either one (1:1) or two (1:2) molecules of a typically monoazo dye that contains groups (such as hydroxyl, carboxyl or amino) that are capable of coordinating with the metal. In the Color Index, metal-complex dyes are included in the acid dye class, though they have distinct differences from nonmetallized acid dyes. The 1:1 and 1:2 metal-complex dyes resemble leveling and milling nonmetallized acid dyes, respectively, in terms of general application conditions. The increased popularity of the dyes, which has occurred mainly at the expense of mordant dyes, can be attributed to health and effluent hazards associated with the use of chromium in mordant dyeing and the comparatively simple application procedures of metal-complex dyes. The 1:1 metalcomplex dyes have been gradually replaced by 1:2 metal-complex dyes due to superior all-round fastness properties and less damaging application conditions of the latter.

Metal-complex dyes depend on formation of co-ordinate links between the dye and metal. The co-ordinate link occurs with atoms such as oxygen and nitrogen having a lone pair of electrons in the outer shell, which can be shared by another atom. In covalent bond, on the other hand, each atom contributes one electron. Thus, with two atoms A and B, the two types of bond formations may be shown as follows (Equations 3.1 and 3.2):

Covalent bond, $A \cdot + \cdot B \rightarrow A$: B	(Equation 3.1)
Coordinate bond, $A: + B \rightarrow A: B$	(Equation 3.2)

The final result is the same, but the mode of formation is different.

Depending on the absence and presence of sulfonic groups, the 1:2 complexes are of the following two types respectively:

- 1) Weakly polar 1:2 complexes
- 2) Strongly polar 1:2 complexes

These complexes are salts of strong acids and they dissociate completely in dilute solution and acquire negative charge $(D - Na^{+})$. The free acids have very low aqueous solubility, whilst the salts show considerable aggregation in solution at room temperature and low solubility in presence of inorganic salts.

There are typically three types of 1:2 metal-complex dyes:

- Unsulfonated
- Monosulfonated
- Disulfonated

The disulfonated type is most soluble and has greater pH dependence. This means that they have a low neutral affinity and require more acid to exhaust. They also exhibit the lowest cross-staining in domestic washing because any desorbed dye has only limited affinity for adjacent fibers at the pH condition maintained by domestic detergent (Parton, 1997).

In the most popular first type, sulfonic solubilizing groups are absent, since their presence leads to dyes that are unsatisfactory from the point of view of leveling and skitteriness. Instead, nonionic groups are incorporated in the molecule to improve the aqueous solubility and decrease the rate of dyeing. These groups, in fact, distinguish the ranges offered by different manufacturers. The most popular are methylsulfonyl (-SO₂CH₃) and sulfamoyl (-SO₂NH₂) groups; their hydrophilic character being due to hydrogen bonding with water. Both have similar solubilizing properties, but the latter exhaust more slowly. Other solubilizing groups reported are mono- or dialkyl-substituted sulfonamide, ethylsulfone and cyclic sulfone. The typical examples are C.I. Acid Violet 78 (Figure 3.5(a)) and C.I. Acid Black 60 (Figure 3.5(b)).

Most of the commercially available acid dyes are based on azo, anthraquinone or triphenyl methane. Although there are other acid dyes like azine, xanthane, nitro, indigoid, quinoline and Carbolan dyes, these dyes are of limited commercial value. The most popular chromophore in acid dyes is the azo group. Following the discovery of the diazo reaction by Griess in 1858, both monoazo and bisazo dyes were produced. The first azo acid dye was formed by diazotizing sulphanilic acid and coupling with β -naphthol. Molecular weights of acid dyes range from 200 to 900. Most of them have one or two -SO₃Na groups which are water-soluble and capable of bonding with fibers having cationic sites. They give a wide range of bright colors on textiles, especially when monoazo and anthraquinone structures are used. Some of the anthraquinone greens and violets are more brilliant than azo dyes. Acid dyes based on the triphenylmethane structure and its heterocyclic forms are not very popular, though they are known for their brilliancy. Carbolan dyes have a high fastness to milling treatment and washing, but are obsolete as they create a lot of foam. Azine dyes get reduced by the action of a reducing agent but their reduced form is soon oxidized by air (Chattopadhyay, 2011).

Acid dyes are characterized by clear and vivid colors and are used for printing fabrics such as those used for swimwear, high-end fashion dresses and accessories. Depending on the selection of dye, the light fastness rating can become problematic for certain applications.

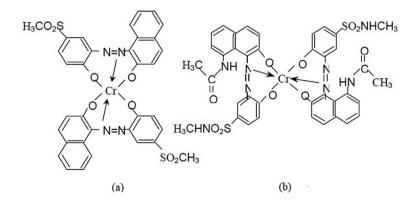


FIGURE 3.5 (a) C.I. Acid Violet 78; (b) C.I. Acid Black 60.

In the printing process, acid dye molecules need to establish ionic bonds with the fibers. Therefore, the print paste typically uses weak acid solutions, such as ammonium sulfate, ammonium tartrate or acetic acid, as a fixing agent to create the negatively charged dye site. The acid is mixed in the print paste together with a thickening agent made from guar gum, locust-bean, crystal gum and so on. The fixation processes are similar to those used for reactive dyes. After steaming with saturated steam, the printed fabrics are washed to remove excess dyes and thickening paste (Ujiie, 2015).

3.2.2.3 Basic or Cationic Dyes

The basic or cationic dyes are historically interesting, as the first synthetic dye, Perkin's Mauve, belongs to this class. Basic dyes like Magenta and Malachite Green are also amongst the earliest synthetic dyes. The basic dyes are so-named because they are derived from organic bases. They are also called cationic dyes as they ionize in water producing colored cations. They are capable of salt-formation as shown in Equation 3.3.

HO-R-
$$\sim$$
-NH₂ + HCI \rightarrow R= \sim =NH₂CI + H₂O

They are usually hydrochlorides or other salts of organic bases. Basic dyes are also called cationic dyes, because in solution the basic dye molecule ionizes causing its colored component to become a cation or positively charged radical. They can be applied to protein fibers directly. However, the use of basic dyes on wool or silk has declined significantly due to their poor light fastness.

The invention of acrylic fibers demanded a new class of dyes, as available dyes were unsuitable for this fiber. The modified basic dyes called pendant cationic dyes were developed by separating ionic charges away from the chromophore. These modified dyes have superior light fastness and they are largely used for both dyeing and printing of acrylic materials.

The outstanding characteristics of basic dyes are the brilliance and intensity of color. The clarity of hue obtained with some basic dyes cannot be matched with any other dye-class. Acid magenta, which is obtained by sulfonation of basic magenta, requires double the quantity of the latter to produce a full shade on wool. The basic dyes are not easily soluble in water and may form a sticky mass, which is difficult to bring into solution. Some of them are decomposed by boiling water and should be applied at temperatures of 60 to 65°C. They are readily soluble in alcohol or methylated spirit. With alkali, basic dyes are decomposed into colorless bases. Hard water or alkaline water should be avoided.

The conventional basic dyes, mainly because of poor light fastness, have virtually fallen into disuse on natural fibers. With the invention of polyacrylonitrile fibers, difficulty in dyeing was encountered due to very compact structure of the fiber. Fortunately, a number of modified varieties of the fiber were commercialized on which cationic dyes are substantive. Moreover, the basic dyes showed much better fastness on these hydrophobic fibers as compared to those on natural wool and silk. The photo-fading of dyes is faster in the presence of water and oxygen, which cannot gain access in the hydrophobic polyacrylonitrile fibers.

The light fastness of conventional basic dyes is better on acrylics than that on wool. However, further modifications in dye structure led to modified basic dyes having excellent light fastness. They belong to three classes:

- 1) Cationic dyes containing a pendent cation with a non-resonating positive charge as in C.I. Basic Blue 49 and C.I. Basic Red 18 (Figure 3.6(a)).
- 2) Cationic dyes with a delocalized positive charge as in C.I. Basic Violet 7 (Figure 3.6(b)) and C.I. Basic Blue 5.
- 3) Cationic dyes with a heterocyclic ring containing a quaternary nitrogen atom, which does not form an integral part of chromogen as in Figure 3.6(c).

3.2.2.4 Mordant Dyes

This group includes many natural and synthetic dyes, the latter usually obtained from anthracene. They have no natural affinity for textile fibers but are applied to cellulosic or protein fibers, which have been mordanted previously or during dyeing with a metallic salt or natural mordant. The acid mordant dyes are a special class of dyes applied to wool or polyamide fibers as acid dyes, and subsequently mordanted to improve wash-fastness. After successful production of premetallized or metalcomplex dyes, the used of synthetic mordant has been discontinued.

A sub-group of mordant dyes, natural dye is the oldest class of dyes being used by human beings since ancient times. These dyes are obtained from various natural sources like different portions of plants (leaves, roots and skins), insects and more. These can be applied with the help of a natural mordant along with several metallic salts. The natural dyes were slowly being replaced by synthetic dyes due to poor supply, poor color build up, poor fastness properties and poor reproducibility of the

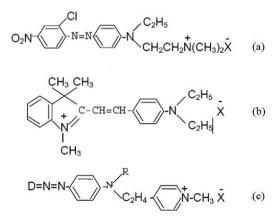


FIGURE 3.6 (a) C.I. Basic Red 18; (b) C.I. Basic Violet 7; (c) cationic dyes with a heterocyclic ring.

former. With worldwide consciousness about pollution and the polluting nature of many synthetic dyes, the use of natural dyes has been revived again in recent years.

Fustic, safflower, madder, and various other types of natural sources have been known to be used to dye various natural fibers like wool, cotton and silk since humans first started coloring their clothes. By the mid-19th century, there was a vast range of colors that could be obtained. Gradually these dyes were replaced by synthetic dyes because of their limited shades and poor fastness properties, and lack of information regarding the methods to improve the fastness and color value. On the other hand, synthetic dyes were cheaper, readily available, easy to apply, and had a wide array of colors as well as better fastness properties.

Two hundred or more years ago, the production of crops such as indigo (and woad), weld and madder was based on labor-intensive agronomy, and time-consuming downstream manufacturing processes for preparing the dye were necessary. The trade of natural dyes began to decline in the second half of the 19th century, and now, more than 100 years later, many of the dyes that were once commonplace are little known and difficult to obtain. Many of the plants have not been cultivated for their dyes on any commercial scale for the last century. Indeed, the original cultivation varieties of plants used for producing natural colors in Holland had been lost; a new variety of similar characteristics has been recently developed. Cochineal cultivation, which was discontinued in Central America, has survived in Peru and the Canary Islands. Despite this success, the reestablishment of some of the old sources of these dyes is not possible and many old dyes are rarely seen. Newer sources are gradually becoming available. Biotechnological routes, like use of microorganisms and cell cultures, are being utilized for manufacture of natural dyes like indigo, alizarin, and more. Although such dyes as madder, cochineal, fustic, brazilwood, sanders wood, cutch, indigo, logwood and weld are obtainable, they are relatively expensive and retailed in small amounts (Roy Choudhury, 1996).

3.2.2.5 Azoic Dyes

Azo dyes are readymade dyes, while azoic colors are not readymade – those are formed inside the textile materials by interaction of some simple chemicals. Insoluble azo pigments are formed inside the textile materials by treating textile material with solubilized aromatic hydroxy compounds (naphthols) followed by development (or coupling) with diazotized aromatic bases (azoic fast colors). They are used to dye cheap shades of high wet fastness on cellulosic materials. They can be applied on protein fibers, but their suitability is doubtful, especially due to high alkaline conditions maintained during dyeing. The azoic color dyeing is a tedious multistep process. The fabric is first soaked in alkaline solution of naphthols; azoic fast color are diazotized (treatment with sodium nitrite and hydrochloric acid) separately; and coupling is done by soaking napholated fabric in diazotized solution. This is widely used for dyeing in hand dyeing or cottage dyeing. In Batik printing, the fabric is first treated with wax or any other resisting agent as per some defined design or randomly keeping portions accessible to dyeing liquid. The treated fabric is soaked successively in naphthol and diazo solution when the accessible portions get colored and the resisted portion remains white.

Diazotization is troublesome and stock solutions cannot be stored because of their lack of stability. In printing, the printing paste is prepared in bulk in order to keep consistency, and is stored for quite some time. The diazotized base decomposes during storage. As a result, there has been a great demand for stabilized diazonium salts, called fast color salts, which can be readily dissolved in water (preferably containing a nonionic dispersant and acetic acid or formic acid for selected salts) and would immediately be ready for use. The various methods of preparation of such salts are:

Two stabilized azoic colors were in use for printing cheap cotton materials – those are basically mixture of naphthol and stabilized diazo compounds. On acidification, the diazo compounds get activated and react with naphthol to form insoluble pigment inside the fiber.

(Roy Choudhury, 1996)

3.2.2.6 Antidiazotates

Diazonium salt: when diazo compounds react with excess alkali (mainly sodium hydroxide), an alkali syndiazotate forms. It rapidly undergoes transformation into antidiazotate (Equation 3.4).

R-N≡NCI →	+ <i>R</i> · <i>N</i> ≡N·OH	\rightarrow	R-N	→ R-N	
	Diazonium	Ν	ll NaO-N	ll N-C	Na
	hydroxide	Sy	ndiazotate	Antidiazo	otate

The latter is more stable and can be isolated in a dry form suitable for storage.

On acidification, the antidiazotate forms the diazonium salt. The fabric may be padded with a mixture of a naphthol solution and an antidiazotate, and on acidification coupling takes place. This is not useful in dyeing, but is popular in printing, and the mixture is marketed as Rapid Fast dyes.

3.2.2.7 Diazoamino Compounds

Diazonium salts react with selected amino compounds to form inactive compounds. Examples of such amino compounds include:

- Sarcosine (CH₂·NH·CH₂·COOH)
- N-methyltaurine (CH_3 ·NH· CH_2 · CH_2 · SO_3H)

The diazo compound regenerates on acidification. Rapidogen dyes are mixtures of a naphthol and a fast base stabilized with such screening agent called stabilizer, and are most widely used in printing.

3.2.2.8 Sulfur Dyes

These dyes are complex organic compounds containing sulfur. They are used to dye cheap shades of high wet fastness on cellulosic materials. The dyes, however, lack brightness and the shade range is limited. They are not used in printing.

3.2.2.9 Vat Dyes

As a dye class, vat dyes are characterized by the highest all round fastness properties; however, these dyes are quite expensive. Their applications in dyeing and printing are limited due to high costs and very complicated application methods.

Some of the trade names of vat dyes are Indanthren (BASF, Bayer, Hoechst), Caledon (ICI), Cibanone (Ciba), Sandothrene (Clariant, at present Enchroma), Navinon (IDI, India) and Novatic (ATIC, India). Vat dyes are divided into two main classes:

- Indigoid vat dyes, which are usually derivatives of indigotin (Figure 3.7(a), where R = NH) or thioindigo (Figure 3.7(a), where R = S)
- Anthraquinoid (Figure 3.7(b)) vat dyes derived from anthraquinone

The anthraquinoid group exhibits superior fastness properties – distinguished by excellent fastness to light – and is the most widely used group.

The derivatives of anthraquinone are more versatile and are made of higher condensed aromatic ring systems with a closed system of conjugated double bonds. The structural elements of several typical important classes of vat dyes are indanthrones, flavanthrones, pyranthrones, dibenzanthrones, isodibenzanthrones, benzanthrone acridones, anthraquinone carbazoles, anthraquinone oxazoles and so on.

The vat dyes are insoluble in water and have no affinity for textile fiber so long as they remain in insoluble state. They all contain two or more keto groups (>CO) which, when treated with reducing agents, combine with hydrogen to form leuco compounds (\equiv C·OH). These secondary alcohols do not dissolve in water but form soluble derivatives (enolate) in the presence of alkalis. Vat dyes are converted into water-soluble leuco compounds by the action of caustic soda and sodium hydrosulfite. These solubilized leuco compounds have a high affinity for cellulosic materials (Equation 3.5).

$$(>C=O)_2 + Na_2S_2O_4 + 4NaOH \rightarrow (\equiv C-ONa)_2 + Na_2SO_3 + 2H_2O$$
 (Equation 3.5)

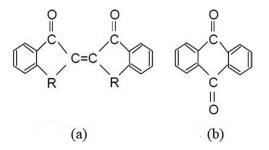
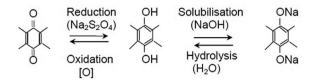


FIGURE 3.7 (a) Indigoid and (b) anthraquinoid vat dyes

After completion of dyeing, they are converted into insoluble form by oxidation. On exposure to air, the sodium compound is converted to the original insoluble pigment (Equation 3.6).

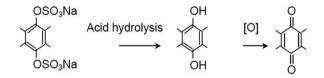


Excellent wash-fast printing is possible with vat dyes, but the printing method is complicated and very difficult to control. They are no longer used in textile printing.

3.2.2.10 Solubilized Vat Dyes

Solubilized vat dye is a vat dye in the form of a soluble sodium salt of a sulfuric acid monoester of its leuco compound. These are water-soluble and can be applied directly on cellulosic and protein fibers at low temperature. Chemically they are sulfuric esters of vat dyes and are converted into parent vat dyes by oxidation after completion of dyeing or printing. In earlier days, it was difficult to get wash-fast prints on cellulosic materials. Vat dyes were known for high wash-fastness. However, it is difficult to get vat-printed materials of consistent color. Hence, a soluble form of vat dyes was developed. The modified form, solubilized vat, was very popular for printing of wash-fast bright shades on cotton. But the dyes were very costly, and the shades were limited. With the introduction of reactive dyes, these dyes lost their importance.

When the textile materials dyed or printed with solubilized vat dyes is passed through a solution containing sulfuric acid and sodium nitrite or potassium dichromate at around 50–70°C, the dye is hydrolyzed and oxidized to original vat dye, which, being insoluble in water, is immediately precipitated inside the fiber (Equation 3.7).



3.2.2.11 Reactive Dyes

The most recent class of dye contains reactive groups, which react with hydroxyl or amino groups of textile fibers forming covalent bonds. These dyes are fast so long as the covalent bonds are intact. As the wash fastness of these dyes does not depend on the molecular size of the dye, dyes of low molecular weight can be used which usually provide brighter shades. These dyes were originally developed for cellulosic materials, but special reactive dyes for wool and nylon are also available.

Reactive dyes comprise of a chromophore and a reactive group. They differ fundamentally from other dye-classes in the fact they chemically react with the textile fiber forming covalent bonds. The conventional dyes, on the other hand, owe their wet fastness to physical association, non-specific chemical bonding (e.g., hydrogen bond) or insolubilization inside the fiber.

The different structural components of a reactive dye are:

- 1) A chromogen responsible for the color.
- 2) Solubilizing groups responsible for the solubility of the dye.
- 3) A reactive group, which forms covalent bond with the substrate.
- 4) An optional bridging link between the reactive group and the chromophoric system.

The variation in chromophore is necessary for the following reasons:

- 1) In order to provide various shades to cover the maximum possible color gamut.
- 2) The reactivity of the dye is affected by the chromophore.
- 3) The chromophore affects substantivity and diffusion coefficient, which in turn determines fixation efficiency and washing-off properties of reactive dyes.

Giles (1974) classified reactive groups into five categories depending on the mechanism of reaction with the substrate, such as:

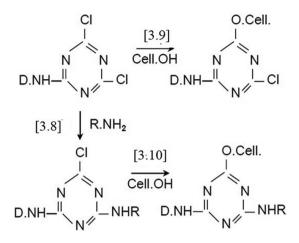
- a) Nucleophilic substitution.
- b) Nucleophilic addition.
- c) Multiple addition-elimination reactions.
- d) Fixation under acidic conditions.
- e) Dyes forming disulfide bonds.

More recently, other classes of reactive dyes have been developed, which provide much higher degrees of fixation than the conventional reactive dyes. These high fixation reactive dyes contain multiple (mostly two) reactive groups attached to each dye molecules. The reactive groups may be identical or different, and accordingly the dyes are known as homo-functional or hetero-functional reactive dyes.

3.2.2.12 Nucleophile Substitution

The most important member of this group is chlorotriazines, obtained by reaction of dye chromogens having NH_2 groups with cyanuric chloride. When cyanuric chloride is reacted with a dye base (D.NH₂), highly reactive DCT dyes, Procion MX (ICI) and Basilen M (BASF) dyes are obtained. When it is reacted with a colorless amine (Equation 3.8), less reactive monochlorotriazine (MCT) dyes – Cibacron and Procion H, Cibacron Pront (-OR instead of NHR) – are obtained. The usual procedure of making MCT dyes is to react cyanuric chloride first with colorless amine before reacting with dye base. Under favorable conditions, nucleophilic groups of the substrate (e.g., –OH groups of cellulose or –NH₂ groups of protein fibers) react with the chlorine atoms on the heterocyclic ring by nucleophilic additionelimination or substitution mechanisms. The functional group of the textile fiber is first added to the dye molecule and then an ion (usually chlorine) is eliminated. The overall reactions for dichlorotriazine (DCT) and monochlorotriazine (MCT)

dyes with cellulose are shown in Equation 3.9 and Equation 3.10, respectively (Roy Choudhury, 1996).



The reaction (Equation 3.9) occurs at around 20°C when one or both chlorine atoms of DCT dyes may be replaced by cellulose. The reaction (Equation 3.10) of MCT dyes occurs at high temperature, around 70°C. The by-product of both the reactions is hydrochloric acid (HCl). Hence, the rate of forward reactions can be increased by addition of alkali. In other words, the reactions are base-catalyzed. A portion, however, reacts with water in the dyebath and is deactivated. This hydrolyzed dye, which is simply the original reactive dye with its labile atom or group replaced by hydroxyl, usually has very similar diffusion and adsorption properties compared to the original. This hydrolyzed or loose dye must be removed by a final washing process in order to produce dyed material of high wet fastness.

The other members of this group are:

- 2,4,5 trihalogen-pyrimidine, e.g., Reactone (Geigy), Drimerene (Clariant) (Figure 3.8(a)), Drimarene K, Drimalan F (Clariant), Verofix, Levafix E-A (Bayer) (Figure 3.8 (b)).
- 2) 2-methylsulphonyl-4-methyl-5-chloro-pyrimidine, e.g., Levafix P (Bayer) (Figure 3.8 (c)).
- 3) 3,6-dichloropyrazine, e.g., Solidazol (CFM) (Figure 3.9(a)).
- 4) 2,3-dichloroquinoxaline, e.g., Levafix E (Bayer), Cavalite (Figure 3.9(b)).
- 5) 2-chlorobenzthiazole, e.g., Reatex (Fran) (Figure 3.10(a)).
- 6) 4,5-dichloropyridazone, e.g., Primazin P (BASF) (Figure 3.10(b)).

3.2.2.13 Nucleophilic Addition

Reactive dyes, based upon chlorotriazines or chloropyrimidines, are acylating dyes that become attached to fibers by the process of nucleophilic substitution, thus forming compounds with cellulose possessing some of the properties of esters (R-CH – O.alkyl). Another type of reactive dyes is conceivable, with which the dye-fiber compound is formed by nucleophilic addition rather than substitution, and has the

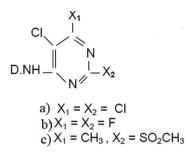
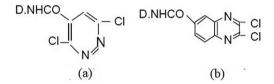


FIGURE 3.8 (2,4,5) trihalogen-pyrimidine





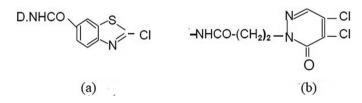


FIGURE 3.10 (a) Reatex; (b) Primazin P

properties of an ether (R.O=CO.alkyl) rather than those of an ester. An ether type of linkage is formed between azo compound and cellulose, either by direct reaction of the sulfuric ester or by desaturation and subsequent addition. However, in the absence of a suitable activating group, such reactions proceed far too slowly to be of any practical use. Various electron-attracting groups have been used to provide such activation, one of the most common being sulfonyl. By interposing such a group between a chromophore and the olefinic group, as in vinyl sulfone (VS) dyes, the double bond becomes sufficiently polarized for nucleophilic addition. The reaction proceeds readily under mild alkaline conditions with alcohols (R.OH) including cellulose; the group –OR becomes attached to the β -carbon atom. It is not necessary that the vinylsulphonyl system is present as such in the dye molecule. The activation, which facilitates addition of cellulose, also enables the corresponding β -sulfatoethylsulfonyl or similar precursor to undergo desaturation very easily under mild alkaline conditions in the dyebath (Equation 3.11), although it is not absolutely certain that this mechanism is involved in dyeing. $DSO_{2}CH_{2}CH_{2} \cdot O \cdot SO_{3}Na \rightarrow DSO_{2} \cdot CH=CH_{2} \rightarrow DSO_{2}CH_{2}CH_{2} \cdot O \cdot Cell.$ (Equation 3.11)

In a nucleophilic substitution reaction, the functional group participates in the addition as well as in the elimination step, while in Equation 3.4, the first β -elimination step is independent of the substrate. Therefore, with the latter class of dyes, it is possible to optimize the rate of formation of the true reactive compound at constant dyebath pH by varying the concentration and type of buffer. This may be of particular significance in obtaining level dyeing. The degree of fixation also depends on the type and concentration of buffer.

The product of hydrolysis, a 2-hydroxyethylsulphone, is generally much less substantive than the reactive dye itself and can be easily washed off after dyeing.

Ever since the Remazol dyes were introduced in the 1950s, the dyeing of dischargeable ground for subsequent discharge printing has been a preferred outlet for them. Largely they have ousted the earlier favorites for this application, namely the direct dyes. No other range of reactive dyes offers such a wide choice of dischargeable dyes, which can be made colorless by the action of a reducing agent at high temperature.

Various reactive groups present in commercial reactive dyes, which undergo similar chemical addition reactions, are listed here.

Groups yielding vinyl sulfone can be represented as:

 $-SO_2CH_2^-CH_2^-X$ (3.16) X = $-OSO_3H$, Remazol and Remalan dyes (Hoechst) X = $-N(CH_3)CH_2_-CH_2_SO_3H$, Hostalan (Hoechst) dyes X = $-N(NH_3^+)CH_2_-CH_2_SO_3^-$, Remazolan (Hoechst) dyes

Groups yielding acrylamide groups can be represented as:

- NH-CO-CH₂-CH₂-X (3.17) X = -OSO₃H or X = -Cl, Primazin (BASF) dyes

Epoxy, its precursor 2-chloro-1-hydroxylethyl, aziridine and 2-chloro-ethyl-1amino groups present in Procinyl (ICI) dyes also undergo nucleophilic addition reactions.

Reactive dyes are primarily for dyeing and printing of cellulosic textile materials. The use of reactive dyes for wool, silk, nylon (special brands) is limited. More than 100 types of reactive groups were developed, but only about a dozen commercialized.

The most popular reactive dyes are:

- 1) Procion cold brand (M, MCT)
- 2) Procion hot brand (H/HE, DCT)
- 3) Remazol (vinyl sulphone or VS)

For textile printing, hot brand and Remazol types are popular because they possess:

- 1) Required reactivity to achieve levelness and reproducibility (balance between exhaustion and reaction);
- 2) Full range of shade for exhaust, padding and printing; and
- 3) Bond stability under normal use.

A comparison between triazine based (Procion) and vinyl sulphone based (Remazol) is shown in Table 3.1

3.2.2.14 Disperse Dyes

The Society of Dyers and Colourists (UK) defines disperse dye as a substantially water-insoluble dye having substantivity for one or more hydrophobic fibers such as cellulose acetate or polyester, and usually applied from fine aqueous dispersion.

Disperse dyes can, therefore, be applied to most of the synthetic fibers, namely acetate, acrylic, aramid, modacrylic, nylon, olefin, polyester, Saran (vinyl) and triacetate fibers. However, for polyester and acetate fibers, disperse dyes are really the only practical means of coloration.

All of these fibers are thermo-plastic; the fibers soften instead of decomposing or igniting when exposed to sufficient heat. Unless the material is heat-set, it will shrink and creases will form during hot aqueous treatments, such as dyeing or steaming/ heat treatment after printing. In order to make the material dimensionally stable, heat-setting may be carried out in a medium of hot air, steam or hot water. The materials are also to be scoured and bleached, if necessary.

Disperse dyes are sold under various brand names such as Dispersol (BASF, earlier ICI), Foron (Clariant), Palanil (BASF), Terasil (Ciba), Tulasteron (Atul), Navilene (IDI), Terenix (JDL) and more.

Because the bulk of the dye is in suspension during dyeing from aqueous media, transfer of dye into the fiber takes place from a very dilute aqueous solution of the

TABLE 3.1Comparison Between Triazine Type and Vinyl Sulfone Types of Reactive Dyes

Triazine type	Vinyl sulfone type
In reactive form more chance of	Reactive form generates with alkali, less chance of
hydrolysis	hydrolysis.
Maximum fixation up to 70%	Maximum fixation up to 95%
Less preferred in printing especially	More preferred in printing due to high fixation – less bleeding,
M-brand (less stable in paste)	ground staining
Requires severe washing after printing	Requires moderate washing
Non-dischargeable	Generally dischargeable
Less bright	Brighter
Unstable in acid	Unstable in alkali and alkaline detergent

dye, at least during the initial stage of dyeing. Such pockets containing dissolved dyes are continuously replenished by progressive dissolution of particles in suspension.

Due to their nonionic nature, disperse dyes are volatile and the dye-vapor is strongly adsorbed by hydrophobic fibers. This is the basis for thermosol (heat-fixation) dyeing and heat-transfer printing processes.

Disperse dyes are mainly used for acetate and polyester fibers. The dyes for secondary cellulose acetate are well established. For highly hydrophobic triacetate fiber, the molecular size of the dye is the limiting factor. Polyester fibers are dyed at high temperature. The dyed and printed polyester materials are often subjected to heat treatment. Hence, dyes of greater molecular size having good sublimation and light fastness and give good color-yield on polyester.

Some characteristics of disperse dyes are as follows (Roy Choudhury, 1996):

- 1) Disperse dyes are low molecular weight substances, mostly derived from azo, anthraquinone and diphenylamine.
- 2) Disperse dyes are crystalline materials of high melting point (>150°C). They are milled with dispersing agents to produce stable dispersions in dyebath, 0.5 to 2μ in particle size. As they are applied in the form of very fine aqueous dispersions, both particle size and dispersion stability are extremely important. Ideally, disperse dyes should disperse extremely rapidly when added to water and give a stable dispersion of very fine and uniform particle sizes. The dispersion should be stable during dyeing and printing in the presence of auxiliaries, including carriers and leveling agents. Some aggregation of dye may precipitate on the fiber surface in the presence of surface-active agents and at temperatures higher than 100°C, which are to be removed after dyeing and printing by reduction clearing.
- Disperse dyes are marketed in both powder and liquid forms. The powder brand contains considerable amount of dispersing agent – a naphthalene sulfonic acid-formaldehyde condensate – and possibly a wetting agent.
- 4) The conventional disperse dyes give insufficient color yield by superheated steam fixation method and also have poor compatibility with synthetic thickeners in printing due the presence of anionic dispersing agents or electrolytes. Nonionic disperse dyes have now been developed which are especially recommended for printing and continuous dyeing, e.g., Kayalon Polyester N paste (Nippon Kayaku). These dyes are dispersed with nonionic dispersing agents.
- 5) The disperse dyes are nonionic in nature devoid of strong solubilizing groups like sulfonic or carboxyl groups, although weak solubilizing groups like aromatic or aliphatic –NH₂, -NHR and –OH groups may be present.
- 6) These dyes have relatively low solubility (at least 0.1 mg/l) in aqueous medium under dyeing conditions. Aqueous solubility at 80°C ranges from 0.2 to 100 mg/l. As solubility increases logarithmically with temperature, a considerable amount of dye may be in solution at 130°C. On cooling, the dye may crystallize as large particles.

- The saturation level of pure disperse dyes in the fiber is relatively high (30–200 mg per g of fiber).
- 8) Due to the absence of ionizable groups, disperse dyes have the tendency to sublime without decomposition. Consequently, color of disperse-dyed fabric may fade while ironing. It is therefore necessary to test sublimation fastness or fastness to dry heat of the dye. The fastness rating is useful for deciding by which method the dye can be applied most successfully and the performance of the dyed material for various end-uses. The test may be mild (M), intermediate (I) or severe (S) depending on the temperature of testing (150°C, 180°C or 210°C, respectively). According to molecular weight and sublimation fastness properties, disperse dyes are classified into 3–4 groups such as A, B, C and D for Dispersol dyes (originally by ICI), and S, SE and E types for Foron dyes (Clariant). Out of these, C and D types of Dispersol dyes and S and SE of Foron dyes are suitable for application on polyester fibers.
- 9) The fastness to heat treatment improves with increase in molecular size.
- 10) The color yield, brightness and shade of disperse dyes remain unaffected in the presence of hard water of 50°e (English hardness). Demineralized water containing sodium ions is alkaline and needs suitable buffering.
- 11) A number of disperse dyes are susceptible to copper or iron and form a blue-violet complex with them. This may cause change of shade or staining. If the use of hard water is unavoidable, it is advisable to use a sequestering agent such as 0.5 g/l of disodium salt of EDTA and pH should be buffered at 4–5. EDTA salts are alkaline. Tetra-sodium salt is not recommended due to its high alkalinity. The addition of sequestering agent (1 g/l) is also to be made in reduction clearing and subsequent processes, if the water is hard. After reduction clearing, it is advisable to treat the goods with 1–2 g/l acetic acid (60%). If the undesirable metal-complex dye is already diffused into the fiber, a treatment with a sequestering agent, anionic dispersing agent and carrier is to be made at pH 4–5 and temperature 130°C for 2 hours. The dyes sensitive to copper and iron are:
 - C.I. Disperse Orange 25
 - C.I. Disperse Reds 55, 60, 75, 91, 92 and 93
 - C.I. Disperse Violet 35
 - C.I. Disperse Blues 79, 94, 128 and 148
- 12) Soon after the introduction of cellulose acetate materials, it was noted that such fibers dyed with certain disperse dyes had a tendency to fade when stored in an atmosphere with fumes from gas heaters. The most susceptible dyes were reds and blues based on amino-anthraquinone, but certain azo dyes were also affected to a lesser extent. It was established that the active constituents of the burnt gas fumes were nitrogen oxides. In the late 1940s and early 1950s, numerous disperse dyes resistant to fading by gas fumes were introduced. The resistance is increased when basicity of the dye is decreased. However, this may lead to inferior dyeing properties and the most

successful of the newer gas-fume-fast dyes have more complicated chemical structure in order to maintain dyeing properties. The fastness to gas fumes can be improved by substituting one of the two $-NHCH_3$ substituents of C.I. Disperse Blue 14 with aminobenzene ($-NHC_6H_5$) substituent as in case of C.I. Disperse Blue 24. However, dyeing properties of the latter is inferior. Better dyeing properties can be achieved by adding CH_2CH_2OH group on amino-benzene substituent and substituting other $-NHCH_3$ groups with hydroxyl groups, as in the case of C.I. Disperse Blue 27.

- 13) With other dyestuff classes, identity of chemical structure establishes all dyeing and fastness properties. But this is not true with disperse dyes. The disperse dyes having identical chromophore (indicated by C.I. number) produced by different manufacturers may not give identical shades on dyeing. The shade produced depends on several factors like shape, size and volume of the dye crystals, colored impurities or isomers, type and amount of dispersing agents and products added for standardization.
- 14) Disperse dyes show thermal migration migration of dye from core to surface while drying of dyed goods at 170°C or above. Migration is more in case of disperse dyes of high molecular weight having high sublimation fastness. Whenever thermal migration poses a problem of low wash fastness, the remedy is to post-scour the dyed material followed by drying at 140°C or below. Some processing aids (e.g., spinning or knitting oils) and finishing agents may also cause thermal migration of disperse dyes. During storing of the dyed or printed material, some disperse dyestuffs have the tendency to be desorbed from polyester and be reabsorbed in the layer of oil or finishing agent, particularly under the influence of heat, humidity and pressure. As the dye migrates from the core to the surface of the material, the fastness to light, sublimation and wet treatments may be adversely affected. Broadly speaking, nonionic emulsifiers and finishing agents are responsible for thermal migration. Anionic and cationic agents are less harmful. Polyvinyl acetate and crosslinking agents like DHDMEU with magnesium chloride catalysts are safe.
- 15) In case of dyeing of polyester with disperse dyes, abnormal light-fading occurs in several combinations of yellows and blues. In case of other dye-classes, blues are selectively destroyed in the presence of yellows, but with disperse dyes both the dyes undergo destruction; for instance, the light fast-ness of the final green shade is lower than expected. The following are examples of compound shades of C.I. Disperse Blue 56 with yellow disperse dyes:
 - C.I. Disperse Yellow 50
 - C.I. Disperse Yellow 83

Similarly, when C.I. Disperse Blue 183 is combined with several red dyes, abnormal fading was observed.

The various chemical structures found among disperse dyes are:

- a) Azo
- b) Nitrodiphenylamine
- c) Anthraquinone

- d) Methine
- e) Heterocyclic rings

3.2.2.15 Azo Disperse Dyes

Azo dyes represent the largest and most important group, and chiefly cover yellow, orange and red hues. The dyes are relatively cheap and generally they do not require numerous intermediate stages during manufacture. The most important sub-group, aminoazobenzene derivatives (Nunn, 1979), has the general formula (Figure 3.11).

Examples for the Figure 3.11 are

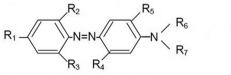
- C.I. Disperse Orange 30, where $R1 = NO_2$, R2, R3 = C1, R4, R5 = H, $R6 = C_2H_4CN$, $R7 = C_2H_4OCOMe$ (class-C dye)
- C.I. Disperse Blue 183, where R1 = NO₂, R2 = CN, R3 = Br, R4 = NHCOEt, R5 = H, R6, R7 = Et (class-D dye, suitable for polyester).

3.2.2.16 Nitrodiphenylamine Disperse Dyes

This continues to be a relatively small class of dyes covering mainly yellow and orange-yellow hues. They are still used on account of their low cost, ease of manufacture, very good fastness to light in pale colors, and their usefulness in producing greens with blue anthraquinone dyes whilst maintaining good fastness to light. By increasing molecular size or by introducing polar groups, sublimation fastness can be improved. The basic type of structure used in dyes for polyester fibers is shown in Figure 3.12, where R1 and R2 = H or Alkyl or aryl, R3 = H or substituent.

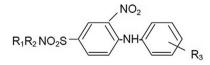
3.2.2.17 Anthraquinone Disperse Dyes

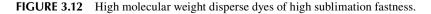
This is also a large and important group and capable of covering the range from greenish yellow to bluish green. However, these dyes are particularly valued for the



Where R_1 = electrophilic group R_2 and R_3 = H or electrophilic groups R_4 and R_5 = H or neucleophilic groups R_6 and R_7 = H or alkyl or substituted alkyl groups

FIGURE 3.11 Aminoazobenzene derivatives (azo disperse dyes).





production of bluish red, violet, blue and bluish green dyeing. The simple anthraquinone dyes are bright and stable under dyeing conditions. Dyes of this class will probably not increase their market share in the near future because:

- 1) They are somewhat weaker in tinctorial value than many azo dyes;
- Several intermediate stages are often required in their production necessitating a relatively high capital investment;
- 3) Many dye intermediates required for their production are derived from anthraquinone- α -sulphonic acid, which require a mercury catalyst. This may create pollution problems and alternate methods are to be established.

Examples are C.I. Disperse Violet 1 (Figure 3.13) and C.I. Disperse Blue 56 (Figure 3.14).

3.2.2.18 Methine (Styryl) Disperse Dyes

This small group was originally introduced for producing greenish yellow dyes for secondary acetate. Dyes having more complex structures than the aforementioned type are prepared by condensing pyrene, triphenylamine and phenoxazine with reactive methylene compounds like malonitrile. They are all fluorescent greenish yellow dyes, with the exception of the latter, which is orange.

3.2.2.19 Heterocyclic Disperse Dyes

A number of heterocyclic dyes are particularly useful for producing bright colors, especially greenish yellow. A member belonging to this group is C.I. Disperse Yellow 206. Although not as green and bright as many of the styryl dyes, they, however, possess good color build-up and good fastness to light with the advantage of a high degree of stability under most application conditions, like anthraquinone dyes.

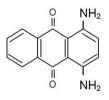


FIGURE 3.13 C.I. Disperse Violet 1.

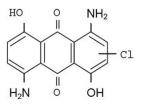


FIGURE 3.14 C.I. Disperse Blue 56.

3.2.2.20 Pigment Colors

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

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

- Azo pigments (yellows, oranges, reds)
- Naphthalene, perylenetetracarboxylic acid, anthraquinone, dioxazine and quinacridone pigments (very fast and brilliant oranges, reds and violets)
- Halogenated copper phthalocyanine derivatives (blues and greens)

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

With aqueous pigment pastes, the dispersion medium is of course water. The surfactants used must have an HLB value >10; nonionic dispersing agents based on ethylene oxide condensates with C12 to C20 alcohols are commonly used. When producing a pigment paste starting from a wet press-cake that contains about 25% pigment mixed with water, it is only possible to make about 20% pigment dispersions. Highly concentrated pigment pastes (with 35–45% pigment content) are obtained from dried press-cake; the drying conditions for this must be as mild as possible, in order to avoid formation of hard pigment agglomerates.

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

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- Naphthalene, perylenetetracarboxylic acid
- Anthraquinone, dioxazine and quinacridone pigments (very fast and brilliant oranges, reds and violets)
- Halogenated copper phthalocyanine derivatives (blues and greens)

A typical recipe of pigment dispersion is as follows:

Pigment powder	25-40%
Glycols	5-10%
Dispersing agents	5-15%
Preservative	< 0.1%
Antifoam	<1%
Water	34–59%

Modern pigment dispersions should have the following physical properties:

- Water-based
- Particle size below 3µ

- Long-term stability up to 50°C
- · Low dry-up behavior
- Good re-dispersibility
- Low influence on viscosity of synthetic thickeners
- No gelling
- Low viscosity (liquid).

Natural colors are decreasing in usage, but not organic pigments – these are synthetic products. They can be printed on any textile materials including blends. They are applied with the help of low-molecular weight polymers called binders. The binder forms a transparent film on the surface of the textile materials and forms crosslinks with it. The colorant molecules are trapped inside the film. The fastness of such colors will depend on the stability of the binder film. As the application is not based on affinity, they can be applied on any textile substrate including blends of different fibers, as well as on inert fibers like glass and metal. Their method of application and fixation are quite different from those of other dye-classes. Pigment colors can be used for dyeing light shades on cotton materials, but are popular for printing cotton materials.

The two main components in this process are the pigments and the binder. The pigments are mostly organic azoic, vat, and phthalocynine compounds and carbon black. The physical state of the pigment is important as it is to be dispersed in the binder. The covering power of the pigment is the most important characteristic for its application. Ebler's rule states that the covering power of the pigment increases with diminishing particle sizes, until this value becomes of the same order as the wavelength of the light reflected or absorbed. With further reduction of particle size, translucency begins. The pigment colors must be fast to light, unaffected by the binder and by the normal treatments a textile material will receive.

3.2.2.21 Mineral Colors

These are not readymade dyes; insoluble metallic oxides and hydroxides are precipitated inside textile fibers by treating with soluble metallic salts followed by treatment with alkali. As mineral compounds are used, the cost is very low. Moreover, the inorganic pigments thus deposited increase the weight of the material and impart anti-fungal properties. Mineral colors were used for dyeing police and military uniforms, but now this usage is obsolete.

Suitability of various dye-classes for various textile fibers may be summarized as follows.

3.2.2.22 Cellulosic (Cotton and Viscose)

Direct, azoic, sulfur, vat, solubilized vat, reactive, ingrain, mineral, pigment, oxidation colors (limited use).

3.2.2.23 Cellulosic (Jute)

Most of the above classes, except those require caustic alkali, additionally acid and basic dyes.

3.2.2.24 Protein (Wool, Silk, Nylon)

Acid and selected direct dyes, basic dyes (limited use).

3.2.2.25 Synthetic Fibers (Polyester, Cellulose

Acetate, and, Less Commonly, Nylon)

Disperse dyes.

3.2.2.26 Other Synthetic Fibers (Acrylic and Modacrylic)

Conventional and modified basic dyes.

3.3 COLOR FASTNESS PROPERTIES

Dyed materials have various uses. Consequently, they are subjected to treatment with several external agents under diversified conditions. The resistance to such external agents is known as fastness properties. Frequently a compromise must be reached between the cost of attaining a particular color of goods and the fastness properties of such goods.

The most important fastness properties are (Roy Choudhury, 1996):

- 1) Washing fastness
- 2) Light fastness
- 3) Rubbing fastness wet and dry
- 4) Fastness to perspiration
- 5) Fastness to bleaching
- 6) Fastness to dry heat

3.3.1 WASHING FASTNESS

Unlike other types of fabric testing, such as flammability, there are no mandatory legal requirements for color fastness testing. But color fastness testing is essential to ensure customer satisfaction with fabric products. Color fastness issues will often prompt consumers to reject the product and return it or submit a claim.

Poor washing fastness of dyes may appear in two ways: dyes may come out from the dyed or printed fabric causing lower color strength of the washed sample as compared to unwashed sample (termed as "color change"). In the first case, the released dyes in the wash liquor may not be recaptured by the washed fabric. In the second case, if the released dye is again captured by the washed fabric, it is called as "staining". Staining on adjacent fabrics is assessed by putting a white cloth along with the dyed or printed sample under test in the washing bath. After washing, the washed white sample is compared with unwashed white sample. Staining is highly objectionable in printed materials as it changes the color of background (i.e., non-printed portion) fabric. Some dyes (e.g., direct dyes) may cause considerable staining, and hence, they are unsuitable for printing. The washing fastness ratings are expressed by two numbers: one number represents rating for "color change", while the other for "staining". Both assessments are made by measuring color contrast between washed and raw (i.e., unwashed) samples. The contrast is compared visually with the contrast represented by Grey Scale.

The degrees of fastness are expressed numerically -1 being the lowest and 5 the highest (8 for light fastness). The fastness grading may be intermediate between two full numbers and may be expressed as 2–3, 4–5 or 2.5, 4.5, and so on. In most of the tests, the grading is decided by the difference in color of the material before and after the test.

For assessment of color change and staining, two different Grey scales are used, namely Grey scale for color change ((ISO 105 A02 or BS 1006 A02, 1978) and Grey scale for assessing staining (ISO 105 A03 or BS 1006 A03, 1978).

The five-step Grey Scale consists of five pairs of non-glossy neutral grey color chips (or swatches of grey cloth), which illustrate the perceived color differences corresponding to fastness ratings 5, 4, 3, 2 and 1. Nine-step scales are now available where chips for half-step ratings 4-5, 3-4, 2-3 and 1-2 are provided (Roy Choudhury, 1996). Each step consists of two grey chips. In the Grey scale for assessing change of color, one chip is a standard dark grey (the Y tristimulus shall be 12 ± 1), while lightness of the second chip increases with decreasing rating. The contrast between two chips is nil in case of rating 5 and the lightness contrast increases for rating 4-5, 4, 3-4 and so on. Figure 3.15 shows a nine-step SDC Grey Scale for assessing color change.

A Grey Scale (ISO 105 A03 or BS 1006 A03, 1978) is also available for assessing staining on adjacent fabrics (Figure 3.16). The Y tristimulus value of the first member (white) of each pair shall not be less than 85.

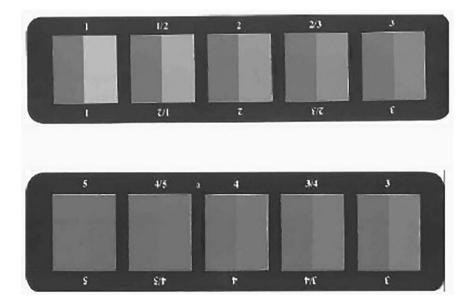


FIGURE 3.15 SDC Grey Scale for color change.

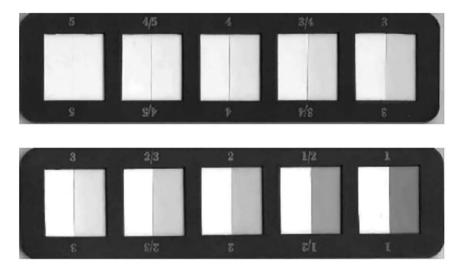


FIGURE 3.16 Grey Scale for assessing staining.

Nowadays, the color contract may be measured in terms of color difference equation using a spectrophotometer and fastness ratings are expressed by comparing those instrumental values with those of various Grey Scale ratings. The color difference in terms CIELAB units using 1964 10 degree standard observer functions under illuminant D65 of the Grey Scale for color change and staining (ISO, 1993) are shown in Table 3.1 and 3.2 respectively.

3.3.2 LIGHT FASTNESS

The light fastness of dyed materials is measured by exposing them to daylight under glass or to an artificial illumination in an accelerated fading lamp alongside a set of standard dyed materials.

Currently, the most common standards for light fastness testing are the blue wool standards. At the time of development of the light fastness standards, wool was found to be the substrate that was least effected by humidity. The scale consists of a set of eight woolen fabrics dyed with different dyes numbered 1 to 8 (British system) in order of increasing fastness – 1 having lowest light fastness and 8 having highest fastness. Blue wool standards developed and marketed in America are designated as Standards L2 to L9. Light fastness of the standard materials is such that the time of exposure required for their fading is in geometric (GP) scale; for instance, each standard would take twice as long to fade to a certain level as the one below it.

The samples under test and eight blue wool standards are cut in small strips and are fixed on black card board with one-quarter covered with black card A. The samples and standards fixed on black cards are simultaneously exposed to daylight or artificial

Fastness grade	Color difference in CIELAB units	Tolerance
5	0	0.2
(4–5)	0.8	±0.2
4	1.7	±0.3
(3-4)	2.5	±0.35
3	3.4	±0.4
(2–3)	4.8	±0.5
2	6.8	±0.6
(1-2)	9.6	±0.7
1	13.6	±1.0

TABLE 3.1

Color Differences of the Grey Chips of Grey Scale for Assessing Change of Color

TABLE 3.2
Color Differences of the Grey Chips of Grey Scale for Assessing Staining

Fastness grade	Color difference in CIELAB units	Tolerance
5	0	0.2
(4–5)	2.3	±0.3
4	4.5	±0.3
(3–4)	6.8	±0.4
3	9.0	±0.5
(2–3)	12.8	±0.7
2	18.1	±1.0
(1-2)	26.6	±1.5
1	36.2	±2.0

light (preferably Xenon-arc lamps) and checked for color fading by judging color contrast between exposed and unexposed areas with Grey Scale for color change.

The standards are inspected at intervals until an alteration of shade in standard 3 is just perceived. At this stage the specimens with fastness no greater than 3 are assessed by comparing specimens and standards 1–3. Otherwise, the card A is then replaced in exactly the same position as it was before. The exposure is continued until a change in standard 4 is just perceived when a second opaque card B is placed in advance to card A overlapping a portion of it. The exposure is continued until standard 6 shows initial fading. At this stage the cover C is placed ahead of card B overlapping a portion of it. The exposure is continued until a contrast in standard 7 equal to Grey Scale rating 4 appears or the fading of specimen equals to Grey Scale rating 3. The specimens and standards will show three zones with the unexposed area at the left side. The zones of specimens are compared with the standards and if the two degrees of fading on the specimen do not correspond with the same standard, the fastness would be the mean between the two (such as 3-4).

3.3.3 RUBBING FASTNESS

A device called a crock meter is used for rubbing fastness test (BS 1006 X12: 1978, IS: 766–1956). It has a finger of 1.6 cm diameter which can move to and fro in a straight 10 cm track on the specimen. The rubbing is carried out by moving 10 times in 10 seconds with a downward force of 6 N. The color change of the rubbed fabric and the staining of the rubbing white cloth are assessed by the respective Grey Scales.

3.3.4 PERSPIRATION FASTNESS

Unless dyes are selected carefully, those parts of the cloth or garment which come in contact with the body, where perspiration is heavy, may suffer local discoloration. Two artificial perspiration solutions (BS 1006 E04: 1978) are prepared by dissolving in one liter of distilled water 0.5 g l-histidine monohydrochloride monohydrate ($C_6H_9O_2N_3HC1,H_2O$), 5.0 g sodium chloride, 2.5 g (2.2 g for the 2nd solution) disodium orthophosphate (Na₂HPO₄,2H₂O); and pH is adjusted to 8 and 5.5 with 0.1 N NaOH and 0.1 N acetic acid for two solutions, respectively.

The material to be tested is placed between two undyed pieces, one of which is of the same fiber and the other of a different fiber as in the case of washing fastness test. The specimens are then placed between glass plates pressed together with a force equivalent to 10 pounds (4.536 kg) and allowed to stand in an oven at $37 \pm 2^{\circ}$ C for 4 hours. The color change of the dyed fabric and the staining of the white cloth are assessed by the respective Grey Scales.

3.3.5 FASTNESS TO PEROXIDE BLEACHING

The fastness to peroxide (BS: 1006 N02: 1978) test is carried out with a specimen sewed with two adjacent fabrics as in case of washing fastness test. The composite specimen is kept inside a test tube by rolling in the direction of the longer side and bleaching is carried out. A reflux condenser is fitted with the test tube to reduce evaporation from the bleaching bath during test. After bleaching, the composite specimen is removed and rinsed for 10 minutes in cold running tap water, squeezed and dried by hanging in air. The change in color of the specimen and the staining of the adjacent fabrics are assessed with the Grey Scales.

3.3.6 FASTNESS TO DRY HEAT

This fastness (BS: 1006 P01: 1978) is to be regularly assessed for disperse dyes on polyester, as these dyes are sublimable. For dyed or printed textile specimens sewed with two adjacent fabrics (one of them usually polyester), the time of treatment is 30 seconds and the three temperatures recommended are $150\pm2^{\circ}$, $180\pm2^{\circ}$ and $210\pm2^{\circ}$ C. The change of color and staining on adjacent fabric are then assessed with the respective Grey Scales.

3.4 TOXICITY OF DYES

Fiber-reactive dyes are dyes that form covalent bond to the fibers like cotton, rayon, and soy. About 100 years ago, some trade journals reported increased risk of bladder cancer for people working in dyestuff production. The cause of these malignant diseases was soon thought to be certain aromatic amines widely used in the production of synthetic dyes in those days.

In 1994 the German Consumer Goods Ordinance was amended to ban specific azo dyes, triggering widespread discussion about textile ecology stating: "Azo dyestuffs which, on cleavage of one or more azo groups, release any of twenty listed amines should not be used in commercial production or treatment of consumer goods". Among all azo dyes, only about 4-5% of dyes release banned amines under certain conditions due to reductive cleavage, and are therefore banned. The epidemiological evidence shows that the following four aromatic amines have a carcinogenic effect in humans, namely:

- 1) Benzidine
- 2) 2-naphthylamine
- 3) 4-aminodiphenyl
- 4) 4-chloro-o-toluidine

These four amines are listed as "definitely carcinogenic in humans". Subsequently, 22 aromatic amines were banned. However, not all synthetic dyes are harmful.

3.5 SELECTION OF DYES FOR PRINTING

Dyeing is a process of uniform coloration of textile material in all three directions, namely lengthwise, widthwise and thickness-wise. The color uniformity in all directions is the prime criteria of a perfect dyeing. On the other hand, textile printing is the application of color in selected portions of the fabric as per design or at random portions of the fabric. Here, non-uniformity of color of different portions of the fabric is the target. In other words, textile printing can be considered as a controlled form of localized dyeing.

In principle, any dyes used for uniform dyeing of fabric could be used to print the fabric. The same mechanisms of dye fixation apply in both dyeing and printing. Careful selection of appropriate dyes for a particular dyeing process is always desirable; however, in the case of printing, proper selection of dyes is essential. The primary concern in printing is the solubility of the dyes in water. High solubility of dyes is essential, even more so than for continuous dyeing processes, which admittedly compare closely with printing. Not only is the amount of water in the print paste severely limited but, also at the fixation stage, the dye must be redissolved in a small volume of condensed steam.

There are further reasons for careful selection. The dye must diffuse through the film of thickener before adsorption on, and diffusion into, the fiber. Unless the dye diffuses rapidly, the required time for fixation will be very high. Consequently, low molecular weight dyes will often be preferred, provided that their fastness levels are

adequate. It is also necessary to choose dyes that can be washed off satisfactorily, without staining the ground or other printed areas in the fabric.

3.5.1 Advantages of Pigment Printing

Pigments of course, may be used for the production of plain-colored fabrics, but they are of much greater importance in printing. Fixation of textile materials printed with dyes are mostly done by a treatment with steam (atmospheric or high pressure). This requires sophisticated machinery and precise control. On the other hand, the pigment printed materials require drying (at around 100°C) followed by heat treatment at higher temperature of around 150°C. The heat treatment process is much simpler than the steaming process and may be made continuous. The principal objection against the pigment application is the stiffening effect of the binder which is used as binding agent for the pigments to the fabric. However, the stiffness is less noticeable in printing where significant areas of fabric are left unprinted (i.e., when the design area is low) and the fabric remains flexible. For this reason, far larger quantities of low-cover designs are printed with pigments than of highcover prints.

Secondly, pigment printed materials do not require after-wash, as in the case fabric printed with dyes. In the latter case, the fabric is thoroughly washed after printing and subsequent fixation, to remove unfixed dyes and thickeners. Pigment printed fabrics do not require any after-wash as there is nothing to remove after heat-treatment or curing. The elimination of the washing-off stage adds extra value to the printer, as regards pigment printing.

Pigment color dyed and printed fabrics have poor rubbing fastness; colors come out on rubbing. However, high color marking of the unprinted or ground portions with the migrated colors from the printed portion during rubbing of pigment printed materials is more objectionable on dyed fabrics than on prints, where the pattern conveniently distracts the eye. Pigments can be applied to all textile fibers, including glass fiber. This is advantageous in case of blended fabrics made from the mixture of multiple fibers. Such blended fabrics cannot be printed with a single class of dye.

3.6 TEXTILE AUXILIARIES

Textile auxiliaries are defined as chemicals of formulated chemical products which enable a processing operation in preparation, dyeing, printing of finishing to be carried out more effectively or which is essential if a given effect is to be obtained.

The main object of printing is the controlled application of dye to exactly defined locations on the fabric leaving the rest of the fabric essentially unaffected. In printing, the colors are fixed in the applied areas by steaming or dry heat in a shorter span of time to prevent spreading of color into the unprinted areas.

The following auxiliaries are used in textile printing (Madhu, 2015):

- 1) Thickeners
- 2) Wetting agent
- 3) Dispersing agents or solvents

- 4) Antifoaming agent
- 5) Hygroscopic agent
- 6) Oxidizing and reducing agent
- 7) Carriers
- 8) Binders
- 9) After washing agents
- 10) Miscellaneous other auxiliaries

3.6.1 THICKENING AGENTS

Thickeners used in textile printing are high molecular weight viscous compounds with water imparting stickiness and plasticity to the printing paste. These thickeners facilitate the preservation of design outlines without spreading, even under high pressure. The main purpose of thickeners in the textile industry is to hold the dye particles on the desired areas of the fabric until the dye transferred onto the fabric surface and its fixation is complete. The thickeners provide required viscosity to the printing pastes, preventing premature reactions between the chemicals of the dyes. They are boiled for 2 to 3 hours with high M:L ratios (say 1:50), depending on the nature of the thickener. This process enhances the absorbance capacity of the fabric and leads to uniform coloration (Harlapur et al., 2020).

The thickening agent must be selected for adhesion to the fiber, film elasticity and ease of removal, as well as the normal requirements. High-solids-content thickeners, like crystal gum or British gum, give optimum sharpness of outlines, but form brittle films that crack and scatter dye by "dusting off". The lower-solids-content thickeners, such as alginates and locust bean ethers, form elastic films and are easily washed out. The latter are most commonly used, often in mixtures with starch ethers. Halfemulsions (gums mixed with kerosene emulsion to reduce solid content) are also used, but tend to give a less sharp mark and a risk of rubbing off.

Thickening agents or thickeners are essential and the most important ingredient of the printing paste.

The main functions of thickeners in printing are (Madhu, 2015):

- 1) To act as a vehicle for carrying the dye onto the cloth.
- 2) To restrict the dyes within the printed area before fixation of dyes by steam or dry heat.
- 3) To prevent the spreading of the color on the cloth by capillary action beyond the limit of the defined portion in the motif.
- 4) To retain moisture during steaming for dissolving dyes before diffusion of dyes inside the fiber.

The quality of printing paste depends on the following desirable properties of thickeners (Meram et al., 2020):

- The thickener should be cheap and easily available.
- It should be stable to storage, pressure and temperature.

- Thickeners are expected to create acceptable adhesion and consistent distribution of the printing pastes to fabric surface.
- The dried thickener film should retain colorants firmly, preventing dusting of colorants.
- The thickener should not affect color yield (e.g., diffusion and fixation) of the print.
- The thickener paste preparation process should be easy and quick.
- The thickener should be homogeneously distributed in the printing paste.
- Environmental impacts by thickeners should be negligible. They should be highly biodegradable in order to prevent any negative impacts on the environment via discharge water. The commonly known thickening agents are natural gums, sodium alginate, starch or customized starch, galactomannan or customized galactomannan, and carboxymethyl cellulose. It is well known that galactomannan and its customized derivatives are more environmentally appropriate than British gum (Sudha and Latika, 2017).
- The thickener should be compatible and stable with different printing ingredients including dyes and auxiliaries.
- The thickener should provide sharp outlines of the print preventing bleeding or spreading.
- The thickener should possess good mechanical properties, to prevent dusting of dry film.
- The thickener should absorb condensed water to provide aqueous medium for dissolution and penetration of dyes into the fibers.
- The thickeners should release the colorants fully during fixation.
- The thickener should get dried quickly to prevent spreading and wetting.
- The thickener should not decompose during drying and fixation.
- The thickener should be easily removable by washing after fixation of dyes.

There are four important approaches to generate thickeners, namely (Meram et al., 2020):

- Low concentration of high molecular weight polymers (low-solid).
- High concentration of low molecular weight materials (high solid).
- Emulsion of two immiscible fluids.
- Dispersion of finely divided solids (e.g., Bentonite).

In the past, polysaccharides were the only polymeric thickening agents employed in textile printing. Subsequent to the arrival of diverse types of colorants including dyes and pigments, the compatibility of some of these thickening agents was established to be very poor. Therefore, a variety of polysaccharides derivatives, synthetic polymeric materials and emulsion thickening agents were developed. Those developed thickening agents were characterized by plasticity and stickiness to clothing with sharp outlines. The choice of a thickening agent largely depends on the type of dye and style of printing. According to compatibility between dye and thickener, broad rules for the choice of thickener have been laid. For example, reactive dyes are used

with sodium alginates which comprise fewer crosslinking properties, while pigments were used with synthetic thickeners, in addition to binder.

The colloidal polysaccharide thickening agents, such as starch, cellulose ether, alginates or locust bean gum (LBG) have been used successfully throughout the history of textile printing in printing pastes for various groups of dyes.

Thickeners are of three types:

- · Natural thickeners
- Modified natural thickeners
- Synthetic thickeners

3.6.1.1 Natural Thickeners

The most important natural thickeners include the following:

- Cereal starch: e.g., marine starch, wheat starch
- Plant exudates: e.g., gum tragacanth, Karaya gum
- Root and seeds: e.g., locust beam gum
- Sea weeds: e.g., Na-alginate

3.6.1.2 Modified Natural Thickeners

Modified natural thickeners are also known as semi-synthetic thickening agents. These are produced by the modification of cellulosic materials, starch and gums by chemical, physical and thermal methods. As they are more appropriate compared to natural thickening agents, their application in textiles manufacturing is increasing. Modified polylactic acid was employed recently as a thickening agent. Biodegradable materials can be considered one of the most significant fields of materials science, in which chemical, medical and ecological researchers are contributing to enhance human healthcare, protect the environment from toxic wastes, and decrease reliance on fossil fuels. There are a great number of biodegradable polymers, such as polylactic acid (Figure 3.17), polyglycolic acid and polycaprolactone, which have been developed for a variety of applications.

The thickener may be a natural or synthetic polymer. The use of man-made thickener in the printing industry leads to several harmful effects on the environment. But this effect can be minimized by using eco-friendly natural thickeners in place of synthetic ones (Yadav et al., 2016). The sources of natural thickeners are being extensively stretched throughout the plant kingdom and easily available to a large extent. The constituents of natural thickeners are non-allergic and non-toxic

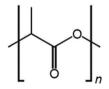


FIGURE 3.17 Chemical structure of polylactic acid.

to human beings and cause no health hazard. The foremost required property of thickeners in textile printing is that they must either be soluble in water or able to absorb water to form viscous solution. This requirement is completely fulfilled by natural thickeners.

A large number of thickeners are available for printing. The choice of thickener will depend upon the class of dye to be printed and style of printing. The compatibility of thickener with other ingredients in the printing paste should also be checked during its selection. Carbohydrates form the most important and largely used varieties of thickening agents. Wheat starch and maize starch have been used as thickeners in printing since ancient times. Starch is not suitable as a thickener in the preparation of paste in which acids are to be added.

3.6.1.3 Gums

Gums act as excellent thickeners. Natural gums are obtained in a natural state such as the tree exudates, extracted from seeds of some legumes or seaweed hydrocolloids. Examples include gum arabica, guar gum and tragacanth.

3.6.1.4 Gum Tragacanth or Gum Dragon

It is obtained from the ligneous plant.

- The advantage of this gum is that it leaves the cloth quite soft.
- Generally, 4–5% gum paste is used in printing.
- It is stable under mildly alkaline conditions but not under strongly alkaline conditions.

3.6.1.5 Gum Senegal or Gum Arabic

- It is obtained from the exudation of the Acasia plant.
- 30–50% gum paste is required for printing.
- It is stable under both strongly alkaline and strongly acidic conditions.

3.6.1.6 Gum Karaya

- This gum is obtained from the Karaya tree.
- It is not much used at present.

3.6.1.7 Guar Gum

Guar gum, also called guaran, is a galactomannan polysaccharide extracted from guar beans that has thickening and stabilizing properties useful in food, feed and industrial applications. The guar seeds are mechanically dehusked, hydrated, milled and screened according to application. It is typically produced as a free-flowing, off-white powder. Guar gum is a gel-forming galactomannan obtained by grinding the endosperm portion of *Cyamopsis tetragonolobus*, a leguminous plant grown for centuries mainly in India and Pakistan, where it is a most important crop that has long been used as food for humans and animals

Guar gum is one of the most important products from Guar which can hydrate rapidly in cold water and also attain high viscosity even in low concentration. Guar gum printing thickener is an important component in textile industry because of its low costs and high viscosity. Guar gum for textile printing aids in direct painting on wool, nylon and silk. It is also used in printing dyes on cotton fabric, carpet printing, acrylic blanket printing, burn out printing and vat discharge.

Guar gum is perfect for the textile industry because it has a perfect film forming and thickening property. One of the main benefits of using it is that it reduces warp breakage and is highly efficient. The fact that it absorbs water very fast makes it vital to prevent ink from spreading all over the clothes.

Since it is a thickening agent, there are many advantages of using it along with dyes, polyester, cotton, silk, nylon and so on. It also enhances the quality of printing by preventing chemical corrosion. It has superior erosive and writing properties, good bonding and hardness, and is thus optimal for the printing industry.

The special feature of guar galatomannan its high viscosity which may go up to 10,000 cps in 1% solution. As this high viscosity is difficult to control, guar gum is rarely used as such. To improve the stability, dispersibility and flow properties, guar is to be modified. The types of reactions that can be carried out include etherification, esterification, oxidation, reduction, cyclic derivatives formation and displacement of the hydroxyl groups by other groups. Reported modified products include easy dispersible etherified guar, sulfated guar and more.

Low-solids, high-viscosity products are preferred and, for purely economic reasons, modified guar gums are particularly popular. The rheological properties of these thickeners vary somewhat, particularly with regard to their property of socalled pseudoplastic flow – that is, a tendency to decrease in viscosity with increasing applied shearing forces. This effect can impact print quality (pile penetration, pattern definition and so on) (Miles, 2003).

3.6.1.8 Locust Bean Gum

Locust bean gum (LBG) is a polysaccharide which is extracted from seeds of *Ceratonia siliqua* (carob tree, or locust bean tree). LBG is also known as carob bean gum or carob gum. LBG is a type of galactomannan with a high molecular weight. LBG bears a close structural and chemical resemblance to guar gum. However, LBG possesses functional properties that are quite distinct different from guar gum. LBG, unlike other hydrocolloids, is only partially soluble in water at room temperature. LBG is soluble in water with the addition of heat, dissolving in water above 80°C. Also, LBG solution does not form a gel by itself, but increases in viscosity at higher temperatures and forms a gel when synergized with other types of hydrocolloids such as xanthan, kappa-carrageenan and agar. The carob tree produces pods which contain the brown colored, hard seeds or beans. The pods are processed to separate the seeds, peel off their skins, split the seeds and separate the germ from the endosperm. The endosperm is milled and ground to produce the LBG flour or powder.

3.6.1.9 Gum from Neem/Babul/Moringa

Thickeners have also been successfully extracted by Harlapur et al. (2020) from the gums of *Azadirachta indica* (neem), *Acacia nilotica* (babul) and *Moringa oleifera* (Moringa or Drumstick; Indian name, Shajna).

Azadirachta indica, commonly known as neem, is an evergreen and wonder tree of the modern era. Since time immemorial it has been used by Indians for various purposes because of its extensive properties. It possesses antibacterial, anticarcinogenic, antiviral, cytotoxic and anti-inflammatory properties. The phytochemical constituents present in neem are nimbidin, nimbin, nimbolide, azadirachtin, gallic acid, epicatechin, catechin and margolone. The chief active constituent azadirachtin is an effective antimicrobial agent.

3.6.1.10 Acacia Nilotica Gum

Acacia is a genus of shrubs and trees belonging to the subfamily *Mimosoideae* of the family *Fabaceae* or *Leguminosae*. In India it is generally known as "babul" or "kikar". It is a moderately sized tree with a spread crown, broadly scattered in tropical and sub-tropical countries. This plant possesses antibacterial, antifungal, antiviral, antimicrobial, antihypertensive, antimalarial and antispasmodial activities. It is a single stemmed plant and stems exude a reddish color gum. *Acacia nilotica* gum is known as "Indian gum Arabic". *Acacia nilotica* gum varies in color from very pale yellowish brown to dark reddish brown depending on the concentration of tannins in the sample. The gum contains galactose, L-arabinose, L-rhamnose and four aldobiouronic acids (Raj et al., 2015).

3.6.1.11 Moringa Oleifera Gum

Moringa oleifera is a fast-growing, drought resistant tree generally known as Moringa or Drumstick. It is the extensively cultivated variety of the genus Moringa of the family *Moringaceae*. This rapidly growing tree was utilized by the ancient Indians, Romans, Greeks and Egyptians for various purposes. *Moringa oleifera* is an important food commodity and received an enormous attention as the "natural nutrition of the tropics". Nowadays it is widely cultivated and has become common in many locations in the tropics. The gum exudates from the stem of *Moringa oleifera* is initially white in color and changes to reddish brown or brownish black on exposure. Gum is sparingly soluble in water. It swells in contact with water and gives a highly viscous solution. *Moringa oleifera* gum is a polyuronide; the purified form contains L-arabinose, D-galactose, D-glucuronic acid, L-rhamnose, D-mannose and D-xylose (Panda et al., 2006). The entire process of extraction of gum laid out by Harlapur et al. (2020) is simple and eco-friendly.

All the printed samples with natural gum thickeners exhibited excellent fastness towards washing and dry rubbing. Even the wet rubbing fastness grade is good to excellent for the fabrics printed with *Azadirachta indica* and *Acacia nilotica* gums as thickeners. Fabric printed with *Moringa oleifera* gum thickener showed fair grade for wet rubbing fastness compared to other two thickeners; the whole process of extraction and printing is environmentally friendly and need not to be removed in effluent treatment plants. It

considerably reduces the dependency on effluent treatment plants. It prevents pollution and reduces the cost of effluent treatment for industries. Harlapur et al. (2020) claimed that by using the gums of *Azadirachta indica*, *Acacia nilotica* and *Moringa oleifera* trees as thickening agents, cotton fabric can be printed with reactive dye satisfactorily. Experimental observations showed that the natural gums of neem, babul and Moringa can effectively be used in printing of cotton fabrics as indigenous and natural thickeners.

3.6.1.12 Modified Starches

Dextrin or dark British gum is a modified starch. It is a degradation product of starch obtained by heating it with mineral acid or roasting at 160°C until it becomes completely soluble in water. Generally, 20–50 parts of dextrin per 100 parts of printing paste is used.

3.6.1.13 Cellulose Derivatives

Cellulose derivatives which are used in thickeners are:

- (a) Methyl cellulose
- (b) Sodium carboxy methyl cellulose (CMC)

3.6.1.14 Methyl Cellulose

Methyl ether of cellulose is prepared from wood pulp or cotton linters. The ether is insoluble in boiling water and also in the presence of alkali but soluble in cold water. It retains its consistency satisfactorily during storage.

3.6.1.15 Sodium Carboxy Methyl Cellulose (CMC)

It is prepared by reacting alkali cellulose with monochloroacetic acid. This thickener is stable to alkali and hence can be used for printing vat colors. The removal of CMC from the cloth after printing is very easy.

3.6.1.16 Sodium Alginate

It is a sodium salt of alginic acid which is extracted from seaweed. Sodium alginate has a similar chemical structure to that of cellulose.

Sodium alginate has the following advantages:

- It is soluble in cold, warm or hot water.
- Only small amounts of sodium alginate are required in the preparation of printing pastes.
- Due to its wetting power, the penetration of the dye in the fabric is superior.
- It can be used with most dyes and is particularly suitable in the printing of reactive dyes.
- Removal of thickener is easy and thus the cloth remains soft after printing.

3.6.1.17 Emulsion Thickeners

An emulsion is a type of colloid formed by combining two liquids that normally don't mix. In an emulsion, one liquid contains a dispersion of the other liquid. Emulsions may be either oil-in-water or water-in-oil. Technically, when generating oil-in-water versus

water-in-oil emulsions, one phase (known as the dispersed phase) is mixed into the other (the continuous phase). In other words, one liquid serves as a sort of base into which another liquid is added. When an emulsion is "oil-in-water", oil is in the dispersed phase and distributed into the continuous phase, water. In a water-in-oil emulsion, the roles are switched. Milk is an example of an oil-in-water emulsion, while butter is water-in-oil. A chief difference involves the use of emulsifying agents, since some are more compatible with one phase than the other. When the disperse or internal phase is higher in volume as compared to the external or continuous phase, the viscosity of the emulsion increases and it becomes thick or it loses free-flowing properties of liquids.

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

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

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

As coarse colloids they are subject to salting-out effects, and small additions of electrolytes reduce the viscosity, which is not the case with white spirit emulsions. Another disadvantage is that, on drying, this type of thickener leaves a residue, depending upon the requirements, 0.5-1% of solid substance remains on the textile. This residue, because of its extremely polar character, produces a hard, inflexible film which can (depending upon its chemical constitution and particularly in the case

of carbonamide groups) react with crosslinking agents. This rigid film has an adverse effect on the handle of the printed goods, although it is considerably less than that of polysaccharide thickeners. The effect on the handle can be satisfactorily balanced by adding suitable softening agents, such as polydimethylsiloxane, mineral oils or synthetic wax. The neutralizing agent, usually ammonia, in the synthetic thickener is removed under drying and fixing conditions; the free carboxyl groups in the polyanion then produce the acid medium which the binder and external crosslinking agents require for the crosslinking reaction. Printing pastes based on emulsion thickeners need about 0.5% potential acid, such as diammonium phosphate, in order to obtain the necessary acid medium during fixation.

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

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

The use of emulsion thickeners in textile printing may be summarized as follows:

- Emulsion thickeners came into existence with the rapid development of pigment colors.
- However, today, emulsion thickeners are also employed for printing other classes of dyestuff.
- In each system of emulsion there is a dispersed phase and a dispersing medium.
- When very stable emulsions are required, emulsification is brought about in the presence of a third component called the emulsifier.
- For textile printing, oil-in-water type of emulsion is popularly used.
- Kerosene-water emulsions have been widely accepted.
- Different types of emulsifiers are available, such as anionic, cationic and non-ionic.
- At present the non-ionic type of emulsifier is preferred, and alkyl-phenolethylene oxide condensates have proved most useful.

3.6.1.18 Synthetic Thickeners

These water-in-oil emulsion pigment pastes were not accepted by the European market, where fastness properties were of more importance. In Europe aqueous pigment systems, for use in oil-in-water emulsions, were developed. The o/w emulsions ultimately drove out the w/o emulsion-based systems, even in the United States. Eventually, synthetic thickeners became available. The aqueous-based synthetic thickeners are high molecular weight polymers containing an acidic monomer as an essential component (e.g., acrylic acid, methacrylic acid, maleic acid).

A synthetic thickener used for textile printing is a polymer dispersion. It includes at least one polymer selected from the group consisting of (A) at least one polymer derived from monomers having an ethylenically unsaturated double bond, (B) at least one ethylenically unsaturated carboxylic acid ester, (C) at least one ethylenically unsaturated carboxylic acid anhydride, and (D) at least one ethylenically unsaturated carboxylic acid amide. It also contains a synthetic carrier medium comprised of at least one biodegradable component, which may have varying respective biodegradability. It is selected from a group consisting of multiple esters (an ester of synthetic origin and an ester of natural origin), which are liquid at room temperature (Willmer and Fischer, 2021).

3.6.1.19 Non-Ionic Thickeners

The most common non-ionic thickening agent is polyethylene glycol ethers. The main commodities include Letexal HVW BASF of Germany, Japan's Dainippon Ink Ryuclve Reclucer 400 cone, thickener M from fatty acids esterified with polyethylene glycol.

Electrolyte did not affect the non-ionic thickeners, good adaptability, but not as an anionic thickening effect, therefore, a larger amount of printing paste glue manufacture hydrocarbons such as kerosene remains, constrained its further.

3.6.1.20 Anionic Thickeners

Anionic thickeners are polymeric electrolyte compounds, the molecules are rich in many ionizable carboxyl group and a lightly crosslinked copolymer characterized by low viscosity and strong thickening ability. They have good stability, good leveling and anti-spatter resistance. These have little effect on gloss of the fabric. The printing paste does not use hydrocarbons, but these are electrolyte sensitive and have poor adaptability.

3.6.1.21 Dispersed Liquid Thickeners

The polymer particles are little dewatered (approximately 1 μ m) and dispersed in hydrocarbon carrier oil, rich in co-stabilizers and emulsifiers. Common lazy hydrocarbon carrier oil is a light mineral oil. The particle size and evenness of spread of the dispersion of fine polymer are better than solid grinding followed by dispersion in a liquid commodity. When the thickener is in alkaline condition, the particulate diameter increases from 1 μ m to 10 μ m, the volume increases by 1000-fold.

The colloid thickener Alcoprint PTF (liquid dispersion type) is a high molecular mass with polyacrylic acid as the main agent in a suitable base (such as ammonia). It generates ammonium polyacrylate, thereby increasing viscosity. The polymer has a micro-crosslinked structure, the onset of swelling in water, and the fetters of each other while suspended in the liquid phase, the constraint between the activists, increased viscosity, rheology similar to emulsion paste. PTF are attributable to pseudoplastic fluid, suitable for flat screen or rotary screen printing mortar, do not cause seepage representation, without adding impermeable agent (Polly, 2016).

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

3.6.1.22 Thickeners for Printing Reactive Dyes

Printing with reactive dyes gives brighter shades with good all-round fastness but the main problem is the availability of suitable thickeners.

- Thickeners based on starches cannot be used as reactive dyes react with these thickeners.
- Most of the natural thickeners are polysaccharides having plenty of hydroxyl groups. Most of them react with reactive dyes and give prints with poor fastness, color yield and rough handle.
- Among natural thickeners, sodium alginate, which is a mixed polymer of O-mannuronic and L-guluronic acid, does not react with reactive dyes. However, the cost of alginate is high and it is increasing rapidly because of non-availability of seaweeds.

To cope with the increasing application of reactive dyes, suitable substitutes were researched. Some of the approaches include:

- 1) Use of carboxymethyl cellulose (CMC); The degree of substitution of CMC should be high in order to get good prints, but highly substituted products are water insoluble.
- 2) Use of synthetic thickeners; These thickeners give good results, but are costly and sensitive to electrolytes.
- 3) The third way is to modify the natural thickener to make it anionic. The raw material should be abundant and cheap. In a study by Gulrajani and Roy Choudhury (1981), carboxy-methylation was carried out by reacting guar gum with monochloroacetic acid (MCA) and sodium hydroxide. The modified guar gum performed satisfactorily with some reactive dyes, but some reactive dyes reacted with the modified gum give stiff handle.
- 4) Sometimes emulsion thickeners are used either alone or in combination with sodium alginate.

Textile printing is mostly done with aqueous paste while in paper printing more rapidly evaporated non-aqueous solvents are used as high-speed drying is necessary. The components of the liquid textile printing paste must include all necessary wetting, dispersing and fixing agents, in addition to the colorants, and may be soluble or insoluble. No separation of insoluble components must occur, and the incorporation of viscosity-increasing protective colloids helps in this respect. Finally, as the viscosity of the print paste must be suitable for the method to be employed and the substrate to be printed, appropriate amounts of thickening agents must be used.

There are two essential reasons for the importance of the viscosity, and hence the flow, of a print paste. It affects the amounts of paste applied as well as the spread of paste, on the surface of the textile material and into its structure. For example, the paste in an engraved roller is transferred completely to the fabric pressed against the roller only if there is time for it to flow into the fabric structure. Highly viscous pastes flow slowly, so that at high speeds the time is often too short for total transfer to occur. Even at low speeds, transfer is viscosity-dependent. If only a small volume of viscous paste is applied, it may not spread to cover all the fibers of the threedimensional fabric. In practice, therefore, the upper limit of the viscosity is determined by the flatness of the fabric surface and the conditions of the printing process. The lower limit also depends on the process conditions, but is mainly determined by the need to keep the print "smart" – that is, having a sharp printed mark surface. The appearance of the print will be unsatisfactory if only the high spots of fabric surface are colored and those parts of the yarn surfaces that are visible, but which lie at a lower level, are left uncolored. The use of pressure helps in this respect, but the amount of pressure must be controlled for other reasons (Miles, 2003).

Wide differences in apparent viscosities between natural and synthetic thickeners, which give rise to their being called long flow or short flow are found only at the low rates of shear that occur in pouring. At the high rates of shear that occur in brushing, spraying, or coating (above 100 s⁻¹), all thickeners examined are highly shear thinning, with similar apparent viscosities and similar slopes for the "viscosity profiles".

Viscosity profiles could be fitted by a power-law equation (that is, were they linear) only within a narrow range of shear rates. Most regression equations required a quadratic or cubic term or both to fit the data adequately.

Process variables and solution properties that alter "single-point" apparent viscosities do not necessarily affect the profiles, by not interacting with changing shear rates. Slopes of viscosity profiles changed with thickener composition, molecular weight, and concentration, and by addition of electrolyte (NaCl). Changing temperature and pH did not alter the profile within the range of variables examined.

Profiles of solutions of different thickeners prepared for equal paste spread in screen printing intersected at a common point, corresponding to an apparent viscosity of about 8,000–10,000 cps at a shear rate of 20 s⁻¹.

The change in apparent viscosity with concentration is less for low-solids synthetic thickeners than for natural gums or for starch or cellulose derivatives. The dependence of apparent viscosity on concentration can be estimated from the initial slope of the viscosity profile for one concentration (that is, the coefficient of the linear term in a regression equation for viscosity on shear rate).

From the estimated or measured dependence of viscosity on concentration and from the measured viscosity profile, the concentration required for any viscosity at any shear rate from 0.1 to 10,000 s⁻¹ can be calculated; in particular, the thickener concentration required for optimum definition, levelness and penetration in screen printing (Guion and Hood, 1985).

3.6.2 WETTING AGENT

The high surface tension of water prevents wetting of the dye powder. Therefore, it is necessary to use a suitable wetting agent while dissolving the dye to obtain a smooth paste of the dyestuff without formation of any lumps. Lumps, if allowed

to remain, get deposited on the cloth during printing, producing dark spots. The wetting agent reduces the surface tension of water and facilitates the wetting of dye particles and ultimately results in solubilizing of the dye. The use of wetting agent is generally beneficial in dissolving dyestuff; for example, Turkey red oil (T.R.O.), Lissopol C, Igepol T and more. During the preparation of printing paste the dyestuff which is usually in the powder form is dissolved in a small amount of water.

For insoluble dyestuffs like vats and Napthols, wetting agents are used to facilitate wetting of the dyestuff. For direct, acid, basic and reactive dyes, which are watersoluble, a wetting agent is not normally required. For such water-soluble dyes, lump formation can take place if water is poured over the dye powder or if the dye powder is added to water.

3.6.3 HYGROSCOPIC AGENT

The function of hygroscopic agents used in printing paste is to take up sufficient amounts of water during steaming to give mobility to dye molecules, to enable them to transfer to the fiber. Urea, glycerin, diethylene glycol and urea are generally used as hygroscopic agents in printing.

3.6.4 DISPERSING AGENTS

These are used to prevent precipitation of dye particles as the concentration of the dyestuff in the printing paste is high. Examples include di-ethylene glycol, thio-di-glycol and sodium benzyl sulphanilate.

3.6.5 FIXATION ACCELERATORS

These are used to improve dyestuff fixation in printing as well as to shorten fixation time by swelling compounds. They are also effective in preventing fixation unevenness that may be caused by fluctuation of conditions for dyestuff fixation such as time, temp, humidity and so on.

Examples of fixation accelerators are:

- P-phenyl phenol is applied for polyester.
- Thiourea is applied for polyamide.
- Resorcinol is applied for polyamide, cotton and acrylic fibers.

3.6.6 ANTIFOAMING AGENT

Dyestuffs have a tendency to froth during color preparation and printing because of the presence of wetting agents, continuous agitation by the printing roller and brush finisher. In the case of roller printing, wetting agents are used in the printing paste and simultaneously continuous agitation of the paste is also taking place in the color box in which printing paste is kept. Thus, a considerable amount of foam is produced in the color box. The print becomes specky and lighter in shade due to the presence of foam. This may also cause overflowing of the color paste, which then falls on the other color box in roller printing machines.

The foam formed in the color box produces faulty prints, and to avoid this, a defoamer should be incorporated in the printing paste. Silicone defoamer, readily emulsifiable hydrocarbon and sulfated oils may be used for this purpose. Perminal KB (ICI) is neutral yellowish-brown liquid containing an aqueous emulsion of sulfated sperm oil and pine oil. It is anionic in nature, miscible with water, and gives milky dispersion which is stable to alkalis. A mixture of ortho, para and meta-methyl cyclohexanol has a power of reducing the foam and is widely used in textile printing. Emulsified pine oil is readily miscible with water and can be used as defoamer. Triactyl phosphate is also a very good defoaming agent.

3.6.7 OXIDIZING AND REDUCING AGENTS

In order to develop the final color in steaming or in subsequent after-treatment as in printing of solubilized vat dye, aniline black and some oxidizing agents are added to the printing paste. They are also used in certain styles of printing such as color discharge/oxidation discharge. The most commonly used oxidizing agents are:

- a) Sodium, potassium, ammonium or aluminum chlorates
- b) Sodium and potassium dichromate
- c) Sodium and potassium chromates
- d) Potassium ferricynide (K₃FeCN₆)

The proportion of oxidizing agent should be carefully calculated. It should be such that it only discharges the color. The oxidizing agents are added during the preparation of printing paste, but it should react with the dyes only during steaming.

"Ludigol" or "Resist Salt", the trade names of m-nitrobenzene sulphonic acid, is used as a mild oxidant in printing vat discharge on direct color ground. It prevents the adverse effect of the reducing atmosphere on unprinted ground during steaming.

Reducing agents are used mainly for printing of vat colors, sulfur colors and so on, as well as for production of reducing discharge effect on the goods dyed with direct, vat, solubilized vat (indigosol) dyes and also in the resist style of printing with insoluble azoic colors.

Commonly used reducing agents are:

- a) Sodium hydrosulfite $(Na_2S_2O_4)$
- b) Sodium sulfoxylate formaldehyde (NaHSO₂.2H₂O.HCHO). This is commonly available in the names of Rongalite C, Formosol, Hydrosulfite NF, etc.
- c) Sodium bisulfite (NaHSO₃)
- d) Glucose
- e) Tin compounds (SnCl₂, SnCOOCH₃)
- f) Ferrous sulfate
- g) Thiourea dioxide [NH₂C(SO₂)NH₂]

3.6.8 BINDERS

Binders are used in pigment printing. A binder is a substance which can form a film at the printed portion. Albumin, casein and glue were historically used as binders cum thickeners. These were later replaced by cellulose esters such as cellulose acetate and cellulose nitrate. Then a large number of synthetic binders were developed, among which the most important are vinyl resins and acrylic resins. Helizarin binder UD (BASF) is formed from acrylic esters with styrene and gives prints with excellent fastness properties.

The binder film in a pigment print is a three-dimensional structure, the third dimension of which is of rather less importance than the other two. The binder is a filmforming substance made up of long-chain macromolecules which, when applied to the textile together with the pigment, produce a three-dimensionally linked network. The links are formed during some suitable "fixing" process, which usually consists of dry heat and a change in pH value, bringing about either self-crosslinking or reaction with suitable crosslinking agents. The degree of crosslinking should be limited, to prevent the macromolecules becoming too rigidly bonded, thus preserving some extensibility.

As the fastness properties of pigment prints are determined by the fastness of the binder film, the quality of a print depends on the quality of the binder.

- The binder film formed on the fiber must be transparent.
- It must be of even thickness, smooth and neither too hard nor too soft. It should be elastic and should have good adhesion to the substrate without being tacky.
- Further, it should have good resistance to mechanical and chemical stresses, but should be readily removable from the printing rollers, screens, backgreys and blankets during operation or shortly afterward.

The binder is a film-forming substance. It is made up of long-chain macromolecules. It produces a three-dimensionally linked network when applied to the textile together with the pigment. During curing or heat fixation, at a particular pH condition, the links are formed. This brings about either self-crosslinking or reaction with suitable crosslinking agents. The degree of crosslinking should not be very high, otherwise the macromolecules become too rigidly bonded, hampering polymer extensibility. The important criteria, which ensure that the pigment within the crosslinked binder film is fast to wear and cleaning, elastic, cohesive and perfectly adhered to the substrate, resistant to hydrolysis, as little thermo-plastic as possible and do not swell in the presence of dry-cleaning solvents. The binders used are all addition polymers, preferably copolymers such as Figure 3.18. The technique used is that of emulsion copolymerization leading to a product containing 40–45% binder dispersed in water.

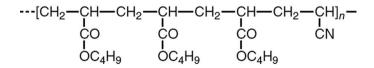


FIGURE 3.18 Chemical structure of a binder molecule.

Depending upon the properties required in the binding film (softness, elasticity, plasticity, solvent stability, light and weather fastness), binders can be "tailor-made" by choosing suitable base products (Schwindt et al., 1971). Typically, unsaturated monomers are used, such as vinyl chloride, dichloroethene, acrylic acid, methacrylic acid, acrylamide, acrylonitrile, acrylic acid esters, vinyl ethers and vinyl esters, styrene and diolefins like butadiene.

The monomers are dispersed by using sufficient amounts of suitable surfactants, and polymerization is initiated by means of free radicals originating from redox reactions, such as that between potassium persulfate and sodium bisulfite (Miles, 2003).

Special binders are also developed for printing polyester/cotton blended fabrics. These are based on styrene-butadiene and acrylonitrile-butadiene, which have good adhesion power for circular cross-section polyester.

Binders containing copolymers with N-methylol groups for "internal" crosslinking may be combined with poly-N-methylol compounds as "external" crosslinking agents. These are especially useful for prints on hydrophobic materials. The watersoluble methyl ethers of tetra- to hexa-methylolmelamines are preferred. They act mainly as adhesive agents between the textile and binder, but also contribute to the crosslinking at the surface of the binder film.

3.6.9 CARRIERS AND SWELLING AGENTS

Dyeing and steaming processes are carried out at high temperature. The compact structure of synthetic fibers, especially polyester, causes the penetration of the dye molecules in the fiber structure to be difficult under the condition of dyeing at boil and steaming at $100-102^{\circ}$ C in ager. It is known that certain hydrocarbons, substituted hydrocarbons, phenol and so on, accelerate the rate of dyeing of polyester with disperse dyes from an aqueous medium at about 100° C. These substances are called carriers and one of their functions is to swell the fibers so that the dye molecules can diffuse easily inside the fiber. Therefore, they are also known as swelling agents. Generally, urea is used as swelling agent for printing various dyes on different fibers.

Some important carriers used for polyester are:

- a) Ethyl alcohol
- b) Diethyl alcohol (DEG)
- c) Diethylene glycol diacetate (DEGDA)
- d) Polyethylene glycol
- e) Ammonium sulfocynide
- f) Thiodiethyl glycol
- g) Ethyl lactate
- h) Diethyl tartrate
- i) Phenols

These carriers should be completely removed from the fabric after dyeing or printing is over. Otherwise, they may decrease the light fastness of the dyed or printed goods. These carriers may also be toxic in nature and therefore they must be used very carefully.

3.6.10 AFTER-WASHING AGENTS

After-washing or soaping of printed goods is an important operation.

It serves two purposes, namely:

- a) It removes the thickener from the printed goods and thereby improves the handle of the cloth.
- b) It helps in developing true shades and improves the fastness properties of certain dyestuffs.

Several after-washing chemicals are available which are probably a mixture of various chemicals like dye-fixing chemicals, anti-staining agents and cleansing agents.

3.6.11 MORDANTS

These are used in the printing of basic dyes on cotton or poor wash-fast acid dyes on wool and silk. A mordant is a substance having affinity for both the fiber and the dyestuff. Tannic acid along with tartar emetic was once very popular as mordant. "Katenol O", which is thiophenol, is also employed as mordant.

3.7 ENVIRONMENTAL ASPECTS

Textile wet processing, including dyeing, printing and finishing, is used in almost all textile products to create colors, patterns and special performance characteristics. These processes have long been criticized for their adverse environmental impacts because dyes and other chemicals are used. Although the textile industry has been working on recycling and reducing waste, the net environmental effect of textile wet processing is still a concern. During the processing of textiles, pollution also comes from the finishing and dyeing/printing processes. So far, several new technologies or materials have been used to reduce the production of waste by-products as well as air and water pollution. For example, to minimize environmental impact, textile manufacturers have provided a database to help mills and suppliers to exchange information on pollution reduction.

A powerful, environmentally responsible catalyst developed by scientists at Carnegie Mellon University significantly decolorizes dyes and removes them from wastewater released from textile mills for recycling (Ward, 2003).

Consumer decisions in product purchasing play a vital role in pushing the textile industry toward "green" or environmentally responsible production However, currently, consumers are faced with a wide range of products, and one can easily find numerous products that are labeled as "environmentally responsible products" or "made from 100% recycled materials". It is not easy for consumers to make informed environmental decisions when purchasing textile products.

Given the large size of the printing industry, and the extraordinary volume of chemicals it consumes, it is not surprising that it also generates a significant amount of pollution. Gaseous emissions have been identified as the second greatest pollution problem (after effluent quality) for the textile industry – and these are largely generated in printing. Speculation concerning the amounts and types of air pollutants emitted from textile operations has been widespread but, generally, air emission data for textile manufacturing operations are not readily available. Air pollution is the most difficult type of pollution to sample, test, and quantify in an audit. According to the US EPA, the printing industry releases 99% of its total Toxic Release Inventory (TRI) poundage to the air, while the remaining one percent of releases are split between water and land disposal. This release profile differs significantly from other TRI industries which average approximately 60% to air, 30% to land, and 10% to water release, respectively. Average VOC emissions per textile print line are 130 Mg (tons)/year for roller and 29 Mg/year for flat and rotary screen (OECOTEXTILES, 2012).

In 1995, more than 41 million pounds of toxic compounds were transferred or released into the environment by the printing industry in the United States alone (EPS, 1997). This table shows some of the polluting chemicals used by the tex-tile printing industry. All ten are petroleum-derived.

Chemical	Releases and transfers in millions of pounds
Toluene	4.2
Methyl Ethyl Ketone	6.3
Glycol Ethers	0.4
Xylene	0.2
Methyl Isobutyl Ketone	0.6
Methanol	0.3
1,1,1-Trichloroethane	0.3
Ethylene Glycol	0.5
Dichloromethane	0.1

These VOC emissions are high because of the great quantity of solvents used in the industry. The volatility that helps minimize ink drying times also presents a health and safety risk. The solvents used in the printing pastes are typically respiratory, skin and eye irritants. But there are also more dire consequences – for example, a study done on Indian printing workers has found abnormal changes in their chromosomes. With such a high percentage of the paste being volatile, solvent vapors are released during printing and present throughout the printing production area. Also, the fabric will continue to off-gas solvents after the material has been printed, especially if it has been rolled up (Sellappa et al., 2010).

Data on ethylene glycol mono-n-butyl ether is used to represent all glycol ethers because it is the most commonly used glycol ether in printing. It can leach into ground water, and reacts with photochemically produced hydroxyl radicals. For humans, moderate exposure may cause central nervous system depression, including headaches, drowsiness, weakness, slurred speech, stuttering, staggering, tremors, blurred vision and personality changes. These symptoms are such that a patient, in the absence of an accurate occupational history, may be treated for schizophrenia or narcolepsy. There are three general types of textile inks (OECOTEXTILES, 2012):

- Traditional solvent-based inks
- Water-based inks
- Plastisol inks

The two inks used most often in textile printing are water-based (used mostly for yard goods) and plastisol inks (used for printing finished goods, such as t-shirts, sweatshirts and tote bags).

3.7.1 SOLVENT-BASED INKS

The solvent has two primary functions:

- 1) To carry the ink to the substrate, and
- 2) To evaporate quickly, leaving only the ink film on the substrate.

While water is a solvent, the name solvent-based ink is used to describe a highly volatile solvent such as 2-butoxyethyl acetate, cyclohexanone and n-butyl acetate.

Solvent-based inks are considered the least environmentally friendly due to the highly volatile solvents given off during printing and drying. The petroleumbased binder used in many solvent-based inks could be replaced with renewable resources such as vegetable oil or soy. The downsides are that the inks dry very slowly, are less durable, and still contain solvents emitting VOCs during printing.

There are now inks on the market called Eco Solvent inks. To most people, "eco" means ecological, and to be fair these inks are not as nasty as full solvent inks. But these inks generally contain glycol esters or glycol ether esters – both derived from mineral oil – hardly a renewable resource or an ecologically sound process. Tony Martin, president of Lyson Inc., suggested we call these inks "mild" – versus the "aggressive" – traditional solvent inks. Also, since these inks are generally used to print onto PVC, the green claim sort of gets overlooked by the elephant in the substrate.

3.7.2 WATER-BASED INKS

These use water as the main solvent. But that does not mean that water is the ONLY solvent used. It is significant to note that many water-based inks contain "co-solvents" which may even be petroleum-based solvents. The reason these co-solvents are used varies, but a common reason is to decrease the time and heat necessary to cure the ink on the fabric. There are two types of water-based inks:

3.7.3 TRADITIONAL (AIR DRY) INK

Traditional air dry ink soaks into the cloth and binds with the fibers providing good colorfastness and wash ability.

3.7.4 DISCHARGE INK

Discharge ink removes the original dye/color from the garment and replaces it with a color/pigment. Discharge inks are now available in formaldehyde free formulations, such as the Oasis Series by Wilflex, making them safer for the user and the environment.

Water-based inks are usually less expensive than solvent-based inks and are similar in quality, gloss and adhesion.

Many printers observe that water-based inks have more vibrant colors and print more crisply than their solvent-based counterparts. The sharper definition possible with water-based inks allows printers to use finer dot patterns in screened process printing. Water-based inks are a good choice when a "soft hand" is desirable. (A soft hand is the condition where the ink film cannot easily be felt with the hand when passed across the surface of the fabric. This effect is often used as an argument for why water-based is preferable to plastisol because plastisol may affect the handle (i.e., stiffness) of the printed fabric.

These inks are inexpensive and easy to manufacture. In fact, with some experience and the proper equipment, printers can even make them in small batches from basic natural components. They have a very limited shelf life and are difficult to re-use, so they generate more wasted ink than regular plastisols or more complex, manufactured water-based inks. While this type of water-based ink is considered a very green alternative, this extra waste is something to consider.

An advantage often cited for water-based inks is that they do not require organic solvents when cleaning the presses. But there is a common misconception that because water can be used for cleaning screens, squeegees and tools, that the wastewater can just be discharged into the sewer. However, the water-based ink is not just water. There are pigments, binders, thickeners, and sometimes even co-solvents in the ink residue.

Many printers believe that screen printing using water-based inks is the cutting edge of textile printing. So why isn't everybody using them?

Water-based inks cure as water evaporates out of the ink so they have a longer – and more difficult – drying time than plastisol inks. This means that the water – along with whatever in the ink evaporates with the water – enters the environment.

If using water-based ink, the facility must have the drying capacity to remove the water. The dryers used for water-based printing tend to be larger than those needed for plastisol. In plastisol printing, the ink film must only reach the cure temperature for a brief moment. With water-based ink, the temperature must be reached and then held until all of the solvent (water) is removed. There are water-based inks that will air dry, but they are usually only acceptable for craft level printing as the room required for curing greatly reduces productivity.

Finally, all water-based inks can start to dry out during use, so care must be taken to prevent the ink from drying on the screen. If water-based ink is left in open mesh for even a short period of time, it can clog the mesh and ruin the screen. Practiced water-based ink printers must always be conscious of how long a screen sits between prints to prevent the ink from "drying in". While modern water-based inks are less prone to this phenomenon, it is still a concern. In addition, overall shelf life is limited. There have been major improvements in manufactured water-based inks in recent years. These newer inks have a number of performance advantages over the basic water-based inks discussed earlier and are as potentially eco-friendly and sustainable as any alternative. For example, they resist drying, and remain useable far longer than traditional water-based and discharge inks. They can be re-constituted with water – and additional binder, if needed – which can cut back on waste. Shelf life of these newer water-based inks is substantially longer as well because the manufacturers have developed technology to encapsulate the water in the ink in such a way that it does not readily evaporate until printed.

Much like traditional plastisol, these water-based inks are sold ready to use as colors or underbases and have a thicker viscosity that yields greater opacity on finished prints. They can be reduced with water and other modifiers for a softer hand.

3.7.5 PLASTISOL INKS

Plastisol inks, commonly used for textile printing and especially for t-shirts, are a PVC-based ink composed of a clear, thick plasticizer fluid and PVC resin. The full name for PVC is polyvinyl chloride. The PVC life cycle results in the release of toxic, chlorine-based chemicals which end up as by-products such as carcinogenic and highly toxic dioxin and PCB. The major health concern about plastisol inks is not that they are PVC-based but that they contain phthalates. Phthalates are added to PVC plastics to transform a hard plastic into a soft, rubbery plastic by allowing the long polyvinyl molecules to slide against each other instead of rigidly binding together. These phthalates used in plastisol ink to make the PVC flexible are also carcinogenic and much research has been done which substantiates the damage phthalates do to us, especially to fetuses and newborns. They are released into the environment during the printing and curing of the ink and they will continue to exhaust toxins when exposed to a radiant heat source, such as a dryer or even sunlight. Plastisol inks contains virtually no solvents at all.

Plastisol does not "dry". In order for a compound to dry, there must be evaporation of some kind of solvent. These inks typically contain less than 1% VOC. Some water-based plastisol inks can contain about 30% VOCs. Since plastisol has little or no solvent, it cannot dry. Plastisol is a thermoplastic ink - meaning it is necessary to heat the printed ink film to a temperature high enough to cause the molecules of PVC resin and plasticizer to crosslink (i.e., bond to the fabric) and solidify, or cure. Crosslinking agents must be used to affect the bonding, and formaldehyde is often a necessary component of these crosslinkers. The temperature at which most plastisol for textile printing cures at is in the range of 300°F to 330°F. Because of this characteristic, plastisol can be left in screens for long periods of time without clogging the mesh, the lids can be left off of the ink containers (although keeping them covered is a good practice to keep lint and dirt out of the ink). And ink left at the end of the job can be returned to the container for reuse without any adverse effects. This last practice is a great benefit in reducing waste product. It is ready to use right out of the container more than 90% of the time. In most applications, it can be printed wet-onwet, which allows for increased production speeds. It comes in formulations that can be printed on light and dark fabrics.

Since plastisol is a thermoplastic, it will remelt if it comes in contact with anything hot enough. For that reason, plastisol prints cannot be ironed. If an iron touches a print, it will smear the ink.

Plastisol ink also creates an ink film that can be felt with the hand. The higher the opacity of the ink, the greater the hand. This heavy hand is considered a disadvantage at the consumer level.

Because both PVC and phthalates are chemicals of concern, many companies are offering phthalate-free plastisol inks. These non-phthalate inks are not as easy to work with as standard plastisols, but it is possible to use them to accomplish most of the common printing techniques. In addition to non-phthalate plastisols, there are some new acrylic-based screen printing inks that are sometimes referred to as non-PVC and non-phthalate plastisols. Why? Well, an acrylic-type resin replaces the PVC resins used in regular plastisol. Also, the plasticizer in acrylic inks is normally non-phthalate, making these inks an even more eco-friendly alternative.

With some experience, acrylic inks can be successfully made into high-density designs. The finished prints lack the soft finish of a standard high-density plastisol print, but this may be an acceptable compromise to some customers.

Acrylic inks are usually a little more costly than standard plastisols and are substantially more expensive than standard water-based inks.

The hazards of plastisol printing inks are not just to personal health but also to environmental health. Garments coated with plastisol inks do not decompose and they are difficult to recycle. The result is that you may soon grow tired of your Rolling Stones concert t-shirt and trash it, but it will live on in immortality in the local landfill. If clothing designed with PVC plastisol ink is incinerated, the trapped dioxins plus hydrochloric acid (a primary component of acid rain) are released into the atmosphere.

New inks have also been developed for digital printing, such as latex, resin and UV curable inks.

The majority of emissions to the atmosphere from textile printing is from the drying process, which drives off volatile compounds. The largest VOC emission source is the drying and curing oven stack, which vents evaporated solvents to the atmosphere. Another source of fugitive VOC emissions comes from the "back-grey" (fabric backing material that absorbs excess print paste), which is dried before being washed. In processes where the back-grey is washed before drying, most of the fugitive VOC emissions from the back-grey will be discharged into the wastewater. In some roller printing processes, steam cans for drying printed fabric are enclosed, and drying process emissions are vented directly to the atmosphere (OECOTEXTILES, 2012).

Other environmental hazards in printing textiles come in the screen and equipment cleaning steps, which use lots of water. When a printing a batch is over, for example, there are still approximately 1.5 gallons of printing paste in the system, predominantly in the tubes that run between the paste reservoirs and the screens. This is simply rinsed out and flushed down the drain. If using plastisol inks, in order to emulsify the ink for easy removal from screens, squeegees, flood bars, spatulas and work surfaces, it is necessary to use some type of solvent. Solvents used to clean printing equipment include toluene, xylene, methanol and methyl ethyl ketone (MEK). In addition, blankets used to transfer the ink-filled image to sheets of paper are cleaned with washes that contain glycol ethers and 1,1,1-trichloroethane (TCA). The type of solvent used depends largely on the equipment to be cleaned. For example, a blanket wash must dissolve ink quickly and dry rapidly with minimal wiping. Conversely, a solvent that is intended to clean a chain of ink rollers must evaporate slowly, to ensure that it does not flash off before it has worked its way through all the rollers. Water based inks contain co-solvents, additives, dyes and/or pigments, which make the water clean-up full of possibly hazardous materials. All of these components must be washed thoroughly.

Irrespective of the type of inks used, all printers attempt to reclaim screens, which are a major cost item. Screen reclamation is a particular challenge to screen printers, because inks and solvents cannot go down the drain and some of the chemicals used to reclaim mesh are restricted. The wastewater will contain particulates comprised of ink pigment, emulsion and emulsion remover. Reclaiming screens involves these steps:

- Removal of paste: Any and all excess paste in the screen should be "carded off" for reused on another job. The screen must then be washed to remove any remaining paste because the paste will interfere with the process of removing the stencil. Screen cleaning solvents are a source of VOC emissions.
- Removal of emulsion: The stencil or emulsion is removed by spraying the screen with a solution of water and emulsion remover chemicals which is comprised mainly of sodium metaperiodate, then rinsing the solution away with fresh water.
- Removal of haze or ghost image: Finally, if any haze or "ghost image" remains, a haze remover must be applied. Some haze remover products are caustic and can damage or weaken the screen. Haze removers make screens brittle and tear easily, therefore only small amounts should be used. Ghost image is a shadow of the original image that remains on the screen caused by paste or stencil caught in the threads of the screen.

The best way to reduce VOCs during screen reclamation are related to technology and best practices, such as using high pressure wash systems and modifying how chemicals are applied to the screens.

The waste ink and the solvent must be disposed of properly in order to minimize environmental impact. There are three major areas of concern for this wastewater:

- Heavy metals, which can be found in the residue of ink, can enter the sewer system and contaminate sewage sludge.
- Heavy concentrations of certain chemicals can disrupt the pH balance at the treatment plant and disrupt the bacterial systems essential to the sewage treatment process.
- Combinations of mixtures with low flash points can cause flammability concerns in the sewage system.

Leftover print pastes cannot be allowed to enter the wastewater treatment system. It must be disposed of as a solid waste. Sites where sludge piles are used can have environmental problems with ground and groundwater contamination. These sludge storage areas should be equipped with waterproof linings to prevent this from occurring (OECOTEXTILES, 2012).

In fact, textile printing is becoming a significant source of wastewater as waterbased materials replace organic solvents. The wastewaters originating from this operation are often strong and may contain toxins, although their volume is still quite low.

The screen printing industry has been very proactive in the creation of products that can minimize the impact of these cleaning processes. Solvents are available that are more environmentally sensitive than traditional petroleum-based solvents. Companies are beginning to market biochemical cleaning solutions, inks and additives to replace current solvents or toxic chemicals – examples include the use of terpene d-limonene (derived from citrus fruit), coconut oil, soybeans, seaweed and fatty amides. In addition, there are many types of filtration and cleaning systems available to capture inks and solvent residues to reduce the amount of solids discharged into the sewer system.

There are some things every printer can do to reduce their environmental impact:

- Minimize downtime on the press.
- · Make rejects history.
- Maintain dryers; is it really worth saving money by buying that second hand dryer? A new one is 30% more efficient, twice the price but the energy savings will pay the difference in 9 months. An average printing line has a nominal power rating of 75 kW, most of which is required for the drying process.

3.8 FUTURE TRENDS

Globalization has changed the fashion industry and its approach towards sustainability. Fast changing trends are majorly focused on synthetic dyes and fabrics. These products have thus far failed to bridge sustainability and eco-friendly designs.

In the eco-friendly environment, it is very important to assure that human beings live in a world of hygiene and freshness. The necessities of human beings are not fulfilled with the provision of food, clothing and shelter alone, but it is important that the environment is clean and livable with pure and safe air as well as water. The sourcing of a truly sustainable fabric is difficult because there is very little transparency about the quality of dyes and chemicals used during dyeing and printing of fabrics, even in the case of organic cloth. Synthetic dyestuffs are made of nasty chemicals and only a few of them are prohibited by laws due to their proven toxicity, which means that many dyestuffs with unsafe ingredients are still permitted and commonly used in conventional industrial dyeing.

For the textiles dyed or printed with synthetic dyes, one should look for suppliers whose products possess eco-labels issued by well-known authorities like GOTS, blue-sign and so on. The textiles dyed or printed with natural dyes should be mordanted (pretreated) with alum; never with chrome, copper or tin. A responsible natural dyer should disclose their mordanting information with no hesitation. Low-impact (less polluting) reactive dyes have been developed, which have been classified by the EU as eco-friendly. These dyes contain no heavy metals or other known toxic substances, and do not need mordants for fixation. Due to the high cost of these dyes, it is cheaper to reclaim the unexhausted dye from its effluent rather than to discharge; this is advantageous from an environmental point of view. The water can also be recycled.

The use of sustainable natural dyes has been in India for thousands of years and is a part of India's cultural identity. In ancient days, dyed textiles were status symbols, and because of their costs, were possessed by the rich people. They were extracted from plants, animals and minerals. Madder and indigo are two major natural dyes used in India since 2500 BC.

Before the advent of synthetic dyes, natural dyes were widely used, often together with mordants such as alum, to dye natural fibers including wool, linen, cotton and silk, but their use declined after the discovery of synthetic dyes. However, interest in natural dyes has been revived recently owing to increasing demands on manufacturers to produce more environmentally friendly alternatives to petrochemical-derived dyes. One main issue associated with the use of natural dyes in the coloring of textiles is their poor to moderate light-fastness, and despite their long tradition, not all natural dyes are especially environmentally friendly. Some natural dyes have no or little affinity for the textile materials, and they require heavy-metal salts as mordants for fixation and color-fastness. Natural dyes may be sustainable but they need sufficient water and land to produce, and there is insufficient dye yield per acre of plant material to sustain industrial-scale production (Roy Choudhury, 2017).

Natural dyes as such are sustainable as they are renewable and biodegradable but they cannot fulfill the huge demand from the textile sector in view of the preferential use of land for food and feed purposes. Production of natural dyes from natural resources may result in deforestation, putting endangered species at stake. For these reasons, the Global Organic Textiles Standard (GOTS) permits the use of safe synthetic dyes and prohibits the use of natural dyes from endangered species. In general, the shortcomings of natural dyes are much less significant than the tremendous environmental advantage they offer. Just because the dye itself is natural, it doesn't mean that the crop is sustainable. Pesticides may have been used on the crop and it may be genetically modified or irrigated unsustainably. Some colors come from forest products, depleting valuable natural resources. Also, other substances used in the coloring process may well be environmentally damaging.

Textile chemicals have a bad reputation of creating pollution globally, and many of them are indeed unsustainable. Thousands of chemicals are in use and the list of such chemicals is changing every day. It is very difficult to keep a track of such chemicals, and creation of pollution goes unabated. The government of Sweden is set to open a substitution center that will facilitate SMEs in finding safer alternatives to hazardous substances, with significant focus on textiles. The center will be located at The Swedish School of Textiles, Boras, and will enable knowledge sharing between large and small companies, associations, academia, authorities and industry, ultimately helping their sustainable development (Textilefocus, 2018).

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4 Various Means of Printing Textiles

4.1 INTRODUCTION

Textile printing is a method of coloration of textile fabric or other continuous strand of material in which colors are applied in selected portions with definite patterns/ designs or in random fashion. In properly printed fabrics the color is bonded with the fiber, so as to resist fading of color on washing and friction during use. Textile printing is similar to the dyeing process but in the latter the whole fabric is uniformly covered with single color, whereas in printing one or more colors are applied in certain portions of the fabric. In dyeing, coloration may be desired to be in all types of shades – pale, medium or dark shades. The shades desired may be dull or bright. However, in printing, leaving exceptions, the desired shades are mostly dark and bright so that the designs or patterns can be clearly visualized. Printing is, therefore, carried out with more concentrated dye solutions than those in dyeing. In dyeing, the dyes are allowed to penetrate uniformly in all directions including interior of the fibrous materials and both sides of the fabric. In printing, the movement of color is restricted to desired portions with the help of thickening agents or viscosity modifiers. The penetration of dyes on the backside (i.e., surface opposite to the printed surface) is prevented or restricted so that the printed design can be prominently viewed on the printed surface.

The dyeing process consists of four stages:

- 1) Transport of the dye to the fiber surface
- 2) Adsorption of the dye on the fiber surface
- 3) Diffusion of dyes into the interior of the fiber
- 4) Fixation of the dye on the fiber

All the above stages may occur in one step or in one machine sequentially. The printing process, however, involves several steps (mostly printing, drying and fixation) and several machines. In printing, wooden blocks, stencils, engraved plates, rollers, or silk screens are used to deposit colors on the fabric. Printing paste contains dyes thickened to prevent the color from spreading by capillary attraction beyond the limits of a pattern or design. The printed fabric is immediately dried to prevent spreading of color paste followed by fixation by steam or dry heat.

Printing processes are, therefore, much more complicated, delicate, multistep operations demanding careful control. The unacceptable dyed materials may be redyed or subject to shade corrections. However, defective printed materials cannot be printed again and is rejected. Such printed materials cannot be rectified. A textile printing process is generally described in two ways:

- 1) Styles or techniques of printing
- 2) Methods or machines of printing

The styles of printing refer to the composition of the printing pastes as well the sequences of operations to achieve a particular printing effect; in other words, the chemical aspects of printing. Methods of printing describe the tools and machines used in the printing process; the mechanical aspects.

4.1.1 STYLES OF PRINTING

Style refers to the manner by which a particular action is performed. Styles of printing mean the printing paste and the sequences of operations to be followed during printing. Styles of printing mean the manner in which a printed effect is produced. There are many styles of printing as follows:

- 1) Direct style of printing
- 2) Discharge style of printing
 - White discharge
 - Color discharge
- 3) Resist style of printing
 - White resist
 - Color resist
- 4) Spray printing
- 5) Flock style of printing
- 6) Crepon/crepe style of printing
- 7) Metallic style of printing
- 8) Emboss style of printing
- 9) Rubber printing
- 10) Burn-out printing
- 11) Transfer printing
- 12) Digital printing

Out of the above styles, the most important and most widely used conventional styles are direct, discharge and resist styles. Transfer printing is popular for the printing of garments. However, the popularity of the digital style of printing is increasing by leaps and bounds and establishing itself as next generation textile printing.

4.2 DIRECT STYLE OF PRINTING

The most common style of printing textile fabric is direct printing. In direct style, the dye is directly applied in the design portions of the fabric. It is the simplest and oldest style of printing. It can be done on white fabric or on dyed fabric. The dye is applied on the fabric in paste form with the help of a machine or tool in selected portions of

the fabric as per design. Any desired pattern may be produced by necessary changes in the machines or tools. Instead of white scoured and/or bleached fabric, the fabric may be dyed in light colors and overprinted in dark colors. The printing paste is transferred to the selected areas of the fabric and the dyes and pigments adhere to the fabric surface after subsequent fixation by steam or dry heat. The fabric is finally soaped and washed to remove unfixed colorants.

The advantages of direct style of printing are as follows:

- 1) It is the easiest printing style to operate.
- 2) It is the least expensive.
- 3) It quickly provides final prints.
- 4) It is suitable for the printing of both simple and complicated designs.
- 5) Color matching with the original design sketch is easy.

Limitations of direct styles of printing are:

- 1) Colored blotches with sharp outlines and free of specks are difficult to produce.
- 2) It is difficult to incorporate small white or colored motifs on dark ground.
- 3) It is difficult to print fine designs with sharp outlines on knitted fabrics/ clothing.
- 4) If not done properly, colors in print may overlap or get displaced.
- 5) If not processed properly, the dyes may come off after a few washes.

4.3 DISCHARGE STYLE OF PRINTING

In this method, the fabric is first dyed with dischargeable dyes which are destroyed by subsequent oxidation or reduction. It is then printed with some discharging chemicals with or without a second non-dischargeable dye. It is finally subjected to steaming, when the dyes are decomposed in the printed portions. The printing paste used in this method contains a discharging agent, which bleach or destroy the dye in the printed areas. The resulting white discharged area brightens the overall design. When the second non-dischargeable dye is added in the printing paste, the ground color is destroyed and a second color is fixed in the discharged area. The discharging agent is an oxidizing or reducing agent capable of destroying colors by oxidation or reduction respectively. Potassium chlorate, sodium chlorate (oxidizing agents), sodium sulfoxalate formaldehyde and stannous chloride (reducing agent) are commonly used as discharging agents. The effects produced are very striking as the white or newly colored area brightens the overall design. This style of printing enables intricate and fine designs to be printed on the fabric. The fabric is thoroughly washed after printing and steaming. The discharge style of printing produces light, bright color on a dark background; printing is sharp and fine and easy to work. However, the major disadvantages of this method are the high costs involved as well as maintenance of perfect discharging condition, the failure of which may cause permanent defective prints.

4.3.1 WHITE DISCHARGE

The fabric is dyed with dischargeable dye following normal dyeing procedures and is then printed with the discharging agent followed by steaming. The discharged portion becomes white while the color of the ground non-discharged portion remains unchanged. A white design is therefore produced on the color ground. Figure 4.1 shows a white discharge fabric.

4.3.2 COLOR DISCHARGE

The dyestuffs, which are strongly resistant to the discharging agents, may be incorporated in the printing paste along with the discharging agent. The discharging agent discharges the color at the printed area. At the same time the non-dischargeable dyestuffs present in the print paste deposit and get fixed on the discharged portion of the fabric. As a result, colored prints on colored ground are obtained. In this way one or more colors may be applied using multiple blocks or screens one after another sequentially.

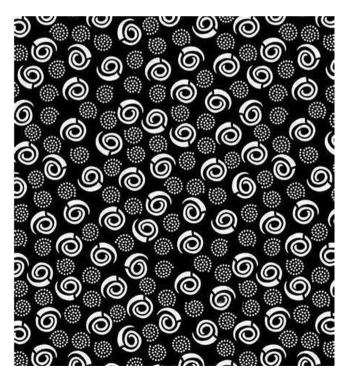


FIGURE 4.1 (a) White discharge printed fabric from Shree Krishna Textiles, Jodhpur, India.



FIGURE 4.1 (b) Discharge printed fabric from R.K. Dyers, Jaipur, India.

The advantages of discharge printing are:

- 1) Printed materials with large areas of ground color can be perfectly produced by discharge printing in terms of depth, levelness and penetration compared to those obtained by the direct and resist styles of printing.
- 2) Discharge printing is famous for the clarity and sharpness obtained in case of delicate, fine and intricate patterns on grounds of any depth. In case of blotch printing by direct style the print paste spreads unequally in different directions losing sharpness of prints and white patterns lose their crispness.
- 3) The extra processes required and the additional costs of discharge pastes result in quite higher production costs. But discharge printed materials are aesthetically superior and enable profit margins to be maintained or even improved. The higher costs of discharge printing are often offset when applied to long-lasting designs used for scarves, ties, cravats and dressing gowns (Miles, 2003).

The disadvantages are:

- 1) The process is very delicate.
- 2) Careless processing may cause permanent defective print.
- 3) The quality of discharging chemicals and steaming conditions should be continuously monitored.

4) The extent of discharge can only be known after thorough washing of prints after steaming and there is no means to rectify incompletely discharged prints at this stage.

Some of the problems faced during discharge printing are:

- One concerns the visibility of the design on the fabric. This is because the print pastes are often almost colorless and, when applied to a dark ground, are virtually invisible, especially in roller printing with the machine running at speed. The incorporation of white pigment improves visibility; fugitive, contrasting sighting colors help, as do fluorescent agents used with ultraviolet lights. This is an inevitable difficulty of the discharge style.
- 2) Controlled rapid drying of discharge prints is imperative if loss of reducing agent is to be minimized.
- 3) Another problem encountered is that of "facing" or "scumming", which is due to partial discharge of the unprinted areas of the dyed ground. This occurs mainly in roller printing and arises if the thin film or "scum" of discharge paste left on the unengraved surface of the printing roller is transferred to the fabric.

4.4 RESIST STYLE

In this method, the scoured and/or bleached fabric is first printed with a paste containing a resisting chemical (mechanical and/or chemical resist) like wax, china clay, acids, alkalis and so on that resists the penetration and fixation of dyes into the fabric. The printed fabric is then quickly dipped or padded in dye bath, so that the resisting agent remains unaffected and only the resist-free areas are dyed. After dyeing and fixation processes, the resist paste is removed, leaving white patterns on a dark background; this style is called white resist. A second dye may be added in the resist paste which fixes in the resisted area giving colored patterns on a dark background. This style is called color resist (i.e., multi-color effect).

Two most popular resist styles of printing are "Batik printing" and "tie and dye" style of printing.

The advantages of resist printing are:

- 1) Multi-color effect can be obtained at lower costs.
- 2) The process is much simpler and cheaper than discharge printing.
- 3) Less stable dyes are used as ground color in discharge style of printing. On the other hand, in resist style of printing, even though stable dyes are used, the contact time of the fabric with dye solution is much less and hence, the wash fastness of colors is lower than those in case of direct styles of printing.

The disadvantages of resist printing are:

1) The performance of resisting agents is limited. Hence, ground colors may penetrate in some portions of the resisted or printed area thereby hampering printing perfections.

4.4.1 BATIK PRINTING

Figure 4.2(a) shows a Batik printed fabric in which wax was used as a resisting agent and azoic colors were used for coloration. The fabric was first block printed with wax and then dipped quickly and successively in two baths – one containing naphthol AS solution dissolved with boiling caustic soda solution and the other containing diazotized azoic fast color base – and finally washed and soaped.

4.4.2 TIE AND DYE STYLE

Tie and dye style ("tie-dye") is a resist dyeing method in which the areas to remain undyed are blocked using different methods of tying and then the fabric is dyed; the areas that are tied remain undyed resulting in beautiful patterns. Dye penetration in the fabric is restricted by folding, knotting, plaiting, tying, stitching or other ways. This style is known by different names in different parts of the Globe such as Bandhani/Badhni/Lahariya/Ikat (India), Adhire Eleso (Nigeria), Shibori (Japan), Tjindai/Chindi (Malaya) and Hol (Indonesia). Ikat is yarn tie and dyed. All the patterns on the fabric are made by compressing the fabric in one way or the other, then binding followed by dyeing it. The fabric can be tied into the cloth to form shapes like circles, stars and rectangles. The bleeding and shading effects can also be done by damping the fabric before dyeing under proper control.

This is a very simple and inexpensive way to decorative plain clothes with beautiful and intricate looking patterns. The dyed areas are not sharply demarcated – there is a blurring of the lines resulting in the beautifully abstract appearance of the tie-dyed fabric

Tying is a very skillful job. A variety of tying methods are used in which the fabric is twisted folded, coiled, crumpled, or even gathered and stitched and then tied with yarn. Small polythene sheets may be used to increase the size of the bound areas. Stones and other small objects may be put inside the bound areas.



FIGURE 4.2 (a) Wax Batik-printed fabric (resist style).

After proper tying the fabric is put into a dyebath containing dyes and auxiliaries at the recommended temperature for a short time; subsequently dyes are fixed as per the conditions recommended for the particular dye class. The fabric should be in highly absorbent condition so that it can absorb sufficient dye during a short period of dipping. After dyeing, fixing and thorough washing, the ties are removed and the fabric is opened in full width. Figure 4.2(b) shows a typical Indian tie-dyed fabric. For tie-dyeing cotton, vat, azoic and cold brand dye reactive dyes may be used; for silk fabric, acid dyes.

Gupta (1990) showed various methods of binding fabric for tie-dye methods. Figure 4.2(c) shows a few methods of binding the fabric shown by Gupta: (a) Pleated,

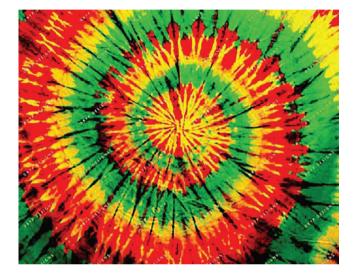


FIGURE 4.2 (b) Tie and dye (resist style) print.

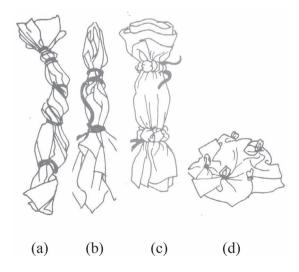


FIGURE 4.2 (c) Various methods of binding fabric for tie and dye.

twisted and tied; (b) Fabric picked up in a peak from the center and bound; (c) Channel sewn into the fabric have a cord threaded through, which is then pulled tight; and (d) Small objects tied into the fabric.

4.5 SPRAY PRINTING

Spray printing is a form of hand printing in which the color is blown through a nozzle under air pressure generated by a compressor. Large spray guns can be used to cover broad areas with dense liquid (like dye solution or pigment paste). This gives a coarse spray when held near the fabric (stippled effect) and fine good coverage as the distance is increased. Different colors can be sprayed on top of each other, as sprayed dyes or pigments have a transparent look. Spraying can also be used with batik and tie-dye to produce interesting effects.

Stencils, especially made of absorbed materials, may be used to restrict spray in selected areas. Fabric is stretched on tabletop and stencil laid on it. Laces, netting or other delicate open weave fabrics may also be used to create novel effects. Spraying is done in short, smooth movements. Fabric may be pleated and crumpled in a totally random or an organized manner and sprayed in this condition. Various novel effects can thus be produced.

4.6 FLOCK STYLE OF PRINTING

Flock printing or flocking is a printing process in which short fibers of rayon, cotton, wool or other natural or synthetic materials are applied to an adhesive-coated surface. This adds a velvet or suede-like texture to the surface. Flock may be prepared from textile fibers by cutting them accurately into pre-determined lengths using a suitable machine. The diameter of the individual flock strand is only a few thousandths of a centimeter and ranges in length from 0.25 mm to 5 mm. With cotton and wool fibers, it is usually prepared by grinding, and lengths may be as short as 0.3mm (0.013 in). The flock may be dyed or uncolored. The effects may be uniform coloration like dyeing or designed/pattered multi-color effects like printed designs. The fibers used in the process are known as flock. They can be applied to paper, plastic, metal, textiles and even glass. Flock printing is an old technique that was in use in China around 1000 BC. In Europe, it became popular during the Middle Ages.

A suitable material is chosen to form the base fabric for the flock and the base material, and the flock may be composed of the same or different fibers. The base fabric may be either coated all over on one side with a suitable adhesive resin, or the resin applied locally in a printed design. When printing is used, a method which transfers a reasonably thick film gives the best results; for instance, a rotary screen printing by the Aljaba or the Stork system or on a smaller scale, flat-screen printing, The resin adhesive must be one which adheres firmly to the substrate being printed, but equally so, must also be capable of anchoring the flock firmly once it is attached. The resin film must be flexible, have a soft handle and possesses a good resistance to washing (Sayed, 2014).

Flocking is used widely in many industrial applications. Flocked surfaces reduce water condensation, act as good thermal insulators, and have been used in the automotive industry for years for items such as glove compartment boxes, door moldings and window trim.

The process uses special equipment that electrically charges the flock particles causing them to stand up. The fibers are then propelled and anchored into the adhesive at right angles to the substrate. The application is both durable and permanent. Flock design applications are also found on many items such as garments, greeting cards, trophies, promotional items, toys and book covers. Figure 4.3 shows two flocked fabric – (a) flocked velvet and (b) flock printed fabrics. The velvets have much higher flocked area so that the fabric has a very thick and soft feel, while flock printed fabrics have comparatively less flocked area as per the printing design.

4.6.1 METHODS OF FLOCK APPLICATION

The flocking operation may be carried out in at least three different ways, which are:

- Spraying by compressed air
- Shaking process
- The electrostatic method
- Flock transfer.

4.6.1.1 Spraying by Compressed Air

This method uses special spray guns and is simple to apply. Various sized spray guns are available, and they are used mainly by handicraft workers as well as painters and decorators. When applied by a spray gun, the flocks land in a completely disordered state and will never produce a clear velvet-like effect.

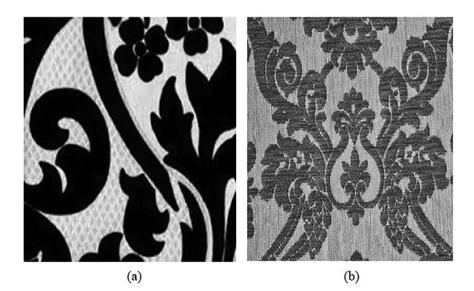


FIGURE 4.3 (a) Flocked velvet and (b) flock printed fabrics.

4.6.1.2 Shaking Process

In this method the flocks are applied merely by shaking, dusting or sprinkling the flock either directly by hand or through a fine sieve. The fabric may be shaken at the same time as the block is being sprinkled. This may be done in the case of small areas of fabric by attaching a wooden rod of hexagonal cross section to the shaft of a small electric motor, and allowing this to come into contact with the reverse side of the printed cloth. As with the previous method, shaking produces a flocked effect on which the individual flocks are attached in a random fashion.

The vibration promotes the density of fibers, which is critical to good fiber coating, and causes the flocking fibers to adhere to the adhesive and pack into a layer. This process is called a beater bar or gravity flocking system and is basically a mechanical process. With this process the flocking fibers are randomly adhered to the surface of the substrate, and each fiber adheres to the adhesive at a different depth, creating an irregular flocked surface.

Since the fibers adhere to the surface of the adhesive, rather than penetrate or embed in it, some fiber shedding occurs. Loose flocking fibers generated during production also have a tendency to migrate, so many of these systems are installed in a separate area to prevent fiber contamination of the factory.

4.6.1.3 The Electrostatic Method

The electrostatic method is perhaps the most viable flocking method, especially for the printer doing more than an occasional flocking job. In principle, a high voltage is generated and connected to two pole-plates, one of which is earthed, the other being effectively insulated. Flocks between these pole-plates will endeavor to close the circuit and spring from one plate to the other in an intense to and fro motion, which results in them becoming aligned vertically. When the resin printed fabric is introduced, the flocks are effectively "shot" into it vertically and adhere in the printed areas. Because of the vertical adhesion of the flocks, the desired velvet-like appearance is achieved. A collection device removes excess flock from the treatment area and returns it to the machine for re-use.

4.6.1.4 Flock Transfer

A much easier way to add flocking to your operation is to purchase and apply standard flock transfers. A large selection of flock transfer sheets is available in the market that can transfer flocks on any fabric when pressed hot on the substrate. One such sheet is a rayon-base fabric that has been electrostatically flocked with a low-gloss nylon pile. Another choice is a patented process, where the transfers are multi-colored and very detailed, and are produced without ink.

Flocked HTV is a special type of heat transfer vinyl that has a lovely raised soft and fuzzy texture. HTV is a type of vinyl that can be ironed onto any t-shirt, sweatshirt, blanket or other cotton or polyester-based fabric. There are different types of heat transfer vinyl. The most common type is standard smooth vinyl, but you can also find HTV vinyl in glitter, holographic, glow-in-the-dark, flocked effects and many more applications (www.thebestvinylcutters.com/ what-is-flocked-htv/).

Flocking is a value-added alternative decorating method for achieving that unusual look. It costs only slightly more than producing a standard screen print, and in conjunction with textiles, it is certainly less expensive than embroidery. This process uses dyed fibers of nylon that are charged with high voltage and driven into the design. This process eliminates fiber shedding, which is common with most other flocked images. Standard flock transfers can also be made in-house.

The pre-press is virtually the same as it is for screen printing with only a few differences. The screens are made from coarser mesh counts and the line thickness of some of the artwork may need to be increased. The adhesive is printed, and a crystalline powder is applied to the transfer and then is sent through the dryer at a low temperature. This removes moisture from the adhesive, but does not melt the crystalline powder. Excess powder is removed and the transfer is sent through the dryer a second time to chemically bind the powder to the adhesive.

Advantages of flocked surfaces are:

- Pleasant appearance
- · Fibered grip
- · Persistence against bounces and scratches
- · Good sliding effect on even surfaces
- Many other specialized properties.

The fineness of the flock, length of fibers and adhesive coating density determine the softness of the flocking. However, fine or short flock is difficult to work with, since it has a tendency to ball-up during processing.

Milled cotton flock has the advantage of being the lowest in cost and the softest, but has the least abrasion and wear resistance. Rayon is a little bit better on wear resistance and nylon is the best. For cut flock, rayon is the least expensive with the least wear resistance. Cut nylon is the best grade of flock and produces a good feel, but is also the most expensive. Cut polyester is used for industrial applications such as automobile window seals, glove compartments and roofing. Besides cutting or milling, flock manufacturing includes several other steps.

After cutting, the flock is cleaned of oils that accumulated during processing. It is vat dyed to any number of colors, and then chemically treated to enable the fibers to accept an electrical charge. Since the fibers are all dielectric, a certain amount of conductivity must be present for the electrostatic flocking process to occur. When the process is complete the fibers are spin dried and then oven dried to a specific moisture content. The flocking fibers are never totally dried, since moisture content adds to their conductivity. Finally, the flock is packaged in moisture proof bags that maintain proper humidity.

4.6.1.5 Flock Adhesives

Flock adhesives are available in both a single and a two-part catalyzed system. There are also plastisol and water-based adhesives. Many of the adhesives have the consistency of plastisol ink. Care should be exercised to select a stencil emulsion or film

that is compatible with the adhesive to be printed. Proper application of the adhesive is the most important part of the process.

A very heavy deposit of adhesive is required, but at the same time the adhesive should not be squeegeed through the substrate. Care should also be exercised not to apply too thin a coating.

4.6.1.6 Electrostatic System

Electrostatic flocking equipment is available in three configurations:

- An automatic carousel for multicolor flocking
- A single station flocking unit that usually attaches to one station of a garment press
- A portable hand-held unit for lower volumes

The cost of the equipment varies from hundreds or a few thousand dollars for handheld units to tens or hundreds of thousands of dollars for automatic multicolor systems. All of the equipment operates using the same basic procedure. In flocking, the electrical charge is generated by the use of two electrodes:

- A high voltage, direct current grid connected to a power generator, and
- A grounded substrate.

An electrostatic charge is generated that propels the fibers at a high velocity on to the adhesive coated substrate. This causes the flocking fibers to penetrate and embed in the adhesive at right angles to the substrate. This forms a high-density uniform flock coating. Controlling the electrical field by increasing or decreasing either the applied voltage or the distance between the electrodes and the substrate controls the speed and thickness of the flocking.

4.6.1.7 Hand-Held Units

The hand-held units are comprised of a metal plate, a generator and a flocking head. The metal plate must be grounded, and it can be placed where it is convenient. It is the equivalent of the plate on a textile press. The generator creates the electrostatic charge, and is wired to a canister that contains the loose fibers. A metal screen is mounted halfway inside the canister opening. The open end of the canister is then passed over the adhesive coated substrate.

This draws flock fibers from the canister through the screen. The electrostatic charge propels the fibers towards the grounded metal plate. The adhesive coated substrate intercepts the fibers and flocking occurs. The substrate is then cured in a conventional textile dryer, and the loose fibers are removed by shaking, vacuuming or by using compressed air.

Having a controlled atmosphere for flocking operations is another essential ingredient for success. Ideally, the flocking area should have a relative humidity of 60%and a temperature of 20° C (68° F). A small variation in temperature or a change in the percentage of relative humidity can result in a 3 to 4 factor change in the conductivity or electrical sensitivity of the flock and the substrate. Flocking fibers are very sensitive to humidity and temperature conditions.

When a new batch of flock fibers is opened, the fibers will give off or receive moisture based on the surrounding environment. Less than 30% relative humidity in the production area will lead to fibers that won't accept a charge. Relative humidity in excess of 65% causes the flock to stick together and flow poorly through the metal screen or plate. For best results the flocking operation should be located in an atmospheric controlled room (Swicofil, 2021).

4.7 BURN-OUT OR DEVORÉ STYLE OF PRINTING

Burn-out printing is also called Transparence process, Corrosion Process or Carbonization Printing (in Japan). A blended fabric containing natural fiber like cotton and synthetic fiber like polyester (Cotton: Polyester:: 40: 60 or 60: 40) is selected. The blended fabric is printed by a paste containing an acidic type of chemicals (say sulfuric acid); cotton fibers in the printed areas are destroyed when heated. Then it becomes a burn-out fabric of translucent style.

Another method uses blended fabrics, containing a protein-based fiber like silk and cellulose such as cotton or rayon. This is used to create the "burn-out" pattern. There is a sodium hydrogen sulphate gel which is applied to a particular fabric in patterns. This then dissolves the cellulose fibers and the protein-based ones are left behind. The protein fibers aren't harmed by the chemicals. The gel is applied by painting onto the fabric or printing onto the fabric by hand (www.tianello.com/blogs/news/ what-is-burnout).

The name Devoré is from the verb *dévorer*, which is French, and it means to devour. This fabric technique is said to have started in France. It was said to be a good alternative to lace, which was cheaper. During the 19th and 20th centuries, the chemical process for the style was developed in Lyon. In the 1920s, this style became quite popular and was used in shawls and evening gowns. In the 1980s and 1990s, the style was revised and used on evening wear and theatrical costumes.

The process for burn-out printing is basically a special type of screen print. The only difference is that instead of traditional print paste composition, an acid chemical is added in the printing paste. It is recommended that this technique be applied by more experienced printers, since extreme care is necessary while printing with those types of chemicals.

Once the chemical is applied through a screen, the garment will need to go through the dryer at 300°F (149°C) about four to five times in order to activate the chemical. The print appears a dark brown color (the color of burnt cotton) when the chemical is activated. The garment is then washed to remove all the burnt cotton fibers, leaving behind only the synthetic fibers in the printed portions.

As for the artwork, since fibers are literally removed from the garment, thinner lines work best. A design that is too solid simply won't work because then the material will become too thin. It's also important to make sure the artwork isn't over any area that is to be sheer (i.e., chest). The production of burn-out printing has a transparent and a concavo-convex feeling. With a natural printing pattern and unique style, it looks much like organdie, which is half transparent, colorful and shiny. Burn out provides a fancy style, which is lucrative for women's wear. It makes fabric very soft and provides very good handle.

The disadvantages are:

- Higher process costs.
- As the method is very much different and hazardous, traditional printers are not willing to print.
- The method is not economic unless it is printed in sufficient volume.
- Low productivity in sewing due to uneven surface and special care required to control shrinkage.

4.8 CREPON OR CRIMP STYLE OF PRINTING

This style is characterized by the appearance of alternate plain and crinkle stripes in the fabric itself. This effect can be brought about by localized fabric shrinkage with appropriate swelling agent.

For example, if cotton fabric is printed in a striped pattern with strong caustic soda, it shrinks in the printed areas and thus causes the unprinted areas to crimp. The greater the shrinkage or contraction of the printed areas, the more pronounced the effect becomes.

Caustic soda up to 50% strength is incorporated in British gum paste and is printed on the cloth. The whole process depends upon the tensionless drying of the printed cloth and slack washing in batches. The fabric must be 100% cotton and lightweight.

4.9 EMBOSS STYLE OF PRINTING

In the printing industry, embossing refers to a method of pressing an image into paper or textile to create a three-dimensional design. Embossing results in a raised surface, with the design higher than the surrounding paper or textile surface.

Embossing is simply raising the surface of your design so that it has some depth. It's a great way to give the design another dimension that print simply cannot do. Emboss can be used by itself or together with foil, coatings or printing.

Textile embossing is generally done on smooth surfaces. This is done by pressing the fabric under high pressure, and at high temperature, in a special backing, creating a three-dimensional effect and giving a unique look to the garment.

This is different from the regular engraving or printing in which plates are pressed against the surface to create an imprint. In embossing the pressing raises the surfaces adding a unique and appealing effect to the fabric. Bleached, dyed or printed fabrics singed with a preliminary finish and chemically unmodified fabrics are used for embossing. Working pressure depends on the quality of the cloth, the embossing design and the different pressing areas of the design. This is durable, with an average life of 50–60 washings.

Embossing may be of various types such as:

4.9.1 BLIND EMBOSS

The embossed image and the fabric surface are the same.

4.9.2 TINT EMBOSS

Here a pastel foil or pearl is used in the raised surface. This is much in demand currently.

4.9.3 SINGLE LEVEL EMBOSS

The image area is raised to one flat level.

4.9.4 MULTILEVEL EMBOSS

The embossed image is raised to different levels to give a depth to the embossing.

4.9.5 PRINTED EMBOSS

The embossed part registers with a printed image.

4.9.6 REGISTERED EMBOSS

The printed image is embossed to give a raised look.

4.9.7 GLAZING

This is a polished emboss used on dark colored surface. More heat and pressure are applied during embossing, which give a shine to the fabric surface. This method is most commonly used for contrasting designs.

Embossing has its utmost applications in advertising and marketing, where it is widely used for making promotional materials. Embossing in textiles is mainly used in non-woven fabrics such as napkins, diapers, tissue papers and so on. In home textiles, it is used in decorating curtains, drapes, bedspreads, cushion covers, table mats and many more. In the fashion industry, embossing appears in embellishing t-shirts, caps and casual wears. Logos are pressed in apparel with embossing techniques. Embossing can be used on fleece, leather, denim, bags and appliques (Jadhav, 2009).

Good quality embossing changes the look of a fabric, and gives a breath-taking appearance. It provides a fabulous depth and texture to the outfit. With a subtle and sophisticated appearance, embossing is an innovative technique for creating fashionable garments. Embossing uses a metal-engraved die/roller along with pressure, temperature and time to press into the fabric a design mark that will not fade or wash away.

Figure 4.4 shows an embossed nylon taffeta fabric.

4.10 TRANSFER PRINTING

Transfer printing is the term used to describe textile and related printing processes in which the design is first printed on to a flexible non-textile substrate and later transferred by a separate process to a textile. In transfer printing, paper is first printed with volatile disperse dyes. The printed paper is heated together with a textile material in



FIGURE 4.4 Embossed-nylon-taffeta fabric.



FIGURE 4.5 Printing of garment with transfer paper.

a thermo-press at up to 200°C for 30 seconds. Under these conditions, the dyestuff is transferred from the paper to the textile material by sublimation. The transferred dyestuff has a good washing fastness.

Sublimation printing is not possible on cotton or on any other natural fiber. For transfer printing on those fibers transfer papers are used (Figure 4.5). Transfer printing by film release technique utilizes transfer paper having a special polymeric

coating. The design is printed on the transfer paper by a standard inkjet printer. The printed paper is placed on garment or other fabric made of any substrate (e.g., cotton, polyester, nylon etc.), the design surface facing the substrate to be printed. The paper-garment (or fabric) sandwich is ironed for 30 seconds or 1 minute.

These papers are coated with polymers, can be printed by inkjet printers, and can transfer the design on any textile fabric by putting the paper facing the printed side in contact with the fabric or garment, which should be in crease-less condition. The transfer paper is pressed by a heated domestic iron on the back side of the paper. The polymeric film on the transfer paper carrying the design is transferred from the paper to the garment/fabric.

This style is very useful for smaller batches. Some disadvantages of traditional printing processes are:

- The printing of textile materials in small batches in any textile printing machine is very uneconomic, because the robust printing machine needs quite some time to get ready for printing. After printing, it takes quite some time for cleaning and preparation for next batches.
- The wastage of unused printing paste is also high.
- The conventional textile printing machines are of high production capacities. The unsold stock of printed fabric adds to the high cost of inventory.
- Due to non-even surface of textile materials exact reproduction of delicate designs are often unsatisfactory.

Transfer printing is very economic for small batches. The advantages of transfer printing are:

- More cost-effective for smaller orders. Low-cost paper may be printed in large quantities and transfer to costly textile material may be done in small batches from time to time as per market demand.
- Easy to print images containing multiple colors and complex designs.
- Affordable setup keeps costs down.
- The paper surfaces are much smoother and perfect printing of delicate artistic designs such as portrait and fine artworks can be easily done on paper.
- As the design transfer on textile is a dry process, delicate designs can be successfully transferred to textiles. It may not be possible to print such delicate designs by direct style of printing.
- Allows for easy production of customized shirts.
- The process is clean and environmentally friendly.

Bismark et al. (2018) has discussed the recent status of transfer printing. Solutions to various limitations of transfer printing have been offered by several authors. Souwer (1975) has discussed the impact of transfer printing on the textile printing industries.

Inventions by accidents are not surprising in the sphere of Science and Technology. Saccharine was invented in the course of an academic investigation of the oxidation of o-toluene sulfonamide at Johns Hopkins University. The sweetness was discovered accidentally when Fahlberg ate a piece of bread and noticed it had a distinctly sweet taste. At the end of the 1950s, N. De Plasse, Chief Chemical Engineer of Filatures Prouvost Masurel (France), got some complaints that a particular batch of printed polyester fabric was giving staining during ironing because of low sublimation fastness of disperse dyes used for printing polyester fabric. Suddenly he was struck with the idea that this property of certain dyes can be utilized for transferring designs to textile substrate from an inert substrate printed beforehand (Roy Choudhury, 1980).

According to Burtonshaw (1972), any process that involves the physical transfer of a design from one substrate to another substrate can be termed as transfer printing process. In conventional printing processes like roller or screen printing, the design is not transferred to the fabric, but the entry of printing liquor is restricted to some selected portions of the fabrics, in order get localized dyeing or printing.

4.10.1 CLASSIFICATION

Four distinct categories of transfer printing are:

- 1) Sublimation, heat transfer, dry transfer or vapor phase printing
- 2) Wet transfer or migration transfer printing
- 3) Melt transfer or thermochrome printing
- 4) Film-release transfer printing

Except the first one, none of the processes became commercially popular because of their inherent disadvantages.

4.10.2 SUBLIMATION TRANSFER PRINTING

In sublimation transfer, an inert substrate like paper is printed with sublimable dyes. When it is sandwiched with the fabric and heated to a particular temperature, the dyestuff volatilizes and goes to the fabric at specific places. As a result, the fabric gets printed. The transfer of designs may be done in a press as a discontinuous process (suitable for garments or piece form) or in a calender as a continuous process. When the paper is heated the dye is preferentially adsorbed from the vapor phase by the textile material with which the heated paper is held in contact. This is commercially the most important transfer printing method.

4.10.3 WET TRANSFER PRINTING PROCESS

Transfer printing in the textile industry usually means the sublimation of volatile disperse dyes from a colored design on paper at high temperature followed by adsorption of the dye vapors by synthetic fibers (mostly polyester) in the fabric. In wet transfer printing, water-soluble dyes printed on paper migrate to fabric in aqueous phase. The principle behind wet transfer printing 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 vapor it is not restricted to the use of dyes that can sublime. The first commercial exploitation of this approach dates to the introduction of the Fastran process in 1971. This involves padding wool garments with stabilized 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 woolen garments, especially when novel design effects are obtained at the same time. The general principles of the wet transfer printing process are:

- The use of Lanasol reactive dyes in the form of Aquatran W papers
- Continuous pre-padding of the goods with a thickened liquor
- Contact between goods and paper for 30–60 seconds at 106°C, with the application of pressure
- Washing-off to remove unfixed dye.

Several attempts have been made to devise continuous wet transfer systems. The DewPrint machine introduced in the late 1970s offered an ingenious solution to the problems posed (Wild, 1977).

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 (Ratee, 2003).

4.10.4 MELT TRANSFER

As the name implies, melt transfer involves solids becoming liquidified, rather than turning into volatile gas, as in case of sublimation transfer printing. This method principally uses wax, resin or oil-based substances as carrier for the ink or dyestuffs. 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.

4.10.5 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. This is very useful for cottage printers who can purchase release paper from the market and print directly on garments as per their chosen design. They can transfer by putting printed paper upside down on the garment and pressing an iron over the paper for 30 seconds until 80–90% dyes are transferred onto the garment. No wash of the printed fabric after transfer is required.

4.10.6 MERITS/DRAWBACKS OF SUBLIMATION TRANSFER PRINTING

Transfer printing offers various advantages over the conventional printing such as (UNEP, 1993):

- 1) Transfer printing involves only the dyestuff and no other chemical is deposited on the textile material, so no after-washing is required and no effluent is generated.
- 2) For conventional printing, 250 kg of water per kg of textile is required. In transfer printing only 2 kg is needed.
- 3) Dyestuff consumption is considerably lower than with direct printing on textiles. A dye yield of 80% can be realized with printed paper transfer, and penetration can be better controlled. With no need for after-treatment, hardly any water is consumed leading to less effluent generation.
- 4) Considerably less energy is consumed during drying. Approximately onehalf ounce of water per square yard is used in transfer printing compared with between 7 to 32 ounces of water per square yard used in direct printing. No after-treatment such as steaming, washing or drying is required.
- 5) It demands less production space and fewer skilled staff, and creates less pollution.
- 6) Capital Investment: Transfer printing eliminates processes like fixation, washing and drying, and costlier components like rollers, screens and so on. Therefore, investment is considerably less.
- 7) Fixed charges: Fixed charges like machine depreciation etc. are obviously less. The cost of storing the printed fabric is on average 2–5 times higher than that of the same amount of printed paper.
- 8) After comparing the costs, Gibson (1977) found that transfer printing has a clear price advantage for the shorter runs and that the keenly competitive costs were found in the region of print orders of about 5,000 yards. But above 5,000 yards, his accounting system failed, as it shows a cost disadvantage in transfer printing (which seems to be wrong).
- 9) The energy requirement of transfer printing is less.

Some of the disadvantages of transfer printing are:

 In its present form, transfer printing is only suitable for some synthetic fibers and cannot yet be used for natural fibers. It has been particularly successful with polyester. Some transfer printing has been done on acrylic, nylon 66 and triacetate. Some wool has been successfully printed by means of the so-called Fastran process after a pre-treatment.

- 2) Low rates of production as well as the limitation to volatile dyes (and to fibers which have affinity with these dyes).
- 3) Due to the nature of the present transfer process as well as the low quantity of dyestuff delivered to the paper, the penetration of the dye into the fiber is also limited. This is a particular problem with knit goods as the base color of the substrate becomes visible when the cloth is stretched.
- 4) The use of exhaust paper may be a cause of headache to the printer. The use of exhaust paper may be a cause of concern to the transfer printer. Suggestions have been made for using these exhaust paper for making up of carrier bags or in similar purposes. The exhaust paper is popular with florists as wrapping paper.

4.10.7 SELECTION OF DYES FOR TRANSFER PRINTING

- Ease of Sublimation: The most important criterion for the selection of dye for dry transfer printing is sublimability or volatility. Volatility can be imparted to a dye molecule in the following ways:
 - (a) by lowering the molecular weight of the dye (best suited range is 240–350)
 - (b) by eliminating ionizing groups from the dye
 - (c) by creating steric hindrance in the dye molecule
 - (d) by introducing silicone atom in the dye molecule (this increases vapor pressure, but the transfer is poor)
 - (e) by increasing hydrogen bonding between polar groups
- 2) Vapor Pressure (Sublimation Pressure): Even if a dye sublimes easily, it may not be suitable for transfer printing due to low vapor pressure at the transfer temperature.
- 3) Thermal Stability: The dye must be thermally stable.
- 4) Compatibility: Dyes in transfer printing are classified as high, medium or low energy dyes depending on the temperature required for 90% transfer in 30 seconds. The transfer of a dye increases with the increase of temperature but the rate varies from dye to dye. Dyes applied in combination must have similar rate of transfer, so that when the temperature fluctuates accidentally on the transfer printing machines or when it is increased intentionally to get stronger colors on the fabric, the hue of the combination may not change drastically towards one of the components.
- 5) Other Physical Requirements: The dye in the ink may be present in disperse or soluble forms. The dye, if soluble, penetrates deeply.

Some disperse dyes claimed to be suitable for transfer printing are listed below:

- C.I. Disperse Yellow 3, 8, 23, 27, 33, 39, 42, 49, 54, 60, 64, 82, 119
- C.I. Disperse Orange 1, 3, 17, 20, 21, 25, 33
- C.I. Disperse Red 1, 2, 4, 11, 13, 15, 17, 24, 50, 59.60, 65, 83, 158
- C.I. Disperse Blue 3, 14, 19, 24, 26, 35, 56, 60, 64
- C.I. Disperse Violet 1, 4, 23, 27, 28, 29

4.10.8 SELECTION OF PAPER

In principle, any paper can be used as the carrier material. But for economic reasons, the paper should release maximum dye during heat transfer. For gravure, flexo and fiat screen printing with solvent-based inks, $60-80 \text{ g/m}^2$ paper, glazed that possibly ligneous provided on one side (printing side) but preferably on both sides with a light starch coat (approx. 3 g/m²) can be used.

When working with water-based inks, there is a risk that the paper will become wavy, particularly when the process is discontinuous. For trouble-free printing with a rotary screen it is advisable to use absorbent papers. But with absorbent papers there is a risk of higher penetration of the dye resulting in poor transfer. To prevent this, suitable filling should be used or adjustment made in the print formulation. The paper surface should be as smooth as possible.

4.10.9 TRANSFER PAPER PRINTING

A number of methods are available for transfer printing of paper such as:

- Gravure printing: Intaglio method of printing where design comes from cells or wells etched into a copper plated cylinder. The unetched surfaces of the cylinder form the nonprinting section of the cylinder. Gravure method gives perfect transfer, especially with solvent-based inks.
- 2) *Flexography:* A rotary web letter press method of printing, characterized by raised image flexible rubber plates and fast drying ink. The results are not very good. Very fine half tone dots are not possible.
- 3) *Lithography and letter press:* Printing from a fiat plane metal plate where the design on the plate is offset or transferred to a rubber blanket from the surface of which it is applied to the fabric. Offset printing requires solvent-free inks of very high viscosity.
- 4) Rotary screen printing: Printing of paper on a textile printing machine is easy and more productive. This has been realized in recent years. A rotary screen printing machine is a textile printing machine where the design carrier is a tubular copper or nickel screen, which is mounted across the bed of the substrate to be printed. Ink is mounted inside the mounted screen and squeezed through the screen by means of a squeeze.

4.10.10 PRINT PASTE FOR PAPER PRINTING

The paper printing inks are broadly classified into:

- 1) Solvent-based inks
- 2) Water-based (aqueous) inks

Solvent-based inks are toxic and costly, hence they are being replaced gradually by aqueous inks. While using solvent-based inks, cleaning with water is not possible, as ethyl cellulose (E-7) is insoluble in water. Cleaning with solvent, on the other hand, will be too costly. Moreover, there is a risk of explosion due to inflammability of the solvents.

A solvent-based recipe is as follows:

The solvent may be ethanol, isopropanol or methyl ethyl ketone. Alternatively, ethyl cellulose may be dissolved in ethanol to make a stock paste in which the dye is mixed in desired quantity. The dye may also be ball-milled in an ethanol-ethylene glycol (9:1 by volume) mixture together with ethyl cellulose thickener for 48 hours.

In aqueous print formulation, combinations of synthetic thickeners and natural thickeners are recommended. Among synthetic thickeners acryl types are of thermoplastic nature, which give tackiness to make for better contact between paper and fabric. Among natural thickeners, Carob flour, guar and alginate products can be used.

4.10.11 TRANSFER PRINTING ON NYLON

Poor wet staining and rubbing fastnesses are the main drawbacks of transfer printing on nylon. That is why transfer printing on nylon is mostly done in pastel shades. To improve wet fastness on polyamide, disperse dyes with reactive moiety may be used that will react with the amino group of the fiber.

4.10.12 TRANSFER PRINTING ON POLYESTER

Heat transfer printing is most successful for polyester. Problem of poor sublimation fastness can be improved by better penetration. Penetration can be improved by the vacuum impregnation technique, but there is a chance of surface deposition and lowering of overall fastness when the rate of transfer is higher than the rate of diffusion.

4.10.13 TRANSFER PRINTING ON ACRYLIC

In 1969 the transfer printed Acrilan acrylic sweater came to markets, developed by Monsanto textiles knitwear manufacturer, in association with two Scottish knitwear manufacturers. Transfer printing on acrylic fabrics is not quite satisfactory as the fiber discolors above 180–185°C and becomes stiff and also exhibits inferior wash and perspiration fastness. Using alkalis in the printing paste, certain basic dyes can be utilized. The dye sublimes in the form of uncharged carbinol base and by reaction with the acidic groups in the fiber reverts to the cationic form.

4.10.14 COTTON AND COTTON/PE BLENDS

The dyes for cotton are not sublimable, hence transfer printing of cotton and cotton blends is difficult. Work has been carried out in numerous directions, some of which are listed here:

mansier rinning conditions for Different Textile Material			
Substrate	Temp. (OC)	Time (Sec.)	
Secondary acetate	190-210	15-30	
Tertiary acetate	190-210	20-40	
Nylon 6,6	190-210	20-40	
Polyester	200-230	20-40	
Acrylic	200-210	15-30	
Wool blend	200-220	20-40	

IADLE 4.1					
Transfer Printing	Conditions	for	Different	Textile	Material

- 1) Transfer printing with a releasable thermoplastic substrate. The method creates various problems and is not popular.
- 2) Migration of water-soluble dyes under wet condition. The method lacks the advantages of dry heat transfer and needs sophisticated apparatus.
- 3) Padding with suitable textile resin and catalyst, drying, curing optionally and transfer printing with disperse dyes. This is the basis of Heberlein Holliday and sublistatic patents.

The best conditions for this process include: padding of about 70% impression for polyester cotton and 80% for cotton, followed by drying at 100–110 °C, and curing at 155 °C for 3 minutes.

The temperature and time required for transfer of disperse dyes by sublimation transfer method are given in Table 4.1.

4.11 DIGITAL PRINTING STYLE

One of the most promising developments in the textile industry is digital fabric printing. It has opened the doors for numerous prospects to enhance the quality and maintain the growing demands of textile printing. Anything can be printed with ease and perfection on fabric using digital printing technology. When digital images are reproduced on physical surfaces, it is called digital printing. The physical surface can be in forms like paper, cloth, plastic, film and so on. In digital textile printing, once the design is created, it can be printed directly onto the fabric from the computer. This process does not require any other step. Just as an image is printed on paper easily, one can print designs on fabric.

To print designs on fabric digitally, a dye-sublimation printer is used, which carries out the printing process by using heat to transfer design onto the fabric. In digital printing, it is necessary to pre-treat the fabric. This will ensure that the fabric holds the ink well, and a variety of colors can be attained through the pre-treatment process.

Digital printing has proved to be advantageous for designers, textile companies and retailers. It allows the user to print quickly and as little as required, and with a high rate of accuracy; while in the case of traditional printing, a minimum quantity must be printed. Thus, the overall cost of producing a sample is considerably reduced. It does not even require color registration of plates or screens.

4.12 SPACE DYEING

Space dyeing is a technique of localized color application in yarn that produces a unique multicolored effect with fabric from specially dyed yarn. Space dyeing is a technique used to give yarn a unique, multi-colored effect. When woven or knitted together for apparel, home furnishing and carpet making, beautiful patterns can emerge depending on the length and variation of each color block. Adequate use of dyes and auxiliary chemicals combined with specialized machines can create finished products that look much like printed materials, without using any printing tools or machine. In some space dyeing methods, carpet and other fabrics are dyed directly by controlling flows coming from jets. Presently the "Space Dyeing" segment occupies a miniscule (less than 1%) share in the textile coloration space (Athalye, 2014). However, considering its potential to offer unique and customized print design effects, it has great potential to grow by many folds in the near future.

Space dyeing is a group of methods of section-wise dyeing or printing of yarn and tow in order to achieve fancy colored effects after fabric manufacturing. The effect obtained is localized application of dyes – an effect similar to that obtained in printing, but through dyeing methods. Though during space dyeing, colors are applied at regular intervals, the effects obtained after fabric manufacture are abstract and random. Thus, the style obtained cannot be imitated by printing directly on the fabric. Space dyeing is the collective term for a variety of methods (Bayer, 1976).

Merits of space dyeing include:

- Yarn dyeing is less costly than stock or top dyeing because the processes are more productive.
- Yarn dyeing permits excellent penetration of dye into the fiber and thus produces a great clarity of color.
- Yarn dyed fabrics tend to be more color fast than those dyed after the fabric is woven.
- When yarns are dyed separately, interesting color effects can be introduced into the weaving process by combining yarns of different colors.
- In general, yarn dyeing is less labor intensive than fiber dyeing.
- Yarn dyeing permits the use of variously colored yarns in a single fabric, thus giving the designer latitude in creating plaids, checks, stripes, muted color arrangements and iridescent effects.

Drawbacks of space dyeing include:

- The major disadvantage of yarn dyeing is the sensitive timing. Applying color so early in the production stage means that color forecast must be extremely accurate to provide adequate yarn for fabric production and avoid a costly oversupply.
- More costly than piece dyeing and printing.

The working methods can be divided into several groups, such as space dyeing methods of:

- Knitted fabrics and deknitting
- Warp yarns
- Hanks of yarn
- Wound yarn packages
- Knitwear, woven fabrics, tufted material and non-woven fabrics.

The term printing has been used here frequently, but it is actually localized application of dyes and not printing with any conventional printing machine. Figure 4.5 shows a few types of space dyeing methods.

4.12.1 KNIT-DEKNIT METHOD

In knit-deknit method (USA), the yarn is knitted, padded with pale color and printed wet-on-wet. After printing, the goods are passed through an ager, where they are steamed for 3–10 minutes in saturated steam. This is followed by rinsing, washing, finishing and drying. The material is then deknitted, reeled, wound on bobbins or section beamed and run into tufting machine.

4.12.2 SPACE DYEING OF WARP

In the Laing method (Edger Pickering Ltd., UK) (Figure 4.6(a)), about 500 threads running parallel to each other are padded and printed. Two rollers of different sizes are used; the lower roller is smaller and dips into the color trough. Color paste is transferred only when the relief patterns of the upper and lower rollers meet. Multicolor effects can be obtained by arranging several print rollers in series.

The Stalwart method (Stalwart Dyeing Co., UK) (Figure 4.6(b)) is similar to the Laing method. The difference is that smooth rollers are used instead of rollers engraved with a relief pattern. The upper roller is pressed on the lower roller for transfer of color and then lifted. Monitoring of the movement of the upper roller is automatic, either electronic or mechanical.

The Martin process (Martin Proc. Int. S.A., Belgium) is similar to Stalwart's, but several independently controlled rollers are used instead of a single roller over the full width of the yarn.

In Zaza printing (Antonis Zanolo, Italy) and also in Vigoureux printing (Figure 4.6(c)), the yarn sheets are passed between an engraved roller and a felt-covered roller supplied with color paste from the trough by means of a rubber roller. The color is transferred to the yarn whenever the raised parts of the engraving press the yarn on to the felt roller.

In the Eastern Colour Dyeing Method (Daito Sangyo Co. Ltd., Japan) (Figure 4.6(d)), yarn is reeled off from bobbins, passed by the side of centrifuges supplied with dye liquor from above, sprayed, dried briefly and wound immediately.

Three centrifuges are arranged on top of each other and up to three shades can be applied on the yarn. Fixation is then affected by steaming.

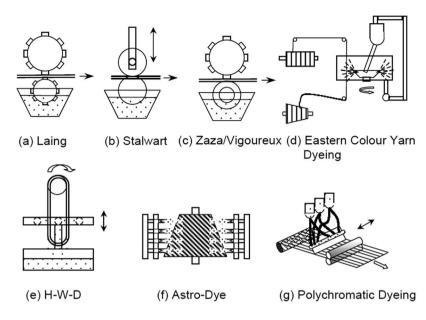


FIGURE 4.6 Space dyeing methods.

The Superba method (Ets. Superba, France) is similar to this, but the color is sprayed in vertical direction and eight threads are sprayed simultaneously.

In the OPI method (Omnium de Prospective Industrielle S.A., France), the desired space-dye effect is produced by the to-and-fro movement of a jet-bar (eight jets) transverse to the running direction of eight yarn threads. Up to three jet bars can be used, depending on the required pattern. The traverse movement is monitored electronically. The excess dye liquor is removed, or the material is dehydrated by compressed air with a specially developed jet acting individually on each thread.

The Unitika-Mixy method (Unitika Ltd., Japan) is similar to the previous methods. The color is applied by jets on the reeled off yarn running at high speed. The yarn is dried and rewound on a bobbin.

4.12.3 Space Dyeing of Hanks

Timmer hank yarn printing machine (J. Timmer, Germany) consists of four pairs of small rolls running through the color troughs and two counter-rolls. Printing is affected in four phases. In every phase, one quarter of the total circumference of the hanks is printed. Movement in longitudinal hank direction is automatic. The hanks are moved in transverse direction and stopped automatically for color application. The machine is suitable for a definite hank length.

In the VH-Syn-O-Flow method (Vald Henriksen A/S, Denmark), the hanks are rolled up in moderate density around a stainless steel drum fitted with slits. Coloration is affected automatically with all 60 dye-liquors at the same time, in 30 to 90 seconds, through the drum slits. The total quantity of wool yarn dyed in one operation is 5 to 7.5 kg.

The multispace dyer machine (Callebaut-De Blicquy S.A., Belgium) was developed for continuous dyeing and steaming of yarn in hanks. For coloration, the yarn hanks are placed in series transverse to the direction of the movement of the conveyor carrying the hanks. The conveyor runs under a series of 40 jets placed side by side and transverse to the conveyor when color is sprayed on the hanks. A group of 10 jets with variable sequence sprays color liquors, hence four color liquors may be applied simultaneously. After spraying, the conveyor passes through a steamer when the colorants are fixed. The speed of the conveyor can be varied between 0.9 to 3 m/min.

The Hussong-Walker-Davis (H-W-D) method (Hussong-Walker-Davis Co., USA) (Figure 4.6(e)) is a mechanized version of Ombré dyeing or shadow dyeing. The hanks are suspended from several arms, which can be turned around their longitudinal axis. The hanks are sprayed from both sides and from inside by means of spray tubes rigidly fixed parallel to the arms, using hot dye liquor. The excess liquor runs down the hanks and is recollected and pumped back to the spray tubes until the dye is exhausted. The height of the arms can be adjusted, so that spray tubes can cover a fairly large area of the lower part of the hanks. The position of the arm determines the length of hank to be dyed. After the first shade is applied, the hanks are moved by a definite length around its circumference. The second liquor is applied. This can be repeated until the hanks are completely covered.

4.12.4 Space Dyeing on Wound Packages

The Astro-Dye method (Astra-Dye-Works, USA) (Figure 4.6(f)) enables spraying of dye solutions in yarn bobbins to obtain coloration up to four shades. The spray arrangement consists of four bars arranged at equal distance around the yarn bobbin. Each bar houses four injection syringes or nozzles, placed on top of each other. Each of these 16 syringes may contain any of the four dyestuff solutions. The yarn must not be soiled and all bobbins must be equally tightly wound. The dyes must have good solubility and a rapid wetting agent must be used. The dye liquor should be accurately metered depending on the type of fiber and method used.

4.12.5 SPACE DYEING OF TUFTED CARPETS, KNITTED AND WOVEN FABRICS

In a Küster continuous carpet dyeing machine, the liquor is taken off a carrier roller by means of a doctor blade and transferred in full width to the surface of the goods. A modification of this process, the TAK space dyeing method (TAG, Germany), utilizes a special doctor blade, which applies the dye liquor in the form of individual thin streams running through narrow channels. By moving the doctor blade to-and-fro at the transfer roll, wavy lines are produced on the running carpet material. However, this is prevented by means of a chain band, which distributes the streams irregularly in the form of drops over the entire material. The irregular application of drops in different colors on pre-dyed material produces a number of mixed colors and overlapping designs. The standard TAK model has two color applicators.

The polychromatic method (James Farmer Norton, UK) (Figure 4.6(g)) can be used to produce a wide variety of patterns in many shades on tufted carpets, woven and knitted fabrics and non-wovens – even on warp threads.



FIGURE 4.7 Space-dyed fabric.

Two or three sets of jets apply the dye liquor to the goods passing below the jets. The individual jets can be connected with dye liquors of different colors by means of a special dyestuff supply tube. A sheet called mirror is placed at an angle below the jets. The angle is so adjusted that the liquor stream coming from one or two series of jets reaches the goods only after running down the slanted sheet, ensuring partial mixing of the dye liquors.

Lateral to-and-fro movement of the rows of jets produces changes in patterns and color mixtures. After applying a constant amount of liquor, which must be fixed beforehand by a suitable choice of jet size, the goods are passed through a padder, when the final pattern is obtained. The goods are then steamed continuously, washed and dried.

Figure 4.7 shows a space-dyed fabric.

4.13 FUTURE TRENDS

Evidence of textile printing was found in China and among the Incas in Peru in the 1st century. In Europe, printed patterns on textiles were introduced much later due to the difficulty in achieving durable printing, which does not fade or wash off. It was not until the development of a durable dyestuff that enabled the first printing of patterns on textiles to emerge. The initial method used was rather primitive and done by hand. The first successful attempt to mechanically print on a fabric was achieved by an engraved cylinder machine which used copper rollers to print on the fabric. The next attempt to improve printing on textiles was done in the mid-19th century by stencil printing, which in course of time developed into mechanized screen printing. The cylindrical screens gave birth to rotary screen. Manual flat screens are popular in small-scale printing, while rotary screens have been popular in large-scale printing for the last few decades. Utilizing these machines and tools, colors may be printed directly on the fabric or by resisting or discharging colors in the design area. The complaint of color fading during ironing of polyester dyed fabrics gave birth to transfer printing has limited use to date, due to several limitations.

Digital textile printing is considered the "next generation" printing, which is quite different from conventional fabric printing. With fabric printing going digital, many textile entrepreneurs are coming forward to invest in digital printing technology, as it is the most budding method of printing. The textile industry is embracing digital printing technology by printing novel designs on most types of textile materials to meet the demands of domestic and international markets.

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5 Direct, Discharge and Resist Styles of Printing

5.1 INTRODUCTION

The four main methods of textile printing are block, roller, screen and heat transfer printing. In each of these methods, the application of the color, usually as a thickened paste, is followed by fixation, usually by steaming or heating, and then removal of excess color by washing.

Note: All recipes mentioned in this book are guide recipes. The relative quantities may have to be changed significantly depending on various factors like physical and chemical properties of the substrate to be printed, the nature and purities of dyes, chemicals and auxiliaries, the tools or machines used for printing, quality of water, weather conditions and so on. It is suggested that a trial be conducted with these guide recipes and consequently necessary changes made based on the quality of printed materials. Various auxiliaries available in the market may also be used as per manufacturers' recommendations during trial, and final recipes may be decided on the basis of these trials.

The most common style of printing textile fabric is direct style of printing. In this method, the dye is directly applied onto the fabric as per design with the help of blocks, rollers or screens. It is the simplest, oldest and most widely used style of printing. It can be done on a white fabric or on colored fabric. The printing may be monocolor or multi-color using multiple blocks, screens or rollers. The dye is imprinted on the fabric in paste form so that the movement of color paste is restricted within the respective design area. Thus, any desired pattern in single or multiple colors may be produced. Dark color prints on lighter background are a characteristic feature of direct style printing. In this style of printing, the printing paste is transferred to the selected areas of the fabric and the pigments adhere to the fabric surface. However, the direct style has a few drawbacks. In this style it is difficult to incorporate small white or colored motifs on dark ground. It is also difficult to print fine designs with sharp outlines on woven or knitted fabrics.

The demand of these types of design has compelled printers to find alternate techniques, such as resist style and discharge styles. In the former, design portions of the fabric are blocked physically by knotting with threads and stones or by coating with melted wax or chemically by printing with acids or other resisting chemicals. In this resisted condition, the fabric is quickly passed through dye solution followed by a required fixation step like steaming or dry-heat treatment for a defined period. Later the knots, stones, waxes are removed, and fabric is washed thoroughly. All resisting agents have limited efficiency. Hence, the fabric after being resisted chemically or physically, the fabric is to be passed for a very short time through colorant solution. During this short time of immersion, the penetration of dyes inside the fibers may be limited, resulting in poor fastness. Moreover, color may penetrate inside the resisted portions hampering sharp boundaries of the resisted areas. The resist style, therefore, provides inferior quality of print, but at a cheaper price.

The third but most delicate and sophisticated style of printing is discharge style. In this method, the fabric is printed on a fabric dyed with dischargeable dyes. The printing paste used in this method contains a discharging agent, which will bleach or destroy the color from the dyed fabric in the printed areas (white discharge). The resulting white area brightens the overall design. Sometimes the base color is removed and another non-dischargeable color is printed in its place (color discharge). The discharging agent is an oxidizing or reducing agent capable of discharging colors by oxidation or reduction respectively. Oxidizing agents like potassium chlorate or sodium chlorate and reducing agents like sodium sulphoxalate or stannous chloride are commonly used as discharging agents. The effects produced are very striking as the white area obtained brightens the overall design. This style of printing enables intricate and fine designs to be printed on the fabric. If the fabric is not thoroughly washed after printing, the strength of the fabric may be affected due to the presence of discharging agents. The discharge style of printing produces sharp, light, bright color on a dark background. The major disadvantage of this method is the high cost involved. Discharge printing is a very skillful job. Due to poor quality of discharging agents and poor steaming conditions, discharging may fail, realized only after final wash, and no correction is possible at that time.

5.2 DIRECT STYLE OF PRINTING OF CELLULOSIC MATERIALS

Cellulosic fabrics can be dyed and printed with dyes belonging to most of the dye classes except acid dyes and disperse dyes. However, fabric made of cotton and other cellulosic fibers are mostly printed with reactive dyes and pigment colors and to a limited extent with vat dyes. If we consider printing of cheaper cellulosic and blended fabrics, pigment colors are undoubtedly the first choice. Reactive dyes are used for high quality bright prints, while pigments are preferred for economic prints on any fiber including cellulosic and their blends. Reactive printing requires a robust steaming unit for fixation, while pigment printed fabrics may also be cured in small curing machines or still smaller domestic stationary curing units. Hence, it is very popular with small scale cottage printers. Vat dyes (mostly liquid brand) are used to a very small extent for prints with very high light and washing fastness.

Three dye classes, namely solubilized vat dyes, rapid-fast and rapidogen colors (both are stabilized azoic colors) were once very popular, but are now more or less obsolete. Various brands of reactive dyes are available in the market. Generally, low reactive monochlorotriazine (MCT) dyes (e.g., Cibacron and Procion H, Cibacron Pront) and medium reactive vinyl sulfone dyes (e.g., Remazol dyes) are suitable for textile printing. Vinyl sulfone dyes have an additional advantage in that they are easily reducible. Hence, these dyes are widely used in discharge printing.

5.2.1 PRINTING WITH PIGMENT COLORS

Pigment printing is probably the oldest printing technique. For more than 3,000 years, mineral pigments have been ground with natural binding agents like oil, albumen and vegetable gums, and applied to textile to form a colored pattern.

However, pigment printing was not important commercially until the Second World War because of its dull colors, and its effect of hampering the aesthetic properties of textiles due to stiffening and poor fastness to wear (rubbing) and washing.

The advantages of pigment print are:

- Pigment printing is the most economical printing process and allows maximum rates of production because of the elimination of washing-off, quick sampling and high printing speeds.
- 2) Properly produced pigment prints, using highly standardized products, possess unsurpassed fastness to light and good general fastness properties.
- 3) Pigments are the only colorants which can be applied to all substrates including glass fibers, PVC and imitation leather, subject to some limitations in color depth.
- 4) It is extremely well suited for color resist effects, for example, under azoic and reactive dyes.
- 5) Pigment printing creates few problems for the printer, with regard to labor costs, equipment and reliability of production.
- 6) The errors in pigment printing are visualized quickly.
- 7) From the ecological point of view, traditional pigment printing using white spirit may cause health hazards and fire hazards. However, pigment printing using pastes free from white spirit is more ecologically friendly than any other system, excepting only transfer printing methods.

The disadvantages of pigment printing are:

- 1) The fastness levels of medium- or dark-colored prints on materials made from polyester and acrylic fibers, as well as on wool, are at best only suitable for articles that will not be subjected to a great deal of wear.
- 2) Dark-colored prints on woven and knitted goods made of synthetic fiber blends are especially susceptible to abrasive wear, as well as to reduction in color strength by frequent use or washing. This applies particularly to men's polyester/cotton shirts.
- 3) The handle of printed goods is often unduly hard because of the large amounts of external crosslinking agents, and this necessitates after-treatment of the prints on breaking machines to produce some improvement.

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

5.2.1.1 Binder

Pigments must be bounded physically to the textile fiber because they have no affinity to the fiber. This is being done with "binders", which form films around pigments and fiber molecules producing a three-dimensional crosslinked network during the dry heat fixation step called curing.

Binders are high molecular weight chains of so-called monomers. Though the chemistry was invented by the end of 1920s, the fastness properties of pigment prints reached an acceptable level for future expansion only after the introduction of emulsion polymerization after the Second World War.

Binders used in pigment printing are usually based on styrene-butadiene, styreneacrylate or vinyl acetate-acrylate copolymers. Water-insoluble monomers are dispersed in a water-emulsifier mixture (= pre-emulsion). Pre-emulsion and initiator (for the chemical reaction to form the chains) are dosed separately to the vessel. The control of this exothermic reaction and the right emulsifying system are essential for the success. The resulting "dispersion binders" are milky liquids which contain around 30 to 45% binder dispersed in water. Depending upon the required properties of the binder film, binders can be "tailor-made" by choosing the right combination and ratio of unsaturated monomers.

Common monomers used for production of binders for textile application (Schklsser, 2010) are n-butyl acrylate, vinyl acetate, ethyl acrylate, styrene, acrylic acid, acrylonitrile, methyl methacrylate, butadiene, methacrylic acid, and so on. The chemical structures of such monomers are shown in Figure 5.1.

5.2.1.2 Crosslinking

Elasticity and improved adhesion of film to substrate is achieved by crosslinking. The crosslinking reaction must produce covalent bonds which are insensitive to hydrolyzing agents (washing liquors, body sweat, and industrial atmospheres). The reaction should be activated only during fixation and not while the binder and the printing pastes are in storage.

The simplest crosslinking reaction would be the condensation of carboxyl groups with hydroxyl groups of film-forming macromolecules. The disadvantages of this

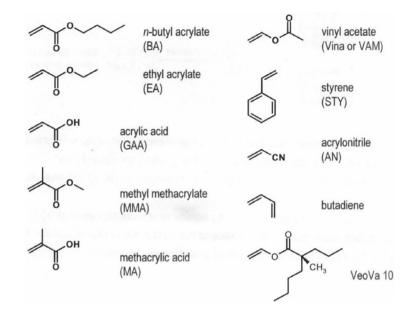


FIGURE 5.1 Chemical structures of various monomers used for the production of pigmentbinders.

process are that it needs very high temperatures and an acid medium, and thus entails the risk of the textile yellowing; and that an ester bond is formed which is relatively sensitive to hydrolysis.

To improve adhesion of the binder-film and to improve crock fastness, crosslinkers are polymerized with the main monomers (around 2–4%). Most universal crosslinking agent is NMA (N-methylol-acrylamide).

Binders containing copolymers with N-methylol groups for "internal" crosslinking may be combined with poly-N-methylol compounds as "external" crosslinking agents. These are especially useful for prints on hydrophobic materials. The watersoluble methyl ethers of tetra- to hexa-methylolmelamines are preferred. They act mainly as adhesive agents between the textile and binder, but also contribute to the crosslinking at the surface of the binder film. Their reaction with the hydroxyl groups of aqueous thickeners and with nonionic dispersing agents based on polyglycol ethers also reduces the swelling of the film and improves the wet fastness of the prints. Because of their large content of very polar groups, the external crosslinking agents themselves form inextensible, rigid networks after the crosslinking reaction, thus hardening the handle of the printed goods a great deal more than does binder film. For this reason, only relatively small amounts – up to about 10%, based on binder quantities – are used. The reaction occurs during curing of binders, as shown here (Equation 5.1):

Binder
$$- CH_2OH + HO - CH_2 - Binder \leftrightarrow$$

Binder $- CH_2OCH_2 - Binder + H_2O$ [Equation 5.1]

Necessary for this reaction are:

- · Removal of water by dry heat to shift reaction equilibrium to the right side
- pH of around 5
- A temperature above 120°C (the higher the better)

The binder film should attach the pigment to the fibers completely and permanently, and it should be soft and flexible enough to have the minimum effect on the handle of the fabric. It should be fast to light washing and normal treatments. The binder must be in liquid form and its viscosity should be readily adjustable to a value suitable for padding.

5.2.1.3 Thickeners

Colloidal polysaccharide thickening agents, such as starch, cellulose ether, alginates or locust bean gum, have been used successfully in printing pastes for various groups of dyes. They are not suitable for pigment printing due to their poor flow properties and because of the formation of brittle films after drying. The prints produced with such thickeners are dull and flat, with poor fastness and a harsh handle.

It is not possible to carry out pigment printing using traditional thickeners or gums. Pigments are water insoluble, and they can only be retained by fibers with the help of a film-forming material called a binder. The fixation is done by dry heat and not by steam. Unlike dyes, washing to remove unfixed colorants is not required after pigment printing and the process becomes very simple and economic.

It is necessary for pigment printing pastes to have pseudoplastic (shear-thinning) flow; they can then be transferred on to the textile material easily, but their penetration is limited. Pseudoplastic flow is usually found in heterogeneous and, physically speaking, coarsely dispersed systems. Flow occurs under shear, but when the shear is removed the pastes return to the consistency of a solid on the surface of the textile. Unlike pastes with no yield value, they cannot penetrate deep down into the textile because of their rheology. Since they therefore remain on the fabric surface, they produce much better color value – a sharp mark and brilliance of color. In addition, because of the superficial coating of the fabric with printing paste, the textile yarns are not bonded to each other by the binders and crosslinking agents, and this results in a better handle to the printed goods.

Typical systems, and the ones most suitable for pigment printing, are the emulsion thickeners, of which the white spirit/water emulsions (o/w type) were of greatest practical interest. They consist of about 70% by mass of hydrocarbons in the disperse phase, 0.5–1% nonionic emulsifiers with HLB in the region 12–15, and 29% water in the continuous phase. The droplet size of the emulsified white spirit depends on the emulsifying agent and the efficiency of the high-speed mixer necessary to produce the emulsion. Efforts must be made to achieve a uniform droplet size. Homogeneous emulsions give maximum stability and yield value. For physiological reasons the white spirit should have as little toxicity and aroma as possible. The other desirable parameters are:

- Flash point of at least 30°C,
- Boiling range of between 160 and 200°C and
- Density of 0.76–0.80 g cm³.

Modern pigment printing was possible only after the invention of emulsion thickening. The emulsions consist of droplets or internal phase which is dispersed in a continuous phase, called external phase. During preparation of emulsions, internal phase liquid is slowly added into the external phase containing emulsifiers under stirring. Initially, the internal phase liquid forms spherical droplets moving randomly inside the external phase. As more liquid (internal phase) is added, the number of droplets increases to a large extent and start colliding each other in increasing viscosity. In a highly thickened emulsion, the total internal phase is much more, compared to that of the external phase. In water-in-oil emulsion (W/O), developed in the United States in 1937, water is the internal phase while oil is the external phase. For very high viscosity, internal phase should be much more in volume. In Europe, oil-in-water emulsions (O/W) became popular after the Second World War. The modern pigment printing process is based on O/W emulsion and the oil (kerosene) is used in much higher quantities than the water used. The type of emulsion is dictated by the type of emulsifier used. The emulsions negligible to no solid content. When emulsions are used in textile printing, volatile oils like white spirit or kerosene are used; they evaporates during drying, leaving behind no solid. The after-wash, thus, becomes unnecessary.

The advantages of emulsion thickening are:

- No solid content
- No influence on handle
- Quick drying
- High definition of prints (W/O)
- No problems with wet-on-wet printing (W/O)
- Water-soluble (O/W)
- Pseudo-plastic flow (shear thinning): high viscosity before and after printing, but low viscosity during printing
- Good penetration through the screens, but low penetration through the fabric matrix

The disadvantages of emulsion thickening are:

- The solvents are costly
- White spirit or kerosene used in this process is not eco-friendly
- They are inflammable
- Inhalation of volatile solvents is harmful
- Creates air pollution
- · Pollutes wastewater

- The printing tools are to be cleaned with solvents
- Pigment dispersions should be water-free

Once, emulsion thickeners were very popular. But due to the above two reasons, their use has declined sharply.

Recent improvements have led to:

- Volatile organic compounds (VOC)-free products by use of high boiling oil
- Lower sensitivity against electrolyte caused by "bad" water quality, possibly by introduction of rheological modifier

In the 1960s, in anticipation, synthetic-polymer thickening agents were developed for pigment printing, with rheology similar to that of emulsion thickeners and extremely low solids content. They are poly-anionic compounds derived from monomers such as acrylic acid and maleic anhydride. A small degree of transverse crosslinking of the polymer molecules is built in, so that packets or bundles of chain molecules are held together. These products have very high swelling power, which is at a maximum pH of 9–10 when ionization increases the degree of solvation in water.

The original polymer with undissociated carboxylic acid groups will be in the coiled chain form. Neutralization leads to a straightening and separation of the polymer chains because the carboxylate ions are fully dissociated and strongly repel one another. This brings about a hundredfold expansion in size and the solvated particles then have dimensions similar to those of the white spirit droplets in emulsion thickeners. When the water-swollen particles are tightly packed they give a paste with pseudo-plastic flow properties.

After printing and curing, the thickening agent remains in the fabric without hampering handle and as such after-wash is not necessary.

The desirable properties of synthetic thickeners are:

- · Water solubility
- High molecular weight polymers
- Polymers are to be branched, but not crosslinked to get big molecules and not too long chains (Figure 5.2(a))
- Similar rheological behavior like emulsions
- · Based on acrylic acid
- No acid donor necessary for binder fixation
- Neutralized with ammonia
- Should not influence the handle or feel of the fabric

5.2.1.4 Mode of Action

When dissolving synthetic thickeners in water, osmotic pressure leads to movement of cations into the water. The remaining negative charges are repelling each other, leading to an expansion of the molecule and therefore an increasing of the viscosity (Figure 5.2(b)).

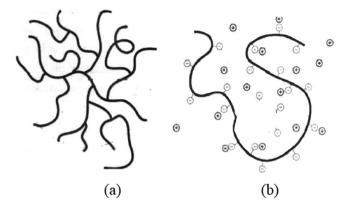


FIGURE 5.2 Synthetic thickeners: (a) branched polymer; (b) ionized polymer.

Alkali soluble emulsion (ASE) polyacrylate thickeners are well known since the 1970s. These are low viscous acrylate dispersions with acidic pH and without any mineral oil. Only by neutralization do they develop their thickening effect. Because crosslinking agents need a slightly acidic pH, only ammonia would be suitable to use due to volatility during fixation. But dosing high amounts of ammonia in a color kitchen is not feasible (strong smell, corrosive).

Hydrophobically modified ASE thickeners may be used as rheology modifiers. Hydrophobically w acrylic polymers that have a comb-like structure with pendant hydrophobic groups randomly distributed along a polyelectrolyte backbone.

5.2.1.5 Printing Process

Printing binder	10 parts
Low viscosity CMC thickener (anti-migrant)	3-6 parts
Urea (hygroscopic agent)	2-3 parts
Water	6–8 parts
White spirit, added under high-speed stirring	79–73 parts
Total	100 parts

Recipe of 10% reduction binder

(The ratio of white spirit and water may have to be varied depending on the quality of kerosene.)

Recipe for printing paste

Pigment emulsion	x parts
10% reduction binder	80-85 parts
Binder	2-10 parts
Water	2-3 parts
Catalyst, diammonium phosphate (1:3)	3 parts
Total	100 parts

The use of white spirit is nowadays objectionable on environmental grounds. White spirit may cause (a) air pollution due to its toxicity and (b) it is a fire hazard. Hence, emulsion pigment printing is replaced by eco-friendly aqueous pigment printing, described as follows:

Aqueous pigment print (reduction binder)

Water with 0.5 ammonia (25%)	X parts		
Aqueous printing binder	12-15 parts		
Aqueous thickener	1.5–2 parts		
Crosslinking agent	1.5-2.5 parts		
Balance (water/thickener)	Y (for viscosity approx. 80 dpa)		

Aqueous print paste recipe

Pigment emulsion	X parts
Reduction paste	Y parts
Crosslinking agent	1-2 parts
Remaining (water or reduction)	Z parts
Total	100 parts

An alternate recipe for aqueous pigment printing reported by a pigment manufacturer (personal communication) is as follows:

Water (pH 7.5) – 6 kgs			
Binder (pH 7.5) Pidicryl binder BN – 1 kg			
Liquor ammonia – 0.5% of total i.e., 35–40 gms			
Check pH, should be 8.5–9.0			
Synthetic thickener, Pidiprint 160/NPF	- 1-1.2% of total i.e., 70-85 gms		
Pidicryl SHRP	0.2-0.3 % or 2-3 gms/kg paste		
(it is alkaline, hence suitable only for water based system)			
Pidimine soft PG (feel modifier) – mainly for knit/dress materials, 1.5%-2% of total paste.			
Pidifix 361 – formaldehyde-based fixer			
Pidifinish FX500 – zero formaldehyde fixer 1–2% of total paste.			
(*Pidilite Industries Ltd., Mumbai, India)			
· 1			

Printed goods are dried, and subsequently cured at 150°C for 3 minutes or 140°C for 5 minutes.

To improve fastness and color strength of pigment colors on polyester fabrics, atmospheric plasma treatment was used. Polyester fabric was treated with argon or air plasma at atmospheric pressure, and plasma pretreatment effect on the pigment printing was evaluated. A printing paste comprising synthetic thickener, binder, and pigment was applied using a flat screen printing technique. The fabric was then dried and exposed to heat. The cured prints were evaluated for color property, color fastness to washing, and dry/wet rubbing. When the properties of atmospheric plasma treated samples were compared to those of untreated sample, higher K/S values were obtained. Also, the fastness of treated samples increased between ½ and 1 point (Yaman et al., 2012).

5.2.1.6 Fashion Printing

Some other special prints called fashion prints developed by PIDILITE Company (India) for creating special effects on garments are discussed subsequently.

5.2.1.7 White Pigment Printing (Khadi Printing)

Khadi, also called as Khari or Tinsel Work, is meant to beautify and enhance the fabric's look. Khadi print is the most recommended form of screen textile printing for printing lighter color shades on darker bases like printing white flowers on blue table mats or yellow lamps on brown bed sheets.

Khadi print is easily identifiable by the fact that the printing ink stays on the surface of the fabric and does not permeate through to the other side. Often light colors like white pigment, titanium dioxide and metal powder like gold and silver are printed using khadi, for the way that the colors stand out. The rubbing and washing fastness is poor as the fabric is not really dyed/printed with the khadi color; instead, the color is standing on the surface of the fabric.

Figure 5.3(a) shows a white pigment (khadi) printing.

TiO ₂	35% or as per desired results
Water	5%
Pidicryl Binder 9400	40%
Pidinon OK HC (emulsifier)	2%
Pidivyl BPX	5%
Reduction binder (as in normal pigment printing)	10–12%
Pidifix 361 (crosslinking agent)	3–10%

5.2.1.8 Typical Recipe

For better results, TiO_2 is to be soaked in binder for overnight, sometimes for a few days. For colored Khadi printing mostly in yellow color, Sandalwood, saffron colors are added.

5.2.1.9 Mica (Pearl) Printing

Pearlescent pigments are coated mica platelets that provide both color and exciting visual effects to a variety of coatings, plastics and printing ink. These luster pigments

are transparent and because of their smooth surfaces reflect light. Although these pigments are non-metallic, they can give paint a metallic look.

The mica in pearlescent pigments is synthetic or natural; coated with titanium dioxide, iron oxide or another metal oxide. Platelets of coated mica can vary in size, shape and thickness. It is the degree of these characteristics along with the thickness of the coating that determine the color and appearance of the pigment. Additionally, thickness and the coarseness of the particles determine the sparkle.

The term "pearlescent pigment" derives from natural pearl and mother-of-pearl. These materials comprise layers that reflect some light while remaining translucent enough to allow light to pass further below the surface. Light is reflected back to reach the observer from several layers, including the top layer, creating a lustrous appearance of reflected light and depth.

While conventional metallic pigments are essentially planar flakes of an opaque reflective material, pearlescent and other effect pigments use a multi-layer structure to produce reflection, refraction and optical interference.

Pearlescent pigment grades include silver (white), interference colors (yellow, orange, red, violet, blue, green), earth tone colors (bronze, copper, russet) and gold colors (light gold and gold).

Mica is a natural mineral (muscovite) of low refractive index (RI) that is transparent in paint because it allows the transmission of light. When these thin platelets (about 500 nm) are coated with high refractive index metal oxides (ranging in thickness from 60 to 165 nm), they have the ability to reflect light. The face size of these particles range from 1 to 150 microns and the thickness ranges from 0.1 to 3 microns.

Luster is a gentle sheen or soft glow, resulting from a substance that is partly transparent and with a partly reflective surface. The reflective property of minerals with vitreous luster is similar to that of glass. This is a very common type of luster and can occur in minerals that are transparent or translucent, such as quartz and calcite. The glitter or sparkle effect of some pearlescent pigments is its ability to shine by reflection with many small flashes of brilliant light. For this purpose, titanium coated with mica powder is used (Ivana et al., 2018).

Figure 5.3(b) shows a pearl printed fabric.

5.2.1.10 Print Paste Recipe

Pearl Powder	20%
Pidicryl Binder KPL (ready binder)	60%
Pidinon OK HC (emulsifier)	2%
Stirred mildly, then add	
Kerosene	18% under stirrer
Pidifix 361	3% at the time of printing
Print – Dry – Cure	

5.2.1.11 Rubber/Puff/Foam/Emboss Printing

Puff ink is an opaque base that rises up on being heat-set to provide a raised print effect. Puff print is also called the Foam Print or Emboss print for the raised print effect. It is also acknowledged by many as a rubber printing technique.

Puff ink is a plastisol that has been modified with the addition of a heat reactive foaming agent. The ink expands when exposed to high temperature heat as the garment is cured. An additive to plastisol inks raises the print off the garment, creating a 3D feel. In this method, when the paste is printed and dries it look like normal printing garments but once it is cured the prints get raised from the fabric's surface. It is better to use a heat press machine instead of a hand dryer machine, because it will make the puff rise evenly.

Plastisol is a suspension of polyvinyl chloride (PVC) or other polymer particles in a liquid plasticizer; it flows as a liquid and can be poured into a heated mold. When heated to around 177°C, the plastic particles dissolve and the mixture turns into a gel of high viscosity that can no longer be poured. On cooling below 60°C, a flexible, permanently plasticized solid product results. Aside from molding, plastisol is commonly used as a textile ink for screen printing. Some important information about plastisol are listed below:

- "Blow temp" temperature Normally between 100–140 °C (As specified by manufacturers)
- Ready to use products Pidicron Foam Binder FB Conc/FBWL

Popular in-house recipe:

Pidicryl FL 9400 (ready binder)	60 %
Foam powder	15 %
Pidivyl BPX (plastisized homo polymer, ready product)	25 %

Dilute to desired levels possible with water-based paste or with white khadi.

• Blow Temp is critical to get best results.

5.2.1.12 Glitter Printing

Glitter print is known as Zari print in the Indian subcontinent. Zari means gold or silver threads. Glitter printing enables the fabric to show glittering granules on the fabric. Glitter powder is generally polyethylene terephthalate (PET) with a size of 1/8" to 1/256", cut into square and hexagonal shapes. Glitter powder is added in the glitter ink, while stirring slowly to avoid lump formation.

Zari or glitters are flat multi-layered sheets produced by combining plastic, coloring and reflective material such as aluminum, titanium dioxide, iron oxide and bismuth oxychloride. These sheets are then cut into tiny particles of many shapes including squares, triangles, rectangles and hexagons.

Figure 5.3(c) shows a zari printed fabric.

- Zari/Glitter Fine powders of polyester films
- · Types of Zaries -
 - Rainbow Zari rainbow effect
 - Superfine Zari milky zari
 - Glitter Zari big particle size

- Pidicryl Binder FJN High performance
- Pidicryl Binder ZER Good performance (ready binder)
- Printing Binder 80 % + Zari 20 %
- Coat/ print binder, spray and press zari
- Print Dry Cure.

5.2.1.13 Metal Powder Printing

The particle size of the metallic powders should be such that they can easily pass through the screen of appropriate mesh. The particle size should be in the range of $0.5-6 \,\mu\text{m}$. Generally, these prints are produced on dark background. The concentration of the metal powder varies between 15% and 25% depending on the covering power of the powder.

- Gold, silver, copper, bronze metal powder, commercial grades available mixtures of metallic powders
- Mesh size -20-120 (suitable for textile printing>60 mesh)
- Critical parameters fastness/choking of screen/blackening of prints
- Recipe
 - Pidicryl Gold Binder MMG 80% (ready binder)
 - Metal powder 20%
 - Pidifix 361 3%
- Sequence
 - Print Dry Cure.

5.2.1.14 Foil Printing

Foil printing is to print some pattern with foil on the fabric for a shiny effect. This printing method is based on the use of metallic foil paper of aluminum or copper. Foil is applied by adhesive. The print fixation method is similar to transfer printing.

Figure 5.3(d) shows a foil printed fabric.

- 1) Print directly with binder GFL
- 2) Place foil paper with the colored side facing you
- 3) Fuse at 150° C for 6 seconds
- 4) Bring the printed material to normal or room temperature and then pill-off the paper

5.2.2 PRINTING WITH REACTIVE DYES

The formation of a covalent bond between dye and fiber makes it possible to use dyes which, unlike the vat and direct dyes, are of small molecular size and good solubility. These dyes can be brighter, faster-diffusing and, in the hydrolyzed form, easily removed in the washing-off process (Davies, 1972).

When selecting reactive dyes for printing, the factors of importance for dyeing must be considered but, in addition, attention must be paid to print paste stability and staining of the ground during washing-off (Miles, 2003).



FIGURE 5.3 Fashion prints: (a) white pigment; (b) pearl; (c) zari; (d) foil prints.

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

5.2.2.1 Fabric Pretreatment

The pretreatment of the cellulosic fabrics is especially important when reactive dyes are used for printing. Woven fabrics must be thoroughly desized as the size reduces azo dyes under hot alkaline conditions in presence of reducing end-groups, leading to lower color yield. Most reactive dyes give full color value on mercerized or semimercerized cotton. For unmercerized cotton, rapid-diffusing and leveling types of reactive dyes may be selected. With regenerated cellulose, suitable pretreatment leads to improved prints. Swelling in a caustic soda solution of concentration 4-6 °Bé at room temperature, under tensionless conditions, improves the color yield of the print. The fabric should be well rinsed, but not neutralized, to achieve maximum effect. An alternative would be to pre-pad with 100 g/l urea and 10 g/l soda ash.

Reactive prints account for about 25% of the total print production throughout the world due to the variety of bright colors, hue and high wet fastness of the print. A successful print involves the correct color, sharpness, levelness, good handle and efficient use of dye (i.e., color yield). All of these factors depend heavily on the type of thickener used and the resulting print paste rheology (Wang et al., 2013). Sodium alginate is the most widely used thickener owing to the mutual anion repulsion between – COO- of sodium alginate C-6 and SO₃ of reactive dyes. However, its limited supply and high cost have spurred effects to find alternatives. In view of excellent thickening, stability and filming properties as well as low cost, guar gum (GG) and its derivatives are the most interesting selectable thickeners (Roy Choudhury, 1981a).

Guar gum is a water-soluble polysaccharide having mannose backbone with galactose side-chains (Figure 5.4).

Guar gum has unusually high viscosity at very low concentrations, unaffected over the broad pH range from 4 to 10.5. However, it possesses many active hydroxyl groups which react with reactive dyes. The chemical modifications of guar gum involve esterification and etherification (Dodi et al., 2011), crosslinking (Huang et al., 2006) and grafting (Abdel-Halim et al., 2011), among which carboxymethylation and hydroxylpropylation (Roy Choudhury, 1981a, Pal, 2009) were the popular methods for preparing thickeners for reactive dyes.

S-triazine di-sulfanilic guar gum (TSG) was successfully prepared by monochlorotriazine di-sulfanilic (TS) and guar gum (GG) in order to improve the printing properties in reactive printing. The results showed that the optimized synthesis

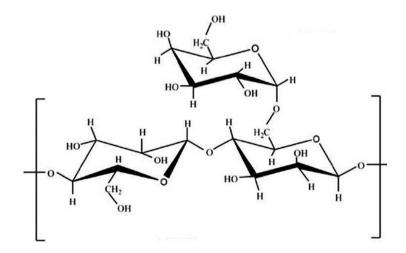


FIGURE 5.4 Chemical structure of guar gum.

condition of TSG was at sodium carbonate solution 1.2 g/L at 90 °C for 75 minutes through the single-factor experiment. Compared to GG, TSG had better flow properties, mainly viscous effects and higher viscosity recoverability, which was more appropriate as a thickener in reactive printing. In the cotton printing experiment, TSG had higher paste add-on, color yield, penetration and levelness than GG. Furthermore, the printing effects of TSG on cotton drew near to those of sodium alginate, which could obtain evenly colored large patterns and excellent outline sharpness (Wang et al., 2018).

Xanthan gum can be produced from simple sugars using a fermentation process, and derives its name from the species of bacteria used, *Xanthomonas campestris*. Xanthan gum, 1%, can produce a significant increase in the viscosity of a liquid. Wang et al. (2013) modified xanthan by deacetylation under alkaline conditions at 90°C. When used as thickener, the xanthan modified by full deacetylation (MXG) could perform as excellently as sodium alginate (SA) in the printing of large patterns, and even had an advantage over SA in fine-pattern printing. Consequently, using SA and MXG as mixed thickeners should be considered for printing with reactive dyes to integrate the excellent rheology of these thickeners for a better printing performance.

With a small addition of MXG to SA, the flowability of the mixed printing pastes is better than with SA alone. Subsequently, with the continual addition of MXG to SA, the apparent viscosity at low shear rates increases gradually, and the mixed printing pastes show increasingly pronounced shear-thinning features. Moreover, the results of dynamic strain sweep tests show that mixed printing pastes with more sodium alginate mainly show viscous behavior under strain, and the liquid-like features become increasingly weak with the addition of MXG. On the other hand, mixed printing pastes with more modified xanthan mainly exhibit elastic behavior within the linear viscoelastic region and the solid-like features become increasingly marked with the addition of MXG. Mixtures of SA and MXG can be used as thickeners in the reactive printing of cotton, affording prints of excellent color yield, levelness and outline sharpness. In particular, mixed printing paste performs best for large patterns when the ratio of SA to MXG is 80:20, and best for fine patterns when the ratio is 20:80 (Wang et al., 2014).

There is a large natural reserve of bentonite that can meet the requirements for printing paste and is applicable to cotton, polyester, blends and silk. It can reduce chemical oxygen demand (COD) of effluents. Huang et al. (2017) studied the rheological properties of mineral clay (OMC) and sodium alginate (SA) pastes using steady shear, dynamic oscillatory and transient tests. The results showed that OMC was a viscoplastic fluid and had more obvious shear-thinning features than SA, which fitted well to the Herschel-Bulkley model in which the strain experienced by the fluid is related to the stress in a complicated, non-linear way. Under strain, OMC and SA exhibited elastic and viscous behavior, respectively, within the linear viscoelastic region. The viscosity of OMC returned to >60% of the initial viscosity after the removal of the high shear stress. In printing experiments, the color yield and penetration of OMC surpassed that of SA and offered excellent outline sharpness, suggesting that it has the potential to be used as a thickener for reactive dyes in cotton printing.

For optimal results, pretreatment of fabric is important, especially before printing with reactive dyes. Various sizes (mostly starch-based) are applied to warp yarn for better weaving. Before printing, especially with reactive dyes, the sizes and other impurities are to be thoroughly removed; they may otherwise react with reactive dye and get reduced. Mercerization increases color yield to a great extent with most reactive dyes. If the fabric is unmercerized, fast diffusing dyes are to be used. For regenerated cellulose such as viscose, caustic pretreatment (tensionless) and subsequent washing without neutralization improve color yield. Alternatively, the fabric is padded with 100 g/l urea and 10 g/l soda ash before printing.

The advantages of reactive printing are:

- No shade limitation full gamut of colors available.
- A number of sub-groups of reactive dyes are available namely hot-brand, Remazol, HE and ME – of varying costs, hues, brightness and fastness properties; hence, a wide choice of dyes.
- Reactive dyes form covalent bonds with the fiber substrates. The fastness of these dyes depends on the bond stability and not on the molecular size of the dyes. These dyes are, therefore, made of comparatively smaller dye sizes. Consequently, the dyes are brighter and fast diffusing. The larger the molecular chain, the higher the light absorption at multiple wavelengths causing greyness. The unfixed dyes are also easily removed during washing.
- Simple and alternate application processes are available, namely "all in", "cold fixation", "two-stage", "print-steam", "print-HT-steam", and "print-thermosol".
- The thickeners of high quality are used in reactive printing. Consequently, faster printing is possible due to better flow of the printing paste and the chances of screen chocking are also less.
- The reactive printed fabrics have smoother handle whereas pigment printed samples have stiffer handle due to the presence of binder in the printed areas.

The disadvantages of reactive printing are:

- The conventional gums react with reactive dyes leading to loss of color and/ or stiffening of the printed fabric.
- The hydrolysis of dyes requiring careful and thorough wash after fixation.
- Hydrolysis of dyes may be very high if print paste alkalinity and steaming conditions are improper, resulting in poor color yields.
- The unfixed dyes may stain the ground (non-printed) portion of the fabric.

5.2.2.2 Choice of Thickener

Most thickening gums are carbohydrates. They react with reactive dyes resulting either in poor color yield or insolubilization of thickeners in the printed areas, and thus, stiffer handle.

Alginate does not react, because of the absence of the primary OH group and also the repulsion of dye anions by COOH groups present in sodium alginate. Sodium alginate has very good flow properties, but it is very costly compared to conventional thickeners. The supply of sodium alginate is diminishing day by day due to the shortage of the main raw material, brown seaweed, partially due to increasing offshore petroleum projects.

The flow-sheet of the production of sodium alginate is as follows:

Brown seaweed \rightarrow digestion with Na₂CO₃ \rightarrow precipitation as Ca-salt \rightarrow purification \rightarrow regeneration as free acid \rightarrow conversion into desired salt of alginate.

Sodium alginate may be substituted as follows:

- Use of carboxymethyl cellulose. But it has poor solubility in water. The lesser the degree of substitution, the more the reaction with reactive dyes. On the other hand, the higher the degree of substitution, the lesser the reaction with dye, but with poorer water solubility.
- Use of synthetic thickener like polyacrylic acid can provide higher color yield and easy removal by washing, but results in more susceptibility to electrolytes.
- Guar gum may be used with a cold method. No stiffening occurs, but the color yield is poorer.

Synthetic thickeners predominate in the printing of pigments due to their low solids content. They additionally offer advantage over natural thickeners in quick and easy paste preparation and viscosity adjustment, and consistency of quality and supply (Abdel-Halim et al., 2008). Today the pressure to print reactive dyes economically with high quality has led to the commercial development of synthetic thickeners for this application (Akcakoca et al., 2000).

Today the pressure to print reactive dyes economically with high quality has led to the commercial development of synthetic thickeners. Madhu and Patel (2016) examined the printing properties of reactive dye pastes based on natural thickeners, a mixture of natural thickeners, as well as two formulated synthetic thickeners to determine if such synthetic thickeners are able to overcome disadvantages, while not losing the advantages for which each is known. There are many variables that might be examined, but generally a printer is looking for a paste that is simple to prepare, stable, prints level and sharp, minimizes the use of dye and auxiliaries and is easy to remove (Madhu and Patel, 2016). They used four different thickeners, including guar gum (GG), sodium alginate (SA), a mixture of guar gum and sodium alginate (GGSA) and two formulated synthetic thickeners (ST1 and ST2). The experiment indicates that formulated thickeners (synthetic polymer, ST1 and ST2) based on thermal polymerization can be used safely for preparing printing paste for screen printing of cotton textile fabric with reactive dye. The highest K/S value obtained with paste is prepared using formulated thickener, which also has fastness properties ranging between excellent and good, compared to samples printed using natural thickener such as guar gum and sodium alginate. The synthetic thickeners perform better than natural thickeners in reactive printing on cotton.

5.2.2.3 Printing Methods with Reactive Dyes

The process flows of various alternate methods of printing with reactive dyes on cellulosic materials are as follows:

All-in Method

Recipe (unit: g or parts) for stock paste	
Alginate thickening (3-12% paste):	400-500
Urea:	100-200
Sodium bicarbonate	20
Sodium m-nitrobenzene sulfonate	10
Water	470-270
Total to make with water/thickener to 1,000	

The required amount of reactive dye may be sprinkled into the stock paste. The solubility of most reactive dyes is sufficient for this sprinkling method, followed by high-speed stirring, to give perfectly smooth prints.

The dye can alternatively be predissolved, using the urea to increase the solubility, in a small volume of hot water. Sodium bicarbonate should only be added after the mixture of dye solution and thickener has cooled to room temperature.

Sodium bicarbonate maintains alkaline conditions during steaming for the reaction between dyestuff and cellulose. Sodium m-nitrobenzene sulfonate, called resist salt, is used to prevent oxidation of dyes during steaming.

Sodium alginate may be sprinkled into hot water under stirring and may be stored overnight for complete swelling. The dye is sprinkled under stirring into thickener paste. Alternatively, dye may be pre-dissolved in hot water and then mixed with thickeners. Just before printing, urea, sodium bicarbonate and resist salt (m-nitro benzene sulfonic acid) are mixed into the dye-thickener paste. A reduction paste may be prepared in the similar way without adding dye. The same paste may be used for preparing pastes of lighter depths from the stock paste prepared previously.

After printing, the fabric is dried at a temperature of below 100°C followed by fixation.

The fixation may be done by one of the following:

- Saturated steam at 105 °C, 10 min \rightarrow wash \rightarrow dry.
- Bake at 160–180 °C for 3 min \rightarrow wash \rightarrow dry.
- H.T. steam 130–160 °C for 30–60 min \rightarrow wash \rightarrow dry.

In addition to the all-in method, a number of alternate printing methods are available as:

• Print without alkali \rightarrow Dry \rightarrow Pad with alkali \rightarrow Flash ageing (1–2 min)

The alkaline solution can be applied on a vertical two-bowl padder at high speed or, if lower speeds are used, on a horizontal two-bowl or nip pad.

- Print \rightarrow dry \rightarrow wet treatment with alkali \rightarrow wash \rightarrow dry
- Pad with alkali \rightarrow dry \rightarrow print with M brand \rightarrow hang \rightarrow wash \rightarrow dry
- Silicate padding method.

Print without alkali → Nip pad with sodium silicate (100° Tw, Na₂O: SiO₂:: 1: 2.1) (Sodium silicate liquor can be padded at 40 °C to reduce its viscosity and assist penetration) →

- The fabric is batched after pad application of the development liquor, at 70-80% pickup.
- Fixation takes place while the batch is left standing for about 6–12 hours. The fabric may be protected from acid in the atmosphere by wrapping the batch in plastic film and prevented drying at the edges. It is finally washed.
- This method is popular in the cottage sector, as expensive fixation machinery can be dispensed of. This method is quite successful with vinyl sulfone dyes. Guar gum and its derivatives may be used instead of sodium alginate as these gums may coagulate in sodium silicate, preventing bleeding in wet condition during batching.

5.2.2.4 Washing-Off of Reactive Prints

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

A good portion of reactive dyes (10–30%) get hydrolyzed during fixation. These unfixed dyes are to be removed completely by washing. Otherwise, these dyes are adsorbed at the unprinted portions causing staining. For large printing production, it is advised to carry washing in multiple steps such as:

- · Cold thorough wash till wash liquor is colorless
- Wash with mild acid (acetic acid or hydrochloric acid) solution
- Hot wash
- Soaping with 1-2 g/l soap or detergent
- Cold wash.

Different approaches have been reported on the elimination or replacement of urea in cellulose printing, including partial or complete substitution of urea by alternative chemicals, mechanical application of moisture prior to the substrate entering the steamer, using two phase printing (flash age printing), pre-wetting with foam and replacement of sodium alginate with synthetic thickener. In this regard, a low-cost alternative chemical, namely sodium edetate (SE) (Figure 5.5) would be of interest as a replacement for urea in reactive dye printing.

The viability of using SE as an alternative to urea in reactive dye print pastes for cotton fibers was explored by Ahmed et al. (2006). The result indicates that SE/free alkali printing shows the best results compared with urea/alkali conventional printing. Besides the low cost of sodium edetate and its use in alkali free

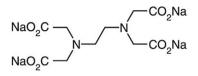


FIGURE 5.5 Chemical structure of sodium editate.

printing of cotton with reactive dyes, the prints obtained have good levelness, outline sharpness, low penetration with considerable dyestuff savings and thus low demands on the print back cloth washing process leading to a reduction of the wastewater load.

Zydex industries (www.zydexindustries.com/) produced Acrylic Thickener-R, a new generation polymeric thickener recommended for reactive printing on rayon/ cotton fabric. Acrylic Thickener R can be used as a partial substitute to sodium alginate or gum. It is a safe product as no cooking is required. It can be used only after high-speed stirring for 10–15 minutes. It is an eco-friendly product.

The further information about Acrylic Thickener are as follows:

- Since Acrylic Thickener-R is water soluble during the washing process, printing gum is removed easily.
- Costs are saved when used with sodium alginate and kerosene half emulsion.
- It helps in preventing tinting of dyes on unprinted portion.

5.2.2.5 Preparation of Stock Paste

Stock A

2.5 to 3.0% Gum Paste is prepared by cooking (Alginate – 2.5 to 3%, Guar Gum – 3 to 6%)

Allow it to cool down.

Stock B

Stock paste of 4% Acrylic Thickener-R is prepared in cold water under continuous stirring.

Stock A	68.0%
Stock B	18.0%
Urea (use pre-dissolved and filtered solution)	10.0%
Sodium Bicarbonate	3.0%
Resist Salt	1.0%
Total	100.0%

Recipe for steam ageing method

- Desired percentage of reactive dye(s) is taken; dissolved in hot water at 70°C.
- The dissolve dyed solution is mixed in above stock.
- Print followed by drying at 125°C.
- Steam for about 10 minutes at 105°C.
- Wash thoroughly.

Recipe for silicate padding method

Printing	
Stock A	80 kg
Stock B	20 kg
Total	100 kg

- Desired percentage of reactive dye(s) is taken; dissolved in hot water at 70°C.
- The dissolve dyed solution is mixed in above stock.
- Print and dry the fabric.

Fixation by Padding Mangle

Black Silicate $(105 \circ Tw^*)$	90.0 kg
Caustic Soda (48 ° Tw)	5.0 kg
Soda ash (10 to 15% Solution)	5.0 kg
Total	100.0 kg
* $^{\circ}$ Tw is the specific gravity measured by Twaddle meter	

- Suitable squeegee pressure is maintained to squeeze fabric properly.
- Squeezed fabric is stored for 12 to 18 hours.
- Wash with cold water.

5.2.3 PRINTING WITH VAT DYES

Vat dyes are characterized by excellent all-around fastness and full range of shades with moderate to high brightness. But these dyes are generally costly. Starchtragacanth mixture thickener is found to be most suitable to give maximum color yield and brightness in printing with vat dyes. For sharp outline and level prints, British gum is recommended. British gum is a modified starch powder mainly used in the textile industry for printing applications. It has good adhesiveness and shine with fast drying properties. British gums are made by heating the starch at a relatively high temperature in the presence of an alkali. British gums have a darker color than do white dextrin. Yellow dextrin is known as a highly modified product, made by heating the starch to relatively high temperatures in the presence of an acid. Before printing, the fabric is to be prepared thoroughly as follows:

- A scour with detergent and alkali to remove oils and waxes from the fabric and make it absorbent is required.
- For cotton and cotton blends, an additional bleaching process may be included to further whiten the fabric and remove motes.
- In the case of cotton woven fabric, it is advantageous although not necessary that the fabric be causticized or mercerized to maximize color value and print appearance as well as to increase fabric luster and sheen. The concentration of sodium hydroxide (NaOH) needed to causticize cotton is 22 °Bé. To produce mercerized fabric, the NaOH concentration needs to be increased to 28–32 °Bé.

For satisfactory prints, a ready for dyeing (RFD i.e., fully prepared fabric) fabric should possess the following properties:

- Uniform absorbency
- Clean (no lint)
- White in color
- Uniform width
- No creases
- Neutral pH (7.0–7.5 is best for all printing)
- Alkalinity ≤ 0.05
- Preferably causticized or mercerized.

Vat dyes are dyed using sodium hydrosulfite $(Na_2S_2O_4)$ as reducing agent, though it is highly unstable and decomposes at room temperature. The printing pastes are prepared beforehand and are normally stored for quite sometimes before being used for printing. To prevent decomposition of the reducing agent, a stronger reducing agent like Rongolite C/Formasol F (chemically sodium formaldehyde sulfoxylate) may be used, which is stable at room temperature and decomposes only during steaming as follows.

NaHSO₂ CH₂O,
$$2H_2O \rightarrow NaHSO_2 + CH_2O + 2H_2O$$
 [Equation 5.2]

$$NaHSO_2 + 2H_2O - NaHSO_3 + 2H$$
 [Equation 5.3]

For printing, the vat dyes should be of high dispersion and low particle size. Hence, paste forms of vat dyes are specially developed for printing. The main advantage of paste form is that they can be printed safely by the Potash-Rongolite method without pre-reduction.

Vat dyes can be printed by the following procedures:

- 1) One-phase printing (all in method)
- 2) Two-phase printing

The two-phase process accounts for almost 100% of vat print application. The resultant color prints are very fast to washing and rubbing. The majority of vat prints are found in the home market in upholstered goods, drapery and decorative items, which requires these vat-printed fabrics to meet their color fastness specifications. The only apparel market that requires similar fastness specifications is the military camouflage apparel sector. One-phase printing is used almost exclusively in vat "discharge" applications for the fashion apparel market. Discharge is where one color is destroyed and another may be put in its place.

One-phase printing (all-in method)

Print – dry rapidly – cool – steam (for 8 to 20 minutes at 103°C in air free steam) – rinse – oxidize – soap – dry.

Maize or wheat starch	100 g
Mixed well with	
Water	160 g
Gum tragacanth (6%)	110 g
British gum	250 g
The mixture is cooked for 30 minutes, cooled to 80 0 C	
Potassium carbonate	180 g
Cooled to 50°C, added Rongolite	150 g
Glycerin	50 g
Total	1,000 g

Recipe for stock thickening

Recipe for print paste

Vat dye paste	50–150 g
Water	250–150 g
Stock thickening	700 g
Total	1,000 g

Print \rightarrow dry well \rightarrow steam immediately in Star ager for 20–30 minutes or in rapid ager continuously for 10 minutes at 102°C (in both cases) \rightarrow Oxidation is carried out in a bath containing 1–3 g/l sodium perborate or potassium dichromate and 2–5 cc acetic acid at 40–45°C \rightarrow Finally it is soaped thoroughly.

An alternate recipe is as follows:

Vat dye paste	7 g
Potassium Carbonate	15 g
C.I. reducing agent 2	8 g
(Rongolite)	
Glycerol	5 g
Thickener	24 g
Water	41 g
Total	100 g

Potassium carbonate is preferred for its high solubility. Glycerol act as humectants, improves solubility of leuco compound and thereby fixation as well as levelness of print. Dispersing agent like Solution Salt-B (dibenzyle sulphanilate) may be used optionally. Choice of thickener affects the reduction rate. British gum is reported to accelerate decomposing of the sulphoxylate. Starch and starch-tragacanth thickeners are the alternatives. Oxidation may be done by airing or passing through 2-4g/l sodium perborate (mild oxidizer to prevent over oxidation) and 5g/l acetic acid at 60–70°C.

One disadvantage of the all-in method is that the printed material cannot be stored long before steaming. Even over-reduction may cause decomposition of sulfoxylate resulting in poor color yield.

Two step method:

Print with dye and thickener – dry – pad with alkali and reducing agent – immediate and short steam – oxidize – wash.

Premature oxidation is avoided and printing is possible with a complete range of vat dyes. The thickener should be alkali coagulable. The best is methylcellulose (i.e., celloresin), hence named the celloresin process. But it is insoluble at high temperature and may be substituted with locust bean or guar gum. Noncoagulable thickener like starch may be mixed for easy removal during washing. As no reducing agent is present, the dried fabric may be stored for a long time without any problem. Steaming follows immediately after alkali padding; hence sodium hydrosulfite may also be used. Steaming time is very short; around 20–30 seconds.

Vat dye paste	250 g
Water	150 g
Starch-tragacanth paste	350 g
Methyl-cellulose (4%)	250 g
Total	1,000 g

Recipe for vat printing paste

5.2.3.1 Mixed Thickeners May Give Better Prints

- Starch ether promotes surface coverage printing and thereby increases color value.
- Guar or guar ether promotes a longer flow that increases print coverage uniformity.
- Sodium alginate (8% low viscosity) may need to be used to give better print outlines and edges.
- Blended products are available in the market.

The alternate sequence of operation for printing without adding reducing agent in the printing paste, known as two phase printing, is given here:

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Printing \rightarrow drying \rightarrow padding \rightarrow steaming \rightarrow oxidation with sodium perborate \rightarrow rinsed \rightarrow soap at boil \rightarrow wash \rightarrow drying.
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After padding, the fabric is guided into the flash ager. The ager is designed to use super-heated steam at 125–130°C (257–266°F). The fabric is supported on the back and travels vertically for 2–6 meters and then reverses direction and vertically descends to an exit. At this point, for the first time, the face of the fabric is contacted by a transport roller and is conveyed out of the steamer exit. The face of the fabric is untouched until the dye fixation is complete and no chance of smearing or other defiling of the print can occur. In this steamer design, the total steaming time can vary from 20–30 seconds to 45–60 seconds depending on fabric weight and print design (Cotton incorporated, 2006).

After exiting the steamer, the fabric usually gets a short, forced air cool-down. Then the fabric is passed through an aggressive open-width spray compartment where it is impinged with both fresh and re-circulated water to reduce pH and alkalinity.

Still in open width configuration, the fabric is passed through an oxidation bath. A constant pump fed mix of hydrogen peroxide and acetic acid is used. Concentration in the bath:

Hydrogen peroxide, 35% 5.0–8.0 ml/L Acetic acid, 56% 2.0–3.0 g/L

The concentration of hydrogen peroxide in the oxidation bath can be controlled by titration. A minimum acceptable range of 2.0 g/L should be maintained.

At this point, the fabric enters a hot wash. Washing with detergent and sodium carbonate, constant agitation, and temperatures of $90^{\circ}-95^{\circ}C$ ($194^{\circ}-203^{\circ}F$) are needed to develop the true shade.

Bath Concentration:

Sodium carbonate 5.0–10.0 g/L Detergent 2.0–3.0 g/L

The fabric is then passed through a hot rinse at 40–50 °C (104–122 °F).

The recipe for padding liquor containing Rongolite or sodium hydrosulfite goes as follows:

	With Rongolite	With sodium hydrosulfite
Rongolite/sodium-hydrosulfite	100 g	200 g
Water	500 g	500 g
Potassium-carbonate	100 g	nil
Glycine A	nil	15 g
Glycerin	100 g	nil
Anionic wetting agent	3 g	3 g
NaOH (70o Tw)	nil	65 cc
Glauber salt	50 g	40 g
Total	1,000 g	1,000 g

Two phase printing is usually used for woven cloths printed with reactive or vat dyes. After printing and drying, the cloth passes through a chemical mangle and then into a steaming chamber for fixation.

Wang et al. (2010) made a study of the thickeners used in two-phase vat dye textile printing. Throughout this complex process, the thickener dispersion undergoes several transformations, especially spreading on the textile material, drying and coagulation. Three different thickeners are considered: guaranate, alginate and modified starch, as well as a combination of these three polymers. Their rheological properties are characterized in both permanent and oscillatory shear flow. Use of a mixture of polymers instead of a simple one avoids undesirable effects of thixotropy, yield stress, and elasticity, for a given value of the viscosity. The process involves the gelation of the thickener by crosslinking of guaranate chains with borate ions. The mechanical properties of such gels strongly depend on the pH, and their stability is affected by the presence of salt. Additionally, thickener films are dried under different conditions, and the morphology of the film is observed at different scales. It is shown that rapid drying at high temperature prevents crystalline structures obtained in the case of slow drying under ambient conditions. This is propitious to a good flexibility of the polymer film, suitable for fabric handling, good swelling in the steamer and easy washing off.

5.2.4 PRINTING WITH SOLUBILIZED VAT DYES

Vat dyes provide a wide range of colors of good all-round fastness properties, but great care, and specialized equipment, is required for their successful use. The solubilized vat dyes offer a simpler method of application, at somewhat higher dye cost. The leuco forms of many vat dyes can easily be transformed into sulfuric acid esters, which can be isolated as stable powders. They are water soluble, have affinity for cellulose and after printing, can be oxidized under acid conditions to the insoluble parent vat dye.

Exposure to light can cause premature oxidation, which must normally be avoided; this can be exploited, however, for the production of photographic effects on fabric. Very deep colors are impossible to obtain, or of prohibitive cost. These dyes have consequently rarely been used alone, but they have found application to supplement the azoic colors.

Two methods of fixation have commonly been used: the nitrite and the chlorate processes. In the former, sodium nitrite is incorporated either in the print paste or in the naphthol preparation. After printing and drying, followed by a short steaming for optimum yield, development is obtained by a short immersion in dilute sulfuric acid.

When sodium chlorate is used as the oxidizing agent, the alkalinity of the color print paste is maintained with ammonia, and an acid generator, usually ammonium sulfocyanide, is activated by steaming. Ammonium vanadate is also needed, in small quantity, as an oxidation catalyst. Solubilized vat dyes are vat dye in the form of a soluble sodium salt of a sulfuric acid monoester of its leuco compound. Solubilized vat dyes are particularly used for pale and light shades. Also known as Indigosols and trade name "Solatic dyes" by ICI and others, these dyes offer various advantages such as ease of use and stability. The solubilized vat dyes are particularly suited for dyeing and printing cotton and viscose material. Before the invention of reactive dyes and binders for pigment printing, it was difficult to get bright and fast prints on cotton fabric. Solubilized vat dyes were the only option for bright and fast print on cotton fabric. However, after the introduction of reactive dyes, they are no longer used for printing. These dyes are no longer available in the market in large scale.

There are several methods of printing with solubilized vat dyes. One such method using sodium nitrite is described as follows:

Solubilized vat dye	1–5 parts
Solubilizing agent e.g., Thiodiglycol	5 parts
Hot water	25 parts
Dissolved and neutralized thickener	60 parts
Sodium nitrite (1:3) solution	5 parts
Bulked to	100 parts

After printing, the fabric is steamed for 5–10 minutes at 105°C and then it is oxidized in a bath containing 20 parts by volume concentrated sulfuric acid (106°Tw) for 30 seconds or padding through the acid solution at 60°C, followed by air passage for 20–40 seconds. Finally, it is soaped with 3g/l soda and 2g/l soda ash followed by thorough wash.

5.2.5 PRINTING WITH AZOIC COLORS

Azoic colorants are formed in the fiber as a result of a chemical reaction. This reaction depends in the first place on the capacity of an aromatic amine to react with nitrous acid to form a diazo compound, and then on the reaction (coupling) of this diazo compound with a suitable organic grouping to form an azo linkage. Both reactions are among the oldest known reactions in organic chemistry.

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

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

Azoic colors were once very popular in small-scale dyeing sector due to low cost of dyeing and the simple method of dyeing at room temperature. The biggest advantage of this method is that the dyeing can be carried out at room temperature. Other dye classes require high temperature for dyeing and it cannot be carried out without a boiler, which is very costly and requires intensive maintenance. The fabric is first treated with naphthol solubilized with caustic soda. The treated fabric is subsequently treated with aromatic amine diazotized with nitrous acid. However, solubilized naphthol can't be mixed with diazotized base as they react prematurely.

In earlier days, the fabric was printed with diazotized base and then quickly passed through naphthol solution or vice-versa (Method A). However, these methods are obsolete because of huge wastage of azoic components.

For Method B, the diazotized base is stabilized or inactivated temporarily so that it can be mixed with naphthol and the mixture can be directly used for printing. After printing and steaming, diazotised base is activated by acid and the color forms.

Stabilization may be done in two ways:

1) Converting syndiazotate (coupling form) to antidiazotate (non-coupling form) by treating with exess caustic soda (Equation 5.4).

$R-N=NC1 \rightarrow$	R·N≡N·OH	\rightarrow	R-N	$\rightarrow R-N$
	Diazonium		aO-N	N-ONa
	hydroxide	Syn	ndiazotate	Antidiazotate

- 2) Forming diazo-amino compound: Diazonium salt is treated with suitable amino compound to give non coupling diazoamino/diazoimino compound. These are stable under neutral and alkaline condition, but under acidic condition they split up, liberating coupling diazonium compound. Amino compounds used as stabilizer may be one of the following:
 - 1) 2-Amino-4-Sulphobenzoic acid:

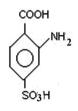
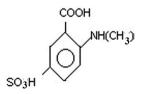


FIGURE 5.6 2-Amino-4-Sulphobenzoic acid.

2) 2-Methylamino-5-Sulphobenzoic acid:



- 3) N-Methyl glycine (Sarcocine) CH₃-NH-CH₂-COOH
- 4) Methyle taurine CH₃NH-CH₂-CH₂SO₃H
- 5) 2-Ethylamino-5-Sulphobenzoic acid

The reaction between diazotized base and sarcosine is shown in Equation 5.5.

 $R-N+\equiv NCl-+CH_3-NH-CH_2-COOH \leftrightarrow R-N=N-N(CH_3)-CH_2-COOH$ [Equation 5.5]

Rapid fast dyes are the mixtures of antidiazotate and naphthol, while Rapidogen colors are the mixtures of diazoamino/diazoimino compounds and naphthol.

Rapidogen is more stable; it requires steaming for fixation. There are limitations to the extent these dyes cannot be mixed. Rapidogen gives brighter and wider range.

> Recipe for printing paste 4 parts Rapid fast/ Rapidogen pasted with 4 parts sprit and T.R Oil and 2 parts caustic soda 25 parts water 60 parts neutral starch/gum 5 parts neutral chromate solution to prevent reduction to make 100 parts

5.2.5.1 Fixation Processes

5.2.5.1.1 Rapid Fast Colors

- Hanging in damp, warm room or open air for 12 to 18 hours preferably followed by treatment with 30g/l sulfuric acid and 30 g/l Glauber salt.
- Neutral steaming for 5 minutes followed by the previous treatment.

5.2.5.1.2 Rapidogen Colors

- Steaming under acetic and formic acid fume for 3 sec at 101–102°C.
- The goods are padded at 90–95°C, then dried on a hot flue or a cylinder dryer. The dried cloth is to be protected from light, moisture and acid fumes.

However, with the proliferation of reactive dyes and pigment colors, Rapid fast colors and Rapidogen colors have become nearly extinct.

5.3 DIRECT STYLE OF PRINTING OF SILK AND WOOL

Printed silk has always formed a high proportion of the total output of the silk industry. Articles like ties, headscarves and "haute couture" dress-wear have traditionally been printed with a range of designs and colors.

Silk and wool both contain amino acid residues, varying in their types and relative quantities. Silk contains simpler amino acids like sericin in large quantities while wool contains sulfur-containing amino acids like cysteine, which give it its reducing nature. Silk provides a beautiful flat surface for a screen print, and being a natural fiber, absorbs ink evenly and effectively. One thing to remember is that the thinner the fabric, the less ink will be absorbed, so expect a subtler effect than on a thicker cotton or wool base. The chemical properties of wool and silk are similar, and the printing methods are similar, varying on minor details.

In recent years there has also been a trend to higher fastness properties for printed silk. This has to do with the changed lifestyles in the course of time and the demand for higher wear and care properties.

It has been observed that in case of wool, dyeing is the most commonly used technique to enhance aesthetic appeal. Printing is not commonly used either at the small scale or large scale to produce beautiful attractive designs. It has been reported that hardly 2% of total wool in the world is printed. This is because of physical and morphological nature of wool. The hairy nature of woolen fabric operates against the production of fine, crisp designs which may be printed on the smooth fabric. Wool does not normally absorb the print paste very well, which may be because of scales on its surface. Bulky wool yarn is mostly used for making winter garments by knitting processes. Dyeing is the most preferred method of coloration of wool. If a print-like, multi-color effect is desired, it can be obtained by space dyeing techniques like the Vigoureux or hank space dyeing methods.

A small quantity of woven wool fabric is printed. In general, the method of printing of wool fabric is not much different from that of silk. Though wool and silk fabrics are chemically very similar, their physical and morphological properties are quite different. Wool is highly absorbent, while silk has moderate absorption properties. The required print paste viscosities for these two types of fabrics should be suitability adjusted. Wool fibers quickly get entangled on agitation under aqueous media. Hence, semi- and poor-soluble matters should be avoided in wool printing as vigorous washing after printing and steaming may cause entanglement or "felting".

Wool fabric should be chlorinated before printing for removing its hydrophobic surface scales partially. Chlorinated wool fabric possesses very good dye affinity. Penetration of dyes into the fiber is very good. The color depths of print improve significantly.

5.3.1 SURFACE CHLORINATION OF WOOL FABRIC

Basolan DC (BASF) is a good chlorinating agent with pronounced anti-felting properties. It retains soft handle and increases color yield.

Pre-scoured wool is chlorinated in three steps:

- (a) Treated with 0.5–2% wetting agent, 0.5–2 ml/l acetic acid 60% for 10 minutes.
- (b) Chlorinated with 2.5–5% Basolan DC, pH 4.5–5.5 with acetic acid for 20 min at 10–25°C and then 20–30 minutes at 30°C.
- (c) Dechlorinated with 1.5% sodium bisulfite at 30–50°C and finally rinsed.

Raw silk is a strong yellow in color. It is inherently poorly absorbent and rough in handle. Before printing, degumming of silk (see Chapter 3) is to be carried out with soap or detergent to remove sericin and other impurities until it is white in color and uniformly absorbent.

5.3.2 SELECTION OF DYES

Acid and acid milling dyes are cheap and easily available. Acid dyes give very bright prints but their fastness to light and wet treatment is poor. Acid milling dyes have medium brightness and good light and washing fastness. Metal-complex dyes are expensive as compared to acid dyes, but they have the advantage of having very good fastness to light and washing. They are not quite as bright as acid and acid milling dyes. Basic dyes can provide extraordinary brilliance in some cases, but do not provide adequate fastness. Specific acid dyes should also be selected to obtain the desired brilliance of hue as well as acceptable light and wet fastness required for the particular end-use.

Metal-complex acid dyes, both 1:1 and 1:2 complexes, offer higher fastness than acid dyes, particularly light fastness, but somewhat duller colors. The metal-complex dyes are applied in for the similar method as those acid dyes, except that these dyes do not require the use of an acid or acid donor. At low pH, in fact, not only is the stability of the paste diminished but the dyes tend to aggregate and give rise to specks. The acid donors can also adversely affect the levelness of prints, and these high-affinity dyes often give leveling problems in blotch printing.

The dissolving process and the choice of print thickener, as well as fixing and after washing are the same for both metal-complex and acid dyes. It is possible, therefore, to mix acid and metal-complex dyes, but printing should be without acids or acid donors (Gutjahr and Koch, 2003).

Reactive dyes produce bright and wash-fast prints. However, they are most difficult to fix, and removal of unfixed dye consumes a lot of energy and time. Natural or vegetable colors give limited dull shades and are liked only by a select customers.

5.3.3 PRINTING COMPONENTS

The print paste contains the following ingredients:

- 1) Suitable dye(s) in required quantities to match the target shade decided by laboratory matching
- 2) Thickener with a high solid content like gum arabic
- 3) Solvent for the dye, such as diethylene glycol (DEG), urea
- 4) Humectant, such as urea, glycerin
- 5) Acid liberating agent, like ammonium sulfate and citric acid
- 6) Mild oxidizing agent such as resist salt, sodium chlorate

5.3.3.1 Solvents, Solution Aids and Humectants

Solvents and dispersing agents are sometimes used to prevent aggregation of dyestuff molecules in a highly concentrated paste of the dye. Commonly used solvents include diethylene glycol and thio-diethylene glycol. These are excellent solvents and used in printing to assist dissolution of the dyes and promote the production of level and deeper print patterns. Use of urea is practiced judiciously, and it is recommended to use thiourea particularly in bright colors to get bright and clear prints. Other items used include glycerin and triethanolamine in optimal quantities to get good sharp prints. In certain cases, addition of benzyl alcohol is also recommended to the print paste for quicker swelling during steaming and better penetration. In fact, non-humectant types of penetrating agents also used to improve the color yield could include phenol, lithium bromide and sodium thiocyanate.

5.3.3.2 pH Controlling Agents

The printing pastes contain an acid donor for fixation of the dyes. Acid liberating compounds which could be used are ammonium sulfate, ammonium tartrate, oxalate or even in some cases acetic acid or glycolic acid. In certain cases of acid-metal-complex dyes at low pH, not only is the stability of the paste diminished but there is tendency for the dyes to aggregate and to give rise to specks.

When using acid dyes in printing, acid is required, in the same way as in dyeing, to fix the dye. Strong acids are usually avoided as these attack back-greys and squeegees. Ammonium tartrate and sometimes also ammonium sulfate are principally used to generate acid.

5.3.3.3 Mild Oxidizing Agent

In order to protect the dye present on the ground, the dyed cloth is first padded with a solution containing a mild oxidizing agent and then dried before the printing of the colored discharge paste. Mild oxidizing agents also protect the dye from the reducing atmosphere of the chemicals prevailing during steaming of the prints.

Certain dyes, especially those having azo groups, are susceptible to reduction during steaming. Small amounts of sodium chlorate or sodium meta-nitrobenzene sulfonate are added to counter the reductive effect of the fiber, and possibly the thickeners, during steaming. In the case of dyes "sensitive to steaming", the addition of sodium chlorate is essential.

5.3.3.4 Thickeners

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

To prevent deterioration of the handle of wool and silk, readily removable thickenings such as locust bean flour and dextrin, reduced with modified starches, are used.

For textile printing, guar gum can also be partially depolymerized in order to promote dye penetration, improve swelling in water and achieve the desired rheological properties. Guar gum is obtained from guar seeds by a thermo-mechanical process that leaves approximately 3% of largely insoluble proteins in the gum, originating from the endosperm's aleurone layer. When printing silk fabrics with acid or premetallized dyes, guar endogenous insoluble proteins bind tightly to anionic dyes, causing deposition of colored aggregates on the fabric. This causes imperfections on the printed fabric in the form of tiny, but visible, "dots", which lowers the quality of the final articles. In order to eliminate "dotting", a novel printing thickener composed of depolymerized guar gum mixed with a bioengineered subtilisin protease has been developed. Upon solubilization of the gum, and during preparation of the printing paste mixture, the protease hydrolyses guar gum insoluble proteins, generating soluble peptides that are washed off by the post-printing treatments of the fabric. This enzymatic application prevents "dotting" and significantly improves the quality of the silk print, without any measurable tensile strength loss of the fabric (Baldaro et al., 2012).

5.3.3.5 Defoamers

Defoamers and printing oils are also often necessary for smooth prints with sharp outlines. Silicone defoamers are quite effective; for instance, Perminal KBI, an aqueous emulsion of sulfated sperm oil and pine oil.

5.3.3.5.1 Steaming

Relatively long steaming times of 30–60 minutes are usually needed to fix acid dyes on wool or silk. The most brilliant and fast prints can only be obtained in saturated steam fixation at 100–102°C. For this reason, it is important to avoid overdrying the goods after printing. Wool is even "spray damped" sometimes before steaming, or put into artificially moistened steam. This, however, means that there is a danger of drop formation. In batch steamers, condensation spots and uneven fixation are less likely if a procedure of alternate steaming and evacuation is used. Festoon steamers, which allow sufficiently long steaming times, are often used. The final wash of the printed goods usually takes place on the winch beck, but it can also be undertaken in one of the washing machines designed for knitted goods.

5.3.4 PRINTING WITH ACID DYES

Recipe for acid dye printing paste

Dye	- 10-40 parts
DEG	- 50 parts
Ammonium sulfate	- 60 parts
Urea	- 150 parts
Thickener	- 500-600 parts
Water	- x parts
Total	1,000 parts
$Print \rightarrow Dry \rightarrow Steam \rightarrow Wash \rightarrow Dry$	

- Print, dry and steam for 40-60 mins in star steamer at 102-106°C,
- Rinse in cold and treat with 1–2 g/l soda ash and specialty fixation chemical, and finally, in dilute acetic or formic acid solution.

5.3.5 PRINTING WITH METAL-COMPLEX DYES

Recipe for printing wool/silk with metal complex dye is as follows:

Dye	- 10-40 parts
Citric acid	- 20 parts
Urea	- 150 parts
Thickener	- 500-600 parts
Water	- x parts
Total	1,000 parts

5.3.5.1 Process Sequence: Same as Acid Dyes

Bright shades are obtainable on wool with reactive dyes. This class of dyes is assured a special position in wool printing because of its high all-round level of fastness and the shorter steaming time required.

5.3.6 PRINTING WITH REACTIVE DYES

Recipe for reactive dye printing paste

Dye	- 10–40 parts
Urea	- 150 parts
Resist salt	-10 parts
Thickener	- 500-600 parts
Water	- x parts
Total	1,000 parts

5.3.6.1 Process Sequence: Same as Acid Dyes

Printing paste for Drimarene R and Drimarene K reactive dyes (earlier made by Clariant, now many others; e.g., Teri Dyes):

Recipe

Dye	- x parts
Urea	- 50 parts
Diethylene glycol	- 75 parts
Boiling water	- y parts
Thickening	- z parts
Glycolic acid/tartaric acid (1:1)	- 10 parts
Or, ammonium tartrate (1: 2)	- 60 parts
Sodium carbonate	- 5 parts
Leveling agent	- 5-10 parts
Total	- 1,000 parts

Alginate thickeners have become well established for printing with reactive dyes. The solid content should not be too low: 5-10%.

Process sequence:

Print \rightarrow Dry \rightarrow Steam 10–20 min at 102°C

Washing off:

To attain good fastness properties, reactive dyes must be washed off at higher temperatures than acid or metal complex types. Care must be taken that no mechanical damage is done to the goods during this treatment.

The following washing sequence must be observed:

- Rinse thoroughly in cold water
- Treat with 1–2 grams per liter soap at 50–60°C
- Treat with 1–2 grams per liter soap at 80–90°C
- Rinse cold
- Possible after treatment with 1-2 g/l dye fixing agent for 10-15 min at 30°C
- Acidification with acetic or formic acid

5.4 DIRECT STYLE OF PRINTING ON NYLON

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

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

Before printing, nylon fabrics are to be properly scoured and heat-set. The methods to be employed are based on fabric structure, cleanliness and dimensions required. It may be advantageous to stenter first to a width 4% greater than the final width, if the fabric is to be gummed down directly on to the blanket of a screen printing machine. This reduces the risk of blistering due to swelling and extension of the first printed areas.

Polyamide (nylon) fabric can be printed with acid, metal complex or reactive dyes (Madhu, 2017a). Dyes are selected from the ranges of acid, metal-complex acid and direct dyes, according to solubility, print paste stability, washing-off properties and fastness properties. Suitable dyes are to be selected so that color build-up is good after printing. Color fastness to water, sea water, perspiration and chlorine is essential.

5.4.1 PRINTING INGREDIENTS

5.4.1.1 Dyes

Acid dyes, metal complex dyes and reactive dyes are the most suitable for printing of nylon. Most of the disperse dyes show poor wet fastness on nylon. They are not satisfactory for printing of nylon. Reactive dyes are used in a limited scale.

5.4.1.2 Thickeners

Thickeners with high solid content are most suitable for this printing.

- Crystal gum is a very good thickener, as it produces print of good color value and washes off easily.
- Alginate thickener produces soft print, and they are easily washed off. In general, low viscosity alginate is most suitable for hard fabric, while high viscosity alginate is suitable for spun and knitted nylon fabric.
- Modified locust bean gum prints well and does not become brittle on nylon.
- British gum produces good color value and paste does not coagulate.
- Emulsion thickener produces print of good sharpness and washes off easily.

5.4.1.3 Solvents

Many dyes have limited solubility. In printing paste, large quantities of dyes are dissolved in small quantities of water, hence, solvents and solution aids are used to assist dissolution of dyes in the printing paste. Urea, thiodiethylene glycol and glycine A are the most commonly used solvents. Urea also increases color value.

5.4.1.4 Swelling Agents

Nylon fibers consist of smooth cylindrical compact hydrophobic polymers with poor swelling properties. As such, it is difficult for dyes to diffuse inside the fiber even at high temperature. Swelling agents such as resorcinol and phenol enlarge nylon fibers during steaming, facilitating penetration of dyes.

The use of both thiodiethylene glycol, to improve dye solubility, and thiourea, which acts as both a fiber-swelling agent and a dye-solubilizing agent, is recommended. The amount of swelling agent, or carrier, required for printing nylon 6 need be only half that for nylon 6,6.

5.4.1.5 Acid Liberating Agents

In order to obtain maximum color fixation and to provide acidic pH during fixation, acid liberating agents such as ammonium sulfate and ammonium tartrate are added in the printing paste.

5.4.2 PRINTING METHODS

5.4.2.1 Printing Method with Acid or Metal Complex Dye

The printing paste is prepared as follows:

Acid or metal complex dye	5-10 parts
Urea	50 parts
Thiodiethylene glycol	30-50 parts
Water	45 parts
Boiling water	200-265 parts
Thickener	600 parts
(*Mypro gum TN or Indalca AGBV)	
Ammonium sulfate/Ammonium tartrate 5 parts	
Antifoaming agent/defoamer 0–1 parts	
Total 1,000 parts	

After printing, fabric is dried and steamed at 103-105°C for 20-40 minutes.

After steaming, fabric is rinsed with cold water and hot water, and soaped with non-ionic detergent.

One of the difficulties of nylon printing with acid or metal complex dye is the staining of white ground during washing. This can be prevented by pre-treatment with dye fixing agent before printing or rinsing.

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

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

Ideally, total washing times of 30 minutes are required. Final rinsing in cold water may be preceded by a "back-tanning" after-treatment with a synthetic tanning agent (Syntan) to improve the fastness to washing at temperatures up to 80°C. Such after-treatments are, however, less frequently used on prints than on dyed fabric because of adverse effects on the white ground, in addition to the 15-minute extension of an already lengthy washing procedure.

Conventional and Coloursafe[®] modified nylon 6,6 fabrics were printed with reactive dyes from various commercial ranges. Maximum color yield was achieved using saturated steam as fixation medium and pH 4–5. The color yield obtained on Coloursafe fabric was higher than that achieved on conventional nylon 6,6. A simple wash-off process was used to remove unfixed dye and print paste from the printed fabrics. The prints displayed excellent fastness to repeated wash testing and to cold water contact fastness. The print paste was stable after up to three months of storage (Burkinshaw et al., 2000).

5.4.3 PRINTING WITH DISPERSE DYE

The printing paste is prepared as follows:

5–50 parts
50-100 parts
200-300 parts
400-600 parts
1 part
1,000 parts

After printing and drying, the fixation of print on nylon can be carried out by any one of the following three methods:

- Pressure steaming: The printed fabrics are steamed at a pressure of 0.5 kg/ cm² for 30 minutes.
- Superheated steaming: This method gives the best color yield and very good feel of the fabric. Fixation with superheated steam is carried out at a temperature 160–190°C for 1 minute.
- Dry heat fixation: In this method, the fixation is carried out with dry air and 170–200°C for 1–2 minutes. The feel of fabric may become harsh in this method.

5.4.3.1 Printing with Reactive Dye

Hot brand reactive dye or Remazol reactive dye can be used for printing of nylon fabric. The printing paste is prepared as follows:

Reactive dye	5–50 parts
Boiling water	100 parts
Thickener	500 parts
Solvent	30 parts
Mild oxidizing agent	30 parts
Total	1,000 parts

After printing and drying, the fabric is steamed for 20 minutes at 7 psi. Steaming is followed by cold rinse, soaping and washing.

5.5 DIRECT STYLE OF PRINTING ON POLYESTER

Because of its inertness and hydrophobicity, polyester cannot be dyed or printed with conventional water-soluble dyes. Hence a new class of dye of low aqueous solubility called "disperse dye" was developed. Polyester fiber and disperse dyes are made for each other. Fixation of disperse dyes in polyester printing depends on the preand after-treatments, selection of dyes, thickeners and other auxiliaries, printing and fixation methods. Developments in all these directions were discussed by Roy Choudhury (1981b).

Polyester fibers, first marketed by ICI in 1952, have become the most important of all the man-made fibers, because of their desirable properties and relatively low cost. By far the most important polyester is polyethylene terephthalate (PET). So-called basic-dyeable polyester has also been manufactured by incorporation of anionic monomers.

For trouble-free printing, polyester fabric should be subjected to suitable pretreatments. Water-soluble sizes and spin finishes must be removed from woven and knitted fabrics, respectively. Anionic surface-active agents are preferred, as residual nonionic products may affect fixation of dyes. The scouring bath should be mildly alkaline and the treatment should be carried out between 40 and 80°C. The paraffin-based lubricants may be removed from knitted fabrics by the use of chlorinated hydrocarbon solvents, either as emulsions in the scouring liquor or as non-aqueous solvents in dry-cleaning.

Heat-setting, preferably after scouring, is normally carried out by using hot air at $190-210^{\circ}$ C for 20–30 seconds on a stenter. It is required to ensure dimensional stability of polyester fabric in subsequent processing and use. The fabric dimensions can be chosen for optimum appearance and properties, controlled by stenter. For fabrics made of bulked yarns a lower temperature must be used, within the region of $150-170^{\circ}$ C.

Bleaching is not normally necessary for polyester fabric. However, sodium chlorite can be used where high whiteness levels are desired. Fluorescent brighteners can be applied by exhaustion processes or by the pad-thermofix approach, exactly as in the case of disperse dyes.

5.5.1 DYE SELECTION

On unmodified polyester only disperse dyes are used; cationic dyes can be used on appropriate copolymers, but light fastness is limited. Azo, anthraquinone, coumarin and quinoline disperse dyes can be used. The commercial products are reduced to optimum particle size by grinding with suitable dispersing agents and finished in powder or granule form (20–40% pure dye) or as liquids (15–30% pure dye). The liquid forms are easier to handle, do not require redispersion and usually give higher color yields. Excellent wet fastness properties are obtained, provided that the fixation and after-treatment processes are correctly carried out. The fiber is hydrophobic and has a high glass transition temperature; thus, washing solutions do not penetrate the fiber and dye inside the fiber is removed only with difficulty.

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

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

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

5.5.2 PRINT PASTE FORMULATION

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

5.5.3 PRINTING INGREDIENTS

Various ingredients of printing paste are discussed by Madhu (2017b).

5.5.3.1 Dyes

Disperse dyes are the most suitable for printing of polyester fiber materials. Dyes with good steaming and thermo-fixation fastness are selected. Azo, anthraquinone, coumarin and quinoline disperse dyes can be used. The commercial products are reduced to optimum particle size by grinding with suitable dispersing agents and finished in powder or granule form (20-40% pure dye) or as liquids (15-30% pure dye). The liquid forms are easier to handle, do not require re-dispersion and usually give higher color yields. Excellent wet fastness properties are obtained, provided that the fixation and after-treatment processes are correctly carried out.

5.5.3.2 Thickeners

Thickeners with high solid content are most suitable for this printing.

• Natural gums, starch ethers and modified locust bean gums (gum indalca) are the most commonly used thickeners.

- Alginate thickener is less suitable since it imparts the brightness of the print with disperse dyes, especially in thermo-fixation.
- Prints with carboxymethylcellulose are normally level and sharp and have good yield.
- Starch ethers do not have satisfactory wash-off properties.
- British gum produces dull prints.
- Emulsion thickeners increase levelness and penetration of the dye in the fiber.

Most of the natural thickeners harden and turn brown when they are subjected to the superheated steam and dry heat. This may be because of:

- (a) The incompatibility of acid donor (e.g., ammonium sulfate with the thickeners).
- (b) The use of other additives such as urea or other fixing accelerators. The recommended recipe is 1/3 starch ether and 2/3 locust bean flour derivative or alginate.

Due to diminishing availability and several shortcomings of the natural thickeners, synthetic thickeners have been developed. These are long chain polymers derived from substituted vinyl polymers.

The advantages of synthetic thickeners are:

- 20–25% higher color yield.
- Due to thixotropic nature a wide range of print viscosities may be tolerated.
- Synthetic thickeners are thermally stable and remain soluble even under high temperature (wet and dry) conditions. As a result, any type of fixation method can be used with synthetic thickeners.
- No fixation accelerator is required.

The main disadvantage of the synthetic thickeners is their sensitivity to electrolytes and dispersing agent.

5.5.3.3 Dispersing Agent

Disperse dyes are insoluble in water, and should be kept in dispersion form. Therefore, paste should contain dispersing agent, like Setamol WS.

5.5.3.4 Wetting Agent or Solvent

For pasting of disperse dye, due to its insolubility in water, the dye should be wetted by wetting agent (e.g., TRO) and solubilized in dispersion form using solvent like ethylene glycol.

5.5.3.5 Acid

Since most of the disperse dyes are sensitive to alkali, the printing paste is kept acidic using organic acid. A small amount of citric acid or tartaric acid is added to bring down the pH about 6.0.

5.5.3.6 Acid Liberating Agent

The print paste should remain acidic during steaming, so ammonium sulfate is used as an acid liberating agent.

5.5.3.7 Oxidizing Agent

Sodium chlorate is used to protect the brightness of the dye against any possible reduction of the dye under prolonged steaming conditions.

5.5.3.8 Carriers and Accelerators

Urea is commonly used in polyester printing for improving the color yield. The use of dimethyl benzyl alcohol and methyl naphthalene as carrier in print paste is suggested.

The prints fixed by H-T steam and dry heat are poorer in color yield and duller in shade than those fixed with high pressure steam. Using urea in higher amount (about 20%), the color yield may be improved, but not recommended, because of

- (a) Inconsistent color yield
- (b) Dulling of shade
- (c) Severe browning and hardening of the thickeners
- (d) Crystallization on the printing machine
- (e) Decomposition of urea forming ammonia which may degrade dye

At present a number of accelerators are available in the market for improving color yield in H.T. steaming or dry heat fixation, which are mostly ethylene oxide condensation products of fatty acids or their amides with ethylene diamine. They have good dispersing and wetting action and promote the diffusion of dyes from the film of the thickeners onto the non-swelling textiles.

The recipe for the printing paste is as follows:	
Disperse dye	50 parts
Dispersing agent	10-20 parts
(Setamol WS or equivalent)	
TRO	10-20 parts
Citric acid/tartaric acid	10-20 parts/ 1-2 parts
Water	160 parts
Ethylene glycol	10 parts
Thickener	710 parts
Ammonium sulfate	5 parts
Sodium chlorate	5 parts
Total	1,000 parts

After printing, fabric is dried and fixation is done by three different methods.

• Pressure steaming: Printed fabric is steamed for 30 minutes at 128°C (30 psi pressure). This system produces full color yield and bright prints. This is a batch wise process and needs more labor.

- High temperature steaming: Printed fabric is steamed at 180°C for 6–8 minutes. This is a continuous process and gives full color yield and bright prints.
- Thermofixation: Printed fabric is thermofixed at 180–210°C for 30–60 seconds. This is a continuous process of fixation and is carried out on a stenter or a backing machine. In this method, the dyes are selected on the basis of their sublimation fastness properties.

After fixation, fabric is rinsed with cold water and hot water, reduction cleared (at 40–50°C for 15 minutes) in the following bath:

Sodium hydrosulfite	20 parts
Sodium hydroxide	30 parts
Polyvinyl pyrrolidone	10 parts
(stripping assistant)	
Total	1,000 parts

Finally, the cloth is rinsed, soaped at the boil, washed and dried.

Burn out style was once very popular for getting higher color yield on printed polyester. In this style, polyester is blended with cheap cotton. The blended fabric is then printed with disperse dyes. Due to the presence of cotton, the fabric absorbs much larger quantities of print paste. During steaming, disperse dyes retained by cotton are released and picked up by polyester and then fixed. After washing and soaping, the fabric is dipped into 70% w/w sulfuric acid when the cotton portion gets dissolved. Pure polyester printed fabric thus obtained has higher color yield and smooth handle. This style is known as burn out style or carbonized style. However, this method is no longer commercially viable due to wastage of cotton and lengthy procedures; it has become obsolete.

Traditional disperse printing on polyester fabric needs reduction clearing and thorough washing procedures to remove unfixed dyes, residual thickener and chemical auxiliaries, which involves high water consumption and large pollution discharge. With the energy-saving, effluent reduction, low-carbon themes of the times, it is vital to develop environmentally friendly auxiliaries and cleaner production technology. In view of the non-washing of pigment printing and the sublimation dyeing of disperse dyes, wash-free printing technology emerges. Using disperse dyes instead of pigments, a similar short process (print-dry-cure) to pigment printing can be adopted. During curing, disperse dyes migrate, diffuse and fix into polyester. The unfixed dyes are encapsulated into the binder film. This can result in high efficiency, energy savings and zero discharge wastewater. Printing binder plays a vital role. The stability, mechanical and adhesion properties of the binder film as well as the migration of disperse dyes into binder film directly affect the color yield (Wang et al., 2018).

The color performances of disperse dye washing-free printing are tightly correlated with the solubility parameters of polymer binders. Based on the solubility parameter theory, ethylhexyl acrylate (EHA) and methyl methacrylate (MMA) were selected as monomers. A series of polyacrylate (PA) binders were prepared by miniemulsion polymerization. The effects of the mixed emulsifiers and the EHA-MMA mass ratios on PA properties were investigated. Results showed that PA emulsion remained more stability, the particle size and distribution were smaller, and the film possessed better tensile performances (at the mass ratio of sodium lauryl sulfate (SDS): fatty alcohol polyoxyethylene ether (O-10): propylene oxide propyl alkyl phenyl polyether ammonium sulfate (V-20S) of 1.5:1:1 at 6 wt %). The larger solubility parameter differences between monomers and disperse dyes could improve color yield of the washing-free printed polyester fabric to a greater extent. At the mass ratio of EHA and MMA of 11:9 (55 wt % EHA), PA achieved the best mechanical and washing-free printing properties and surpassed the commercial binders (Wang et al., 2019).

5.6 DIRECT STYLE OF PRINTING ON ACRYLIC

Acrylic fabric can be printed with cationic dye. Printing of acrylic differs from dyeing as follows (Madhu, 2017c):

- Dyes of modified and conventional basic classes can be used in combination with each other.
- No blocking effect occurs.
- Color build-up is better.

5.6.1 INGREDIENTS

5.6.1.1 Dyes

Cationic dyes are the most important and most widely used class of dyes for printing of acrylic fabrics. Prints produced with cationic dyes have excellent wet and rubbing fastness. Disperse dyes give dull shades when printed on acrylic fabric.

5.6.1.2 Thickeners

Since the acrylic fabric is hydrophobic in nature, thickener selection is an important factor. Thickeners with a high solid content are most suitable for this printing.

- Modified guar gum, gum tragacanth and British gum etc., are suitable thickeners for printing of acrylic.
- Modified guar gum is alkaline in nature and hence must be neutralized with acid.
- The mixtures of British gum and gum tragacanth perform well.

5.6.1.3 Swelling Agent

To increase the diffusion of dyes in the fiber and color value, fiber swelling agents are added in the paste (e.g., Resorcinol, phenol). Excessive use of swelling agents may result in increased bleeding of dyes.

5.6.1.4 Wetting Agent or Solvent

Thiodiethylene glycol is a solvent for the cationic dyes, some of which may be sparingly soluble in water, especially at low temperature. Addition of swelling and oxidizing agent decreases the solubility of the dyes, hence addition of solvent is desirable.

5.6.1.5 Acid

The print paste contains acetic acid as well as tartaric acid to improve the solubility of the dyes and to adjust the pH of paste. Since acetic acid is lost by evaporation during drying of the prints, non-volatile acid (tartaric acid) supplies the necessary acidity during steaming.

5.6.1.6 Oxidizing Agent

Sodium chlorate is used to protect the brightness of the dye against any possible reduction of the dye under the prolonged steaming conditions.

5.6.2 PRINTING METHOD

The printing paste is prepared as follows:

Cationic (basic) dye	50 parts
Acetic acid (50 %)	20 parts
Thidiethylene glycol	20-30 parts
Tartaric acid	20-30 parts
Water	165 parts
Sodium chlorate	5 parts
Thickener	680 parts
Resorcinol/phenol	20 parts
Total	1,000 parts

After printing, fabric is dried and steamed in star ager at 103°C for 40 minutes. The maximum allowable steaming temperature is 105°C. If it exceeds 105°C, undesirable effects such as alteration of handle, bleeding and fabric shrinkage may result.

The steamed fabric is then treated with a bath containing 1 to 2 g/l anionic detergent at 60°C for 30 minutes. Finally, the cloth is rinsed, washed and dried.

5.7 RESIST STYLE OF PRINTING

In the direct printing style, the final effect is obtained in one operation, followed by fixation and washing. Originally the term "direct" indicated that no prior step of mordanting nor following step of dyeing was required.

Resist printing can be used to produce white or multicolor print. Instead of applying print paste in the design portions, as in case of direct style of printing, the design portions are printed with resisting agents or suitably covered, thereby blocking or resisting physically or chemically the penetration of dyes in those portions. The remaining portions are then dyed quickly by short dipping or nip padding of the resisted fabric. The dyes in non-design portions are subsequently fixed by a suitable method, followed by washing to remove resisting agents and unfixed dyes. Resist mechanisms may be chemical or physical, the maximum effectiveness being ensured by using a mixture of both types of resist agent. A physical resist inhibits absorption of dye, and a chemical resist inhibits fixation. Colored resists require the addition to the print paste of dyes or pigments that are satisfactorily fixed in the presence of the resist agent, either before the fixation of the ground color or during the process. If the ground color is not too dark, it may be that the required effect is obtainable by "overprinting". This is simply direct printing onto a pre-dyed fabric. Tone-on-tone effects, which use colors of similar hue, are often produced in this way, but contrasting color combinations are also possible. For example, blue dyes may be printed on to a yellow fabric to obtain green areas. Overprinting requires no elaboration, but discharge and resist styles must be considered in more detail if the full range of possibilities and problems are to be appreciated and understood.

The mechanical resisting agents commonly used in resist printing are waxes, fats, resins, thickeners and pigments, such as china clay and the oxides of zinc and titanium. Such mechanical resisting agents simply form a physical barrier between the fabric and the colorant. They are mainly used for the older, coarser and, perhaps, more decorative styles in which breadth of effect and variety of tone in the resisted areas are of more importance than sharp definition of the pattern. A classic, and nowadays almost unique, example of a purely mechanical resist is batik printing, using wax applied in the molten state. In a true batik the wax is applied by hand brush, but the process has been developed and mechanized for the production of styles that now come under the general heading of "African prints". It is not possible to apply an illuminating color with a wax resist but, after removal of the wax, another color can be printed within the resisted area by rewaxing and redyeing. Two physical resisting methods, namely Batik printing and tie and dye styles of printing, are discussed in the previous chapter (section 4.4).

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

Most reactive dyes can only be fixed on cellulosic fibers in the presence of alkali. Consequently, nonvolatile organic acids (such as tartaric or citric acid) and acid salts (such as monosodium phosphate) may be used as resist agents for preprint resists under such dyes. Hence, the thickeners used should be acid-resistant. Hydroxyethylated and methylhydroxyethylated cellulose ethers, locust bean gum and tragacanth are suitable for this purpose. When printing with deeply engraved rollers the concentration of acid- or alkali-binding substance can be kept low, but an increase in the concentration may be required if sharp effects are to be obtained with shallow engravings. A typical preprint resist paste would have the composition as shown in the following recipe:

Citric acid	50 g
Thickener	600 g
Water to	1,000 g

The colorless resist print pastes may be made visible by tinting with a fugitive dye such as CI Acid Blue 1, or by adding a fluorescent brightener, which is detected with the help of an ultraviolet lamp.

After the material has been printed and dried, it is nip-padded, overprinted or padded with a solution of a high-reactivity reactive dye containing a minimum concentration of sodium bicarbonate. If the material is to be immersed in the dye liquor, it may be necessary to increase the acid concentration in the print paste to 80 g/kg paste. Immersion times should be short. Drying must follow immediately; then an appropriate fixation step and washing. A typical padding liquor is as follows:

Reactive dye	20 g
Resist salt	7 g
Hot water	393 g
Cooled to 40°C and diluted with	
Cold sodium bicarbonate solution (3%)	500 g
Thickener	80 g
Water to	1,000 g

Certain alkali donors may be employed instead of sodium bicarbonate, in which case the steaming time should be increased to 7–10 minutes to allow for adequate breakdown of such compounds and subsequent fixation of the dye (Miles, 2003).

Colored resists under reactive dyes can be produced by preprinting the fabric with a pigment print paste containing an acid to act as resist agent. The pigment binder should preferably be one that can be fixed by steaming. A typical stock paste will be made up as shown in the following recipe:

Thickener (cellulose ether)	100 g
Emulsifier	8 g
Water	100 g
Pigment binder	120 g
White spirit	612 g
Tartaric acid (1:1)	60 g
Total	1,000 g

The actual print paste would be prepared from this stock paste by adding the requisite quantity of pigment emulsion. The sequence of operations would then be as follows:

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

The recipe uses an emulsion thickening system, but due to environmental legislation, restrictions as to the use of systems based on white spirit resulted in the promotion of further developments using aqueous systems based on synthetic thickeners. Prior to this, the synthetic thickeners used to prepare aqueous pigment thickeners were unacceptable as the acid required for the resist produced an unacceptable drop in viscosity (Miles, 2003).

Vat resists under vat-dyed grounds are not a widely used style, but it has been, and could be, used where the fastness properties associated with vat dyes are necessary. The material is first printed with a normal all-in vat print paste with addition of sodium thiosulfate. After steaming, to reduce the vat dye, the material is padded in a solution containing a vat leuco ester and sodium nitrite, followed by passage through a sulfuric acid solution. The alkali in the vat print neutralizes the acid and the sodium thiosulfate is preferentially oxidized, preventing development in the printed areas. The goods are finally after-treated in the normal manner prescribed for vats (Miles, 2003).

5.8 DISCHARGE STYLE OF PRINTING

In the discharge style, the fabric is dyed first with dyes that can be destroyed by printing with selected discharging agents. The discharge paste is printed onto the dyed fabric and, usually during subsequent steaming, the dye in the pattern area is discharged. A white discharge is thus produced. It is also possible to add a discharge-resistant ("illuminating") dye to the discharge print paste, to produce a color discharge. The area of dyed fabric surrounding the pattern areas is described as the "ground", because it is a background from which the illuminating colors (often called head-colors) shine. This is especially true when the ground is black or dark color, and the colors seem to have extra brilliance. The use of the term "ground" is naturally extended to describe the dyed fabric before printing.

5.8.1 DISCHARGE PRINTING OF CELLULOSIC MATERIALS

Vinyl sulfone reactive dyes are easily reduced and can be used for discharge printing on cellulosic materials. The monochlorotriazine (MCT) dyes are non-dischargeable and hence, they can be used as illuminating colors. These dyes are mixed with printing paste containing reducing agents.

In the discharge printing process, the fabric is first dyed with vinyl sulphone dyes in the usual way. The dyeing may be done by exhaust method in jigger, winch or any other batch machine. Alternately, the fabric is dyed continuously by pad-steam method.

In theory, Remazol dyes can be applied to cotton at $20-30^{\circ}$ C. However, this temperature is not generally recommended. Some members of the range give good color yields on cotton at this low temperature and in a commercially acceptable time only if the pH is adjusted to a certain value with sodium hydroxide. When trisodium phosphate is used as an alkali, the dyeing time needed is far too long for practical use. Cotton can be dyed with Remazol dyes in long liquor at temperatures at and above 60° C with a corresponding decrease in alkalinity. Some of the Remazol dyes, such

as turquoise blue and green dyes, can be best applied at 80°C. The temperature of dyeing is generally 45-60°C, but it is also possible to dye at 40°C using strong alkali and allowing more time for fixation – say, 90 minutes. These dyes have good leveling properties. Hence, as a rule, it may not be necessary to add salt and alkali in portions. The shades are very bright. It is preferable to use Glauber's salt and trisodium phosphate instead of common salt and soda ash, as both of them may have metallic contamination, especially iron salts. However, those can be used, if slight alteration of shade is permissible. Generally, for discharge printing, the fabric is dyed in higher depths ($\geq 3\%$ on the weight of material) and the concentrations of salt and alkali are 50 gpl and 20 gpl respectively.

The Remazol or vinylsulphone dyes are well suited for the short-time pad-batch method. The alkali used in this method is sodium hydroxide. Besides alkali, a salt is added to improve the color yield and an alkali-stable wetting agent for better penetration. Dye and wetting agents are dissolved together, and sodium hydroxide and salt together. The padding liquor contains:

x g/l Remazol dye 10–30 ml/l sodium hydroxide solution (32.5%) depending on the depth of shade 30 g/l common salt or Glauber's salt 5 g/l (or as required) wetting agent

After padding, the fabric is batched up without selvedge overlap; then the roll of fabric is wrapped with polyethylene sheet. Dye fixation is affected at room temperature and takes 2 to 6 hours. To be on the safer side, especially with large yardage, batches are left for 10 hours or overnight, and washed off in an open-width washing machine (Roy Choudhury, 1996).

Thickener	500 parts
Sodium sulfoxalate formaldehyde	
(reducing agent, trade names: Rongolite or Formosul)	150-200 parts
Titanium dioxide (1:1) (whitening agent)	100 parts
Caustic soda (75º TW, 450 gpl)	100-200 parts
Water or thickener)	х
Total:	1,000 parts

White discharge paste

The printed fabric is dried at a temperature less than 90°C and then steamed for 10–15 minutes at 105°C, washed thoroughly, soaped and dried.

5.8.2 DISCHARGE PRINTING OF SILK AND WOOL

Discharge printing of wool and silk is a very specialized form of printing, with substantial value-add in terms of profitability being a key consideration. Due to the high fabric value, the principle of "get it right the first time" should apply. A high proportion of silk on the market is claimed by discharge printing; this applies to both classic articles such as neckties and scarves as well as to fashion wear. Unlike other natural or synthetic fibers, silk articles must meet high requirements as to brilliance and coloristic effects; compromises must often be made on account of the fastness properties. For this reason, several dye classes are often used alongside one another.

One of the limiting factors in this process is the small number of dyes which can be used as illuminating colors with good fastness due to the requirement that they must be stable in the presence of reducing agent.

5.8.2.1 Reducing Agents

Generally, for discharge printing, reducing agents are used. Though discharge printing of wool is not popular, these reducing agents are listed here and used whenever such conditions are needed. These could be:

- · Zinc dust and sodium bisulfite
- Stannous chloride
- Sodium formaldehyde-sulfoxylate
- · Zinc formaldehyde-sulfoxylate
- Calcium formaldehyde-sulfoxylate
- · Thiourea dioxide

For getting good white discharge, white pigments like titanium dioxide and zinc oxide help to get superior white effects. When thiourea dioxide is used as the discharging agent, the whiteness is improved by the addition of zinc sulfate. Discharge resistant fluorescent brightening agents are also useful in improving white discharges.

Another product used to improve the discharge effect of a reducing agent is anthraquinone. Anthraquinone paste is generally used, which gets reduced to hydroanthraquinone during steaming, which in turn reduces the dye and itself gets reconverted to anthraquinone. This cycle of reactions continue until the reduction is complete. Thus, the presence of anthraquinone improves the whites and renders them more stable in air by retarding any oxidation of the fission products.

Certain specialty chemicals capable of forming a loose complex with the unfixed dye help in preventing redeposition on the wool fiber. Generally, in the case of metal-complex dyes, no after-treatment is necessary but good all-around fastness is obtained with chemicals like fatty amine ethoxylates. In fact, for good prints, good steaming to cause fixation and optimum conditions for washings is desired.

5.8.2.2 Discharge Style with Acid Dyes

This involves printing with reducing agents and, in the case of illuminated discharges, discharge-resisting dyes on pre-dyed material. In the subsequent steaming operation the dyeing is destroyed and the discharge resisting dyes are fixed. To counteract any fiber damage, both urea and glycerin are added to the print paste, and care must be taken to ensure that the steam is sufficiently moist. This forms a specialist field in wool printing and the working conditions play a critical part. The following standard formula should therefore be adapted to suit the conditions.

Constituents	Illuminated (color) Discharge	White Discharge
	0	0
Non-dischargeble dye	x parts	nil
Urea	50 parts	50 parts
Thiodiethylene glycol	40 parts	50 parts
Water	y parts	x parts
Thickening	500 – y parts	500 – x parts
Resist salt	20 parts	nil
Ammonium chloride	20 parts	nil
Zinc formaldchye	80 parts	80 parts
sulfoxylate		
Glycerin	50 parts	50 parts
Total	1,000 parts	1,000 parts

Recipes for Discharge Print Pastes

5.8.3 DISCHARGE AND DISCHARGE-RESIST PROCESSES ON POLYESTER FIBER

The colored ground is applied using selected disperse dyes, while the illuminating colors are selected discharge-resistant disperse dyes. The discharging agent can be either a reducing agent or an alkali. Dyes that have diffused into polyester fibers in conventional dyeing are virtually impossible to discharge because the hydrophobic properties of polyester make penetration of the reducing agent and removal of the reduced disperse dye extremely difficult. Results obtained are not acceptable commercially except for lightweight fabrics. Consequently, the discharge-resist process was developed.

Polyester fabric is impregnated with dischargeable disperse dye by pad mangle or lick roller, and dried at low temperature to keep the dye on the fiber surfaces. Discharge pastes containing water-soluble zinc formaldehyde sulphoxylate (CI Reducing Agent 6) or tin (II) chloride are printed onto the fabric, and the dye is destroyed during drying and subsequent processing.

Disperse dye (dischargeable)	x g
Water at 20–30°C	y g
Thickener (locust bean ether)	500–100 g
Wetting agent	2 g
Resist salt (1:2)	30 g
Total	1,000 g

Recipe of pad liquor for ground color

The safest approach is low-temperature (102°C) steaming, which will not fix the ground color, followed by a high-temperature fixation of ground and illuminating dyes.

An alternative method is to produce a discharge-resist effect using alkali on disperse dyes containing diester groups. These groups hydrolyze in the presence of

TABLE 5.1 Print Paste Recipe for Polyester (All in g)

Component	With reducing agent	With alkali
White discharge paste		
Locust bean ether thickener	500	500
Zinc formaldehyde sulphoxylate	80-150	
Caustic soda solution (38 °Be		50-80
Discharge-stable FBA		5
Carrier	10	
Polyethylene glycol (r.m.m. 300-400) g		50-80
Glycerol		5-80
With water/thickener to make	1,000	1,000

Notes

1. Tin (II) chloride may be used as an alternative to CI Reducing Agent 6.

- 2. Formaldehyde or methanol is incorporated to stabilize the reducing agent after printing, but before steaming.
- 3. Urea has been found to protect some discharge-resistant dyes, especially the anthraquinone pinks and blues, from attack by the reducing agent.
- 4. To prevent diffusion of dye into the fiber before discharge can occur, low-temperature steaming should precede fixation.

alkali to produce a water-soluble carboxylate salt. The soluble sodium carboxylate form has no affinity for polyester. In practice, the diester disperse dye is padded onto the fabric, low-temperature dried and then overprinted with a print paste containing alkali. As with the process involving a reducing agent rather than alkali, the fixation is done with high-temperature steaming followed by a reduction clear process. A guide recipe is given in Table 5.1.

Of the three alternative methods described below, the first two are to be preferred. The third is used when only a high-temperature steamer is available.

- 1) Initially, to destroy the dischargeable dye, the fabric is steamed for 5 minutes at atmospheric pressure. The pressure is then raised to 140 kPa (21 lbf in $-^2$) and steaming carried out for 20 minutes to fix the discharge-resistant illuminating colors and the colored ground.
- 2) Steam for 5–8 minutes at atmospheric pressure in saturated steam and then for 6–8 minutes at 175–180°C in superheated steam.
- 3) Discharge and fix in one high-temperature steaming operation for 6–7 minutes at 175–180°C.

5.9 FUTURE TRENDS

Direct, resist and discharge styles of printing are three means of getting designs or patterns on textile fabric. Both the print area and non-print area or ground areas may

be white or colored. Depending on design type, color may be applied directly in the design area of white or dyed fabric. Alternately the design portions may be resisted physically or chemically followed by quick dyeing. In discharge printing, the fabric is dyed with dischargeable dyes followed be printing with dischargeable chemicals and subsequently steamed to destroy dyes in these areas. All these styles are complicated multistep processes conducted manually or by traditional block, screen or roller printing machines. The sustainability of traditional printing methods is in question, as they consume lots of dyes and chemicals as well as create water and air pollution. Nowadays, fashion trends demand quick changes in design and color combination. The traditional printing methods become uneconomic when batch or lot sizes are small.

The world of textile printing is rapidly changing. Customers are demanding a greater variety of color and design. Responding to this demand is a necessity in today's marketplace. Printers are forced to find new and innovative ways to provide printed samples while minimizing cost and waste. Digital printing technology allows customers to streamline the entire design, sampling and production process. The majority of all textiles are printed using rotary screen print machines. While this technology offers high speed and inexpensive output, there are many drawbacks. The average order size is rapidly decreasing, and textile companies are printing shorter runs. Rotary screen technology offers obvious benefits during long runs, but does not provide economical short run production (Tippett, 2001).

The global printed textile market is huge, estimated at over 32 billion square meters of output annually. Printing with inkjet is becoming increasingly significant as fashion trends become ever more changeable – the adoption of inkjet textile printing is supporting "fast fashion", with much quicker response times available to retailers. Inkjet printing allows the supply chain to be shortened and made more flexible. There are many t-shirt printers offering a web-to-shirt service where the buyer uploads their own unique image to be printed onto a garment on demand. The printing takes a large part of the value and is done close to the buyer (FESPA, 2017).

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6 Manual Printing Methods

6.1 INTRODUCTION

As discussed in the previous chapters, the styles of printing refer to the chemical aspects of textile printing, while the methods of printing refer to the mechanical aspects like the tools and machines used in textile printing.

The word "printing" implies a process that uses pressure, being derived from a Latin word meaning pressing. The German word $dr \ddot{u}ck$ for print also means pressure. There are six distinct methods to impress colored patterns on cloth, namely:

- 1) Hand block printing
- 2) Perrotine printing
- 3) Stencil printing
- 4) Manual screen printing
- 5) Screen printing machines
- 6) Roller, cylinder or machine printing
- 7) Digital textile printing

Hand painting and block printing on textiles have been reported to be practiced in India for thousands of years. Hand painting involves directly drawing an image using color. Alternately, patterns are created on fabrics with the help of the resist technique, in which the pattern is drawn on the fabric with clay, starch, gum, or wax, which forms a barrier to dye penetration. Dyeing the fabric then reveals this pattern. The block printing method was practiced in Sind (now in Pakistan) region in the 8th century, from where it went to India. Some early blocks were made of clay or terracotta, others of carved wood. Wooden blocks carrying design motifs were found in tombs near the ancient town of Panopolis in Upper Egypt. In the same area, a child's tomb contained a tunic made of fabric printed with a design of white rectangles, each enclosing floral motifs on a blue background. Pliny (born AD 23) described in his book *Historia naturalis* how in Egypt they applied colorless substances to a fabric that quickly produced several colors when immersed in a dyebath (Sherif, 2021). As Pliny also records that the best-quality alum was obtained from Egypt, it seems likely that alum was one of the mordants used and that the dye was madder.

By the 14th century, the use of wooden blocks for printing was certainly established in France, Italy and Germany, but the craft was practiced by "painters", using mineral pigments rather than dyes. One of the early European uses of blocks was to produce church hangings that imitated expensive brocades and tapestries. Cennini, writing in 1437, described in some detail the production and use of brick-sized wooden blocks to print a black outline on brightly colored cloth, which was then hand painted with other bright colors (Brunello, 1973). In 1460 the nuns of a convent in Nuremberg described the block printing method with mineral colors in boiled resinous oils, of gold and silver leaf, and of wool "flock" on to a printed adhesive. In the 15th century, Portuguese traders were discovering the potential for trade with India, where the dyed style was used to produce cotton fabrics of great beauty that were quickly in demand in Europe. As early as the 1st century AD, there was an Indian center famous for the production of painted fabric, and the use of madder was by then long established. Early in the 17th century, hand-painted Indian cottons were reaching London in significant quantities. They were both colorful and color-fast, and introduced a richness of novel and stimulating design styles. Paisley designs, for example, were derived directly from one of these styles, and the words "calico" and "chintz" were adopted into the language.

Stencil printing was also practiced in India during the Gupta period (6th to 8th century). The stencil was placed on a fabric and the color was then brushed or sprayed in the cut-out portions, giving beautiful designs. Machine roller printing came in the latter part of the 18th century and its development could be traced to the block printing process. This eventually transformed the slow and costly block printing process into cheap mass production, which revolutionized the cotton print industry.

The stencil printing process led to the development of screen printing which works on the resist principle described earlier. In the early days, fine silk meshes were used as the screen. Towards the end of the 19th century, this process was well developed in Japan. Flat screen and rotary screen machines had by that time made this process very popular for printing.

6.1.1 BLOCK PRINTING

Wooden blocks are made by slicing logs of wood horizontally, and the required designs are chiseled on to the hard, smooth block surface. A design was carved on the smooth surface of a wooden block and the raised surface of the block was smeared with the dye paste. The design was then stamped on to the fabric; repetition of this equidistantly all over the fabric gives rise to an attractively printed fabric.

Block printing (also called Relief printing) is the process of carving patterns, shapes and designs into a "block". The "block" could be made of wood, acrylic plastic sheet, lino (linoleum) or metal. Wood and lino are more suited for bolder images.

Linocuts and woodcuts are called relief prints since the ink is transferred from the area that stands out from the background. Relief printing, in art printmaking, is a process consisting of cutting or etching a printing surface in such a way that all that remains of the original surface is the design to be printed.

The carved-out design on the block is smeared with thick dye paste and then stamped on to the fabric transferring the design as cut in the block. Each separate color will require a separate block. The process is repeated until the design covers the fabric. A hand block printer ensures that each print fits exactly on the first. Hand block printing is carried out as a cottage or small-scale industry. It is slow and expensive but is ideal for exclusive designs on limited quantities of fabrics.

Block printing is the oldest and generally considered the most artistic of all methods of printing textiles. It is a slow process; subtle gradations of tint and stipple, the fine, sharp outlines, the clear-cut edges of the masses, and the absolutely invisible joining up of the repeats are very difficult to obtain by block printing. Block printing has its own advantages in that patterns containing any number of colors and on any scale can be reproduced with ease and certainty. It is unsurpassed for its effect, its decorative value, and is free from elaborate color shading and fine details.

6.1.2 PERROTINE PRINTING

The perrotine is a block-printing machine invented by Perrot of Rouen in 1834 and is now only of historical interest. Practically speaking is the only successful mechanical device ever introduced for this purpose. For some reason or other it had rarely been used in England, but its value was almost immediately recognized on the Continent, and although block printing of all sorts has been replaced to such an enormous extent by roller printing, the perrotine was still largely employed in French, German and Italian works until the beginning of the 20th century.

The machine's mode of action is roughly as follows: Three large blocks (3 ft long by 3 to 5 in wide), with the pattern cut or cast on them in relief, are brought to bear successively on the three faces of a specially constructed printing table over which the cloth passes (together with its backing of printer's blanket) after each impression.

The faces of the table are arranged at right angles to each other, and the blocks work in slides similarly placed, so that their engraved faces are perfectly parallel to the tables. Each block is moreover provided with its own particular color trough, distributing brush, and woolen color pad or sieve, and is supplied automatically with color by these appliances during the whole time that the machine is in motion. The first effect of starting the machine is to cause the color sieves, which have a reciprocating motion, to pass over, and receive a charge of color from, the rollers, fixed to revolve in the color troughs. They then return to their original position between the tables and the printing blocks, coming in contact on the way with the distributing brushes, which spread the color evenly over their entire surfaces (Cole, 1911).

At this point the blocks advance and are gently pressed twice against the color pads (or sieves) which then retreat once more towards the color troughs. During this last movement the cloth to be printed is drawn forward over the first table, and immediately once the color pads are sufficiently out of the way, the block advances and, with some force, stamps the first impression on it. The second block is now put into gear and the foregoing operations are repeated for both blocks; the cloth advancing after each impression a distance exactly equal to the width of the blocks. After the second block has made its impression the third comes into play in precisely the same way, so that as the cloth leaves the machines it's fully printed in three separate colors, each fitting into its proper place and completing the pattern. If necessary, the forward movement of the cloth can be arrested without in any way interfering with the motion of the block, an arrangement which allows any insufficiently printed impression to be repeated in exactly the same place with a precision practically impossible in hand printing.

For certain classes of work, the perrotine possesses great advantages over the hand block; for not only is the rate of production greatly increased, but the joining up of the various impressions to each other is much more exacting; in fact, as a rule, no sign of a break in continuity of line can be noticed in well-executed work. On the other hand, however, the perrotine can only be applied to the production of patterns containing not more than three colors nor exceeding five inches in vertical repeat, whereas hand block printing can cope with patterns of almost any scale and continuing any number of colors. All things considered, therefore, the two processes cannot be compared on the same basis: the perrotine is best for work of a utilitarian character and the hand block for decorative work in which the design only repeats every 15 to 20 inches and contains colors varying in number from one to a dozen. Though block printing is in use in handicraft industries to a small extent, perrotine printing is now of historical interest.

6.1.3 STENCIL PRINTING

Stencil is a thin sheet of card, plastic or metal with a pattern or letters cut out of it, used to produce the cut design on the surface below by the application of ink or paint through the holes. A design shape is cut out of a piece of thin, hard nonabsorbent material, and when this is placed on a fabric and the color brushed or sprayed in the cut-out portions, the design is transferred on the fabric.

6.1.4 ROLLER PRINTING

Roller printing on fabrics, also called cylinder printing or machine printing, is a textile printing process patented by Thomas Bell of Scotland in 1783 in an attempt to reduce the cost of the earlier copperplate printing.

Modern roller machine printing is a development of the engraved block method. The design is engraved onto a set of copper-surfaced rollers, the number depending on the number of colors in the design. The rollers are situated in sequence around the circumference of a large pressure cylinder whose surface is padded and protected from staining by dyestuff being pressed through the printed fabric with the help of a grey cloth. Copper roll printing enabled users to print larger pieces of textile at a faster printing rate than with hand block textile printing.

6.1.5 FLATBED SCREEN PRINTING

A screen consists of a square or rectangular hollow metal or wooden frame on which a light cloth is mounted. The screen-cloth is called "bolting cloth". The design to be printed is transferred onto the screen before it is considered ready for printing. The design portions of the screen are kept open, while the non-design portions are blocked by resin and/or paint. The color paste is poured on the bottom portion of the screen and moved up along the screen surface by pressing with a rubber blade or rubber roller called a squeegee. During the movement of the squeeze, the color paste passes through open design portions, while the non-design portions are deprived of color paste. For multiple color effects, a number of screens (one screen for each color) are used. The screens are placed one after another and each color is printed as above maintaining a common reference point.

Printing of textile materials using a screen is either done manually (called flat screen printing) or it may be mechanized. Flatbed screen printing machines are of two types. In semi-automatic machines, the screen movement is automatic, while squeeze movement is manual. In the second method, both movements are automatic

in fully automatic screen printing machines. However, flatbed printing machines have intermittent motions and hence, the production speed is limited.

6.1.6 ROTARY SCREEN PRINTING

In 1963, a breakthrough in textile printing resulted in the invention of rotary screen printing by Stork (today named SPG Prints). Unique to rotary screen printing is that a round, seamless screen is used instead of a flat one. The use of circular screens enables users to continuously print (without intermittent stoppage, as in the case of flatbed printing machines) larger pieces of textile at a faster printing rate. The cylindrical screen is covered with a lacquer, but the design portions of the screen holes are kept open for the flow of color paste. In the past this was done by applying a film over the light-sensitive lacquer, but today most screens are engraved by laser. The printing paste is applied inside the screen and pushed through the holes by means of a squeegee.

6.1.7 DIGITAL TEXTILE PRINTING

Considerable money and time are consumed in rotary screen printing as for every design new screens must be engraved, one screen for each color – a very time-consuming and costly practice. There was a demand for a more efficient printing technique that enabled faster and cost-effective printing. Digital textile printing filled this gap by enabling manufacturers to directly print a digital design on textile. For digital textile printing, no printing screen is needed. This not only saves money, it also enables manufacturers to print unique designs rather than the designs that repeat itself every turn of the rotary screen (typically 64 centimeters).

Digital printing is the latest innovation in textile printing and is slowly making its entry into the textile industry. At this moment, about 5% of the textile industry has made the transition to digital textile printing. The main reasons for manufacturers to choose digital textile printing are the short delivery times, the design flexibility, the high image quality and unlimited colors, the speed, the flexibility to bring ideas faster to the market and the possibility to print precise geometric designs.

6.2 BLOCK PRINTING METHOD

The art or craft of block printing consists in cutting a design in relief upon blocks of wood, so that the raised parts when charged with color will transfer the design to whatever fabric the block is stamped upon. In its practical application, it is more strictly limited to certain styles of design.

Rich and colorful prints can be created through block printing. In olden times it was done with natural dyes but nowadays, it is done with artificial colors and synthetic dyes. The colors commonly used for printing are saffron, yellow, blue and red. The wooden blocks are used for printing.

The first textile-printing technique (making impressions) was that of using blocks with raised printing surfaces, which were inked and then pressed on to the fabric. By repetition, the image from a single block builds up into a complete design over the fabric area. Some early blocks were made of clay or terracotta, others of carved wood. Wooden blocks carrying design motifs were found in tombs near an ancient town in Upper Egypt. A combination of block printing and painting (usually described as penciling) was used for some time. The biggest problem was that of achieving bright and fast colors. Madder (madder is a fast, rich red color natural dye stuff obtained from the root of an herb) was the most important dye that was suitable.

In wood engraving – or "block cutting", as it is termed technically – the design is cut or otherwise raised in relief on a thick, flat block of wood. Color is then applied to the raised parts, and the impression of the design obtained by stamping the block smartly by hand on the cloth to be printed. In copper roller engraving the opposite course is pursued, the design being cut out in intaglio on the rounded surface of the roller, and the impression taken by filling the incisions with color and pressing the cloth into them, both these latter operations being affected by the machine. Intaglio means an engraving or incised figure in stone or other hard material depressed below the surface so that an impression from the design yields an image in relief. Intaglio printing (as in die stamping and gravure) is done from a plate in which the image is sunk below the surface.

Further, in the case of block cutting, it is quite impracticable to leave either comparatively fine lines or minute spots in relief, since not only is the utmost skill required to cut them without breaking the grain of the wood, but because, even when successfully cut, they are too weak to withstand the wear and tear of printing. In copper roller engraving, on the contrary, all qualities of line and dot, from the coarsest to the finest possible, may be cut easily, safely and without the slightest fear of their subsequent damage in printing.

The typical hand block print had no large, uniform areas of color but was skillfully built up from many small colored areas, because wooden surfaces larger than about 10 mm in width would not give an even print. This had the advantage that a motif such as a flower would have an effect of light shade obtained from three or four blocks, each printing a different depth of the same color or shade.

Thus, the restrictions imposed upon the treatment of ornament by the nature of "block cutting" limit the application of block printing to such designs as depend for their beauty upon breadth of effect and boldness of handling.

Blocks are made of wood that must be fairly hard and close grained such as box, holly, sycamore, plane or pear wood. It should be of fine, even grain and free from all defects such as knots, cracks and so on. Generally, blocks are either square, oblong or diamond shape and frequently irregular in form. They should not exceed 35 cm by 35 cm in size, as the bigger ones are difficult to handle and may also go out of shape. They should be between 6 cm and 8.5 cm thick as thicker blocks are less liable to wrap, crack or get twisted out of shape during prolonged contact with printing paste during the printing operation.

In the 19th century, some blocks were made with the printing surface entirely in brass, which gave very delicate prints. Another technique used for complex designs was to prepare a mold to cast the image from molten type metal, fasten the casting to the block, and then grind the surface perfectly flat.

When large areas of solid color were required, the areas within metal or wooden outlines were filled with felt, which would absorb and print the paste uniformly.

Finally, each block required corner "pitch pins", which printed small dots; these allowed the succeeding blocks to be correctly positioned by accurately locating the pitch pins above the already printed dots.

Advantages of block printing are:

- Simplest method of printing
- Hand-made art
- No special printing equipment required

Disadvantages of block printing are:

- · Tedious and time-consuming process
- Expensive
- Irregular color shade
- Overall production is low
- Carving of blocks is difficult and laborious

6.2.1 BLOCK CUTTING

Block making required patience and skill. The size of the block is limited by the weight that the printer can handle for long periods without undue fatigue. The pattern must invariably be fitted both across and along the cloth.

The design was traced on to the surface and a fine chisel used to cut away the nonprinting areas to a depth of perhaps 1 cm. To obtain more detail from some blocks, strips and pins of copper or brass (more commonly) were hammered into the wood. Many textile designs are constructed with several colors. For each color a separate block is required. If a design consists of four colors, four separate blocks are required. Block printing is a very slow process. For commercially viability, the block designs are chosen with a minimal number of colors. The majority of blocks are made largely of wood, but metal may be used to reinforce parts of the design. Such blocks are used to apply thickened dyestuff pastes at normal room temperatures. A completely different type of block fashioned from copper strips soldered into a copper lattice is used to apply hot waxes in the traditional Javanese Batik industry (see Chapter 4, section 4.4).

Distinct differences in block construction are distinguishable between those used in Europe (largely for factory production) and those evolved in the East, particularly in India. In Europe, supplies of wood suitable for cutting into blocks are scarce and expensive. Although a block may be about 40 mm (1.5 inch) thick, the cutting necessary to raise the design in relief seldom penetrates deeper than 5 mm (0.2 inch). By bonding together a layer of carefully selected, fairly hard, closegrained wood (e.g., sycamore, pear or lime) with cheaper woods, cost reduction is possible. The layers in the bonded wood are arranged so that the grain runs in directions at right angles to each other. The size of the block may vary slightly to allow for a design to be fitted in and have an irregular outline to encompass the pattern area. Because the block must be lifted and transferred to the cloth repeatedly during the printing operation, its weight and size must be restricted. Dimensions greatly in excess of 500 sq. mm x 40 mm height (18 sq. in x 1.5 in) are unusual but may be required for special designs.

A block intended for commercial use must be constructed robustly and requires craftsmanship of a high order to produce it, whether European or Eastern techniques are used. Multilayer blocks are common in Europe, but in India blocks are more often fashioned from a single piece of wood and are smaller in size. The type of design and fabric to be printed determines the method of block making, particularly the area of a given color required. It is difficult to apply printing paste evenly over large areas from a wooden surface; therefore, any large, plain areas of the design are usually recessed, leaving a wooden outline wall, the cut-out portions then being filled in with a hard wool felt pad. Again, very fine lines in the design are fragile if left in wood, and these are therefore built-up with copper strip.

Double copper strip outlines interleaved with felt are also widely employed. A large proportion of the blocks rely solely on the use of raised wooden areas. To enable the printer to fit his block lays in correct register on the cloth, "pitch pins" are often fixed around the block sides. These pins are arranged so as to coincide with certain well-defined points in the pattern printed during the previous lay.

As a general rule, blocks are either square or oblong, but sometimes they are diamond shaped, and frequently take an irregular form. In any case, of whatever size and shape, and whether simple or composite, wood blocks for textile printing must always be between $2\frac{1}{2}$ inches and $3\frac{1}{2}$ inches thick, for the reason that the thicker they are, the less liable are they to warp, crack, or get twisted out of shape by the prolonged contact with wet color to which they are subjected during the printing operation.

A suitable piece of wood of fine, even grain, and free from all defects, such as knots and cracks, must be chosen and cut to size. Its working surface is first planed up to a dead level and then smoothed with fine sandpaper. The evenness of the resulting print depends upon the perfect flatness of this surface.

The desired print design is first drawn on a drawing sheet with all colors. The smallest unit of a design is known as "repeat", the size of which should be within the permissible size of the block. The drawing should carry the whole design drawn with multiple colors, as expected in the final print with all colors (usually 3–4 colors). Figure 6.1(d) shows the final print; the combination or overlap of three colors, which are printed with three blocks carrying designs as shown in Figures 6.1(a), 6.1 (b) and 6.1 (c) successively with three different color pastes.

There should be four reference points at four corners of the drawing sheet carrying the whole design. Now a transparent sheet is fixed on the drawing sheet, the reference points are marked on the sheet. A careful outline tracing of the design of a particular color, say color I as in Figure 6.1(a), is made with a mixture of lampblack and linseed oil. Transparent tracing-paper is laid face downwards upon the level surface of the block, and transferred there by rubbing it gently from the back with the thumbnail. The outline tracing of the design is now transferred onto the block. The block I is now ready for cutting. In a similar way, outline tracing for the remaining colors, Color II and Color III are made and transferred to block II and block III. All three blocks are now cut in relief – the non-design portions of the each block are cut so that the design portions remain raised to take up color paste.



(a) Color I

(b) Color II



(C) Color III

(d) Combination of Colors I, II and III

(Note: not in scale)

FIGURE 6.1 Designs in three colors, each separately as well as their combination.

The cutter first thoroughly dampens the block and then cuts away the non-tinted portions. The block is maintained in the damp position until the end of the cutting. The cutter removes the wood around the larger objects, leaving the more delicate work until last. The depth to which the ground is sunk for larger objects is between 0.5 cm to 1.5 cm, but it decreases in proportion as the objects become smaller or are massed closer together. The sides of the outstanding parts of the block slope outwards a little instead of being cut vertically downwards. This is done to retain as much of the strength and solidity of the block as possible.

The tools used in "wood block cutting" are practically the same as those used in ordinary fine carving. They include various sizes and shapes of chisels, gouges and drills, together with instruments such as surgical scalpels or penknife blades, which are employed chiefly for trimming up edges and cutting straight lines. When the whole of the uncolored portions of the block have been cut out to the required depth, the pattern stands up in relief in the same way as letterpress type, only more so. It only remains now to verify the accuracy of the "repeats" by a practical trial.

After the cutting is complete, the pitch pins are added at all four corners. These are small brass pins driven down to the level of the printing surface and are used for matching the blocks while printing. The blocks are immersed in mustard oil for about 24 hours, followed by washing in warm soapy water and rinsing. The blocks are then ready for use. As each block only represents one color, separate tracings must be made of the portions of the design occupied by each color and transferred by the putter-on method to separate blocks, which are then cut.

Sometimes, to prevent the block from absorbing an unnecessary amount of moisture from the printing color, the cut-out portions are varnished; but when this is done great care must be taken not to drop any varnish on the printing surface, as any difference in texture is apt to give rise to unevenness of color in the resulting work.

The number of blocks required to realize any ordinary design must correspond to the number of colors employed in that design. As each block, therefore, only represents one color, separate tracings must be made of the portions of the design occupied by each color, and transferred by the "putter-on" to separate blocks, which are then "cut" and treated as already described.

Figure 6.2 shows a set of four blocks manufactured by M/s A K Wood and Handicraft, Bareilly-243005, Uttar Pradesh, India. (Thanks to the owner, Mr. Chanchal Rajput, for providing the picture and gave kind permission to use the figure.)



FIGURE 6.2 A set of four blocks manufactured by M/s A K Wood and Handicraft, India.

6.2.2 THE PRINTING TABLE

A very solid table is needed for printing with blocks. It may be topped with flat slabs of stone or iron covered with a resilient blanket and a sheet of waterproof material. A back-grey of plain cotton is usually stretched over the table to absorb any surplus color. Ideally the back-grey would be gummed to the table and the fabric to be printed pinned to it, for tight-fitting patterns. The length of the table may vary from 2 to 12 meters or more depending on the length, quantity and nature of the material to be printed. Generally, it is 6 meters or multiples of 6 so as to accommodate sari lengths. The height of the table is between 75 cm to 90 cm. The width is about 125 cm for Indian sari printing. It can be wider if bedcovers must be printed.

The top surface is leveled and 18–20 layers of jute cloth is tightly stretched and nailed on it. A layer of woolen or cotton blanket may then be pinned on it followed by 2–3 layers of grey fabric (Markin or Madarpath cloth). The back-grey can be regularly changed when it gets soiled. The prepared tabletop should have good resiliency so that a sharp print is obtained and the block is also not damaged when in use.

6.2.3 PRINTING PAD

The printing pad (Figure 6.3(a)) is made in a double walled wooden trough about 45 cm x 45 cm x 12 cm in size. It has a false bottom made of a waterproof material like thick Rexene. In between the wooden and false bottom, gum paste is filled. This gives the pad resiliency due to which the block is evenly charged with the printing paste and paste does not get inside the crevices. A number of materials are placed layer by layer (Figure 6.3(b)) inside the trough. A layer (lowermost layer) of Rexene followed by a woolen blanket, then a layer of fine muslin or mosquito net (topmost layer) is placed over the false bottom. The printing paste is evenly spread in-between the layers. The block is gently pressed into the pad to charge it with the paste. Separate troughs (along with padding layers) are to be maintained for each color.

Instead of a double layer trough, two troughs may also be used. A small trough is placed within a bigger trough and thick gum paste is kept between two troughs to provide a cushion effect. Nowadays, thick foam is used instead of gum paste. A single trough is kept over a thick sheet of foam to provide a cushion effect.

The process starts by design selection and making of the blocks. Printing may be done in two ways:

- Matching each repeat;
- Otherwise, block may be placed in discrete intervals. In this case, printing may be done by mixing and matching different blocks.

The blocks and color combination are selected. Subsequently, the bleached or dyed fabric is selected, as the case may be. The fabric to be printed is spread on the table and pinned along one edge, stretching it slightly. The other edges are subsequently

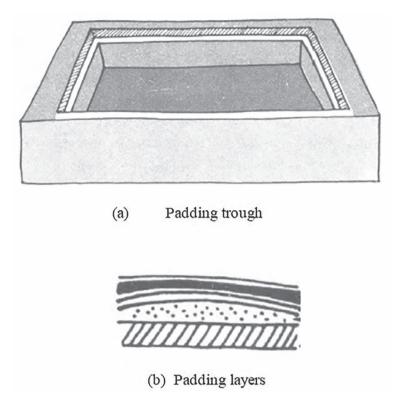


FIGURE 6.3 (a) Wooden trough and (b) padding layers.

pinned in the same way. The areas to be printed are then marked off using a string or ruler and chalk. The pinned fabric should be free of creases and must not move or shift during printing. The fabric is then printed, one color at a time starting with the printing of outline first. The block is placed adjacent to the previous print and aligned using the pitch pins. The printing pad is carried on a trolley from one end of the table to the other. The block is charged with the printing paste and stamped on the fabric and hit on top with the fist to assure an even color transfer. The block is recharged with the paste and the process is repeated. Once the entire length on the table is printed with all the colors, the cloth is allowed to dry on the table.

The instruction note, RSA (TC HLM 03) for block printer written by Textile committee (India) (http://textilescommittee.nic.in/search/node?keys=block%20printing), describes the block printing process step by step as follows:

- Select the fabric batch for printing as instructed.
- Wash the fabric selected and bleach if required as per instructions.
- If the borders are to be made, tie the cloth at the border area and take for dyeing as instructed.
- When the fabric is ready for printing spread the fabric on the printing table and fix firmly with small pins on the table.

- Spread the fabric is laid on the table uniformly; no creases/holds.
- Keep the color tray ready with required colors of proper mixing as instructed by the supervisor.
- Dip the wooden block up to design level in the color tray to transfer color paste on the design portion of the wooden block.
- Ensure even immersion of the design portion of hand blocks.
- Ensure the prevention of over inking or unevenly inked blocks.
- Now take the ink-immersed hand block on the fabric and apply (printing on fabric) by pressing it hard on the cloth in a uniform manner.
- Always commence the process of block printing from left to right.
- Repeat the printing by following the point marked on the block, which facilitates sequential order of printing on the fabric.

Figure 6.4 shows the hand block printing process. Figure 6.4(a) shows pick-up of color paste from the trough by gently pressing the block on the wet blanket inside the trough. Figure 6.4(b) shows transfer of color paste from the block by pressing it on the fabric to be printed matching repeat points followed by knocking the top of the block by hand.



FIGURE 6.4 (a) Color paste pick-up by the block.



FIGURE 6.4 (b) Printing of the fabric with the block.

After printing, the printed fabric is unpinned from the table and stored for a while before steaming it, generally in a hot room. Steaming is carried out to fix the prints. If the fabric is printed using pigment colors then the fabric only needs to be cured for 3-4 min at 140° C (no steaming). With all other colors, the fabric is steamed for half an hour to 2 hours depending on the steamer and the requirement of the printing procedure. A layer of back-grey fabric is provided in-between the layers of printed fabrics during steaming. Sometimes the printed fabric is wrapped in newspaper for steaming. This is done to remove excess moisture which would otherwise be absorbed by the fabric which may result in spreading of color from the printed area.

After the print is fixed, the fabric is thoroughly washed to remove the gum, residual chemicals and unfixed dye. In the small-scale industry, cement tanks are used for washing. The washing process consists of a cold water wash followed by a hot water or hot detergent wash and finally another cold water wash. Finally, the fabric is dried in the open air or on drying machines and then sent for finishing.

6.3 STENCIL PRINTING METHOD

Definition: color is applied to fabric by brushing or spraying through open spaces of a pattern cut-out from a flat sheet of metal or waterproof material/sheets.

A stencil is a flat sheet of paper or metal out of which a design has been cut. A waterproof sheet of plastic, laminate, cartridge paper or metal may be used to make stencil. The stencil suffers from the defect that complete rings or circles fall out of the pattern and some form of "tie" is necessary to link such shapes to the main stencil. Most authorities credit the Japanese with the ingenious adaptation that led to the development of screen printing. Stencils were cut from paper and hair was used to hold to the main design those areas that would otherwise fall out. These fine lines did not show on the final pattern because the dyestuff diffused sufficiently to cover the thin unprinted line originally protected by the hair. The art of stenciling on textile fabrics has been practiced from time immemorial by the Japanese, and found increasing employment in Europe for certain classes of decorative work on woven goods during the late 19th century.

6.3.1 MAKING OF STENCIL

A waterproof sheet of plastic or laminate or cartridge paper or metal is taken. The required design is drawn on the selected sheet. The design is cut out from the sheet with help of a surgical blade. The cut spaces make up or form the design on the selected sheet. If the design is too complicated, then cutting may lead to the design dropping/falling away from the sheet. As only open spaces make up the design, a set of patterns are used to form the design. In case the cut open spaces are too near, the patterns are held together with connectors. Metal sheets are expensive and get damaged during work. Cartridge paper is a better option.

The peculiarity of stenciled patterns is that they must be held together by ties. For instance, a complete circle cannot be cut without its center dropping out, so its outline has to be interrupted at convenient points by ties or uncut portions. This limitation influences the design.

For single-color work a stenciling machine was patented in 1894 by S. H. Sharp. It consists of an endless stencil plate of thin sheet steel that passes continuously over a revolving cast iron cylinder. The cloth to be ornamented passes between the two and the color is forced onto it through the holes in the stencil by mechanical means.

6.3.2 PRINTING WITH STENCIL

The stencil is laid completely flat on the fabric to be printed. The stencil designed is aligned with the place where the design is to appear on fabric. The stencil is held in place with Scotch tape/pins/clips or weights. Color paste is then brushed through the perforations or gaps of the stencil sheet with a brush. The stencil sheet/plate is then lifted, which exposes the design on the cloth as a colored silhouette of the cutout parts of the stencil. If a pattern requires more than one color, then that many stencils are made. Cut-outs correspond to each color's place in the design. The cloth is stencil printed with the first color throughout and followed with the next color in sequence. Color may be brushed or sprayed or dabbed or sponged to get different effects. Another variation is to use different colors on different parts of the stencil and then brush them over each other, giving a merging color effect. This effect cannot be achieved in block or machine printing.

This method is limited to use in home decorative and home upholsteries. Any dye/pigment may be used. Oil colors and acrylic colors may also be used for stencil printing.

A simple stencil printing method on garment is described by a company named "Garment Printing" as follows (Garment Printing, 2021):

Stencil printing could be compared with screen printing in that a different material will be used to block out the areas which are not to be printed. Both methods follow the process of applying ink or paint through an open area and onto a substrate.

In screen printing, a treated screen is exposed to UV light which means the ink will only go through the area of the custom logo or design. This requires a relatively expensive set-up and expertise in the process. Stencil printing, on the other hand, can be done using a home printer, a cutter, paper or card and some imagination!

Step 1. Making of own design

The design can be created by own using a graphics package; for example, Photoshop or Illustrator (Word will work for simple designs and text!). The size of the design is compared with the surface area to be printing and the size is determined accordingly. Some materials which can be printed in this way are custom printed t-shirts, backpacks, posters and walls – the possibilities are endless!

Step 2. The printing of the design is done in black and white so that the areas that will need to cut out can be easily identified. Ideally, if the printer allows, printing may be carried onto thick paper, card or poster board. This will allow stencil to be re-used, and make it easier to cut it out.

Step 3. The design is cut using a sharp blade. In stencil printing the white part of the stencil is called the positive whilst the black part is called the negative. Using a blade or a cutter, the black part of the design or the negative is cut while the positive portion remains uncut. One should try to cut in an unbroken line and follow the perimeter. For a complicated design, one may have to be creative and use some extra lines to make sure that no details are lost.

6.4 GET CREATIVE

Once the stencils (positive and negative) are prepared then one should be ready to get creative and begin printing. The stencil is simply placed in the position to be printed and fixed down with some tape. A piece of cardboard is kept underneath the area to be printed to give a hard and flat surface.

Figure 6.5 shows printing with white pigment on a dark colored fabric using stencil.

Advantages of stencil printing are:

- Low budget, no investment.
- · Exclusive designs and intricacy.



FIGURE 6.5 Printing with white pigment on a dark colored fabric using a stencil.

Disadvantage of stencil printing are:

- Unevenness on printing table leads to uneven printing.
- Less versatile; limited designs.

6.5 FLATBED SCREEN PRINTING

The screen printing process can be accomplished with a minimal amount of equipment. Basically, all that is required is a screen, a squeegee and a table. Besides these, there should be arrangements for steaming, washing, drying and finishing of the printed material.

The idea of screen printing came from stencil printing, which originated in Japan during the 17th and 18th centuries. It evolved from Kata-gami paper stencils, and the method was used worldwide by the 19th century (Storey, 1992). In the second half of the 19th century, woven silk fabric was used as a continuous support for the paper stencil to improve its durability. Within a short span of time, it was observed that durable paint on screen fabric could replace the paper stencil, which prevented the flow of printing paste into the non-design portion of the screen. Accurate multicolor printing was enabled by further improvements of the screens using silk, cotton, viscose rayon and cellulose diacetate yarns, which ensured stable screens with non-aqueous print pastes. Later, the hydrophobic synthetic yarns, such as nylon and polyester, in combination with metal frames instead of wooden ones, were introduced. This allowed for greater tension to be applied on the fabric while stretching it over the frame, ensuring constant tension during printing. The process of flat-screen printing was mechanized and fully automated by the second half of the 20th century. Additionally, improvements were made in dryers, and UV curable inks were introduced, which popularized screen printing techniques even more. Continuous screen printing was achieved using rotary screen printing presses that allowed much higher printing speeds and simultaneous printing of both sides of the fabric. Due to its nature, screen printing uses much lower printing pressure compared to the other direct printing techniques. This allows greater ink volume to be transferred while maintaining precision (ink is not pushed into the fabric structure which improves color strength and maintains the textured surface of the fabric). The cost efficiency and simplicity of this process and the machinery used throughout allow a wider range of inks and dyes to be used in screen printing – more than in any other known printing technology.

The screen printing process is based on forcing the ink through the openings in a fine screen mesh. Non-printing areas are covered by the stencil in the past and now by durable paint, which blocks the ink from passing through the screen onto the substrate material surface. The screen printing process typically consists of five prerequisite elements that ensure reproducible prints:

- Suitable printing medium (printing ink or color paste).
- Screen made of perforated fabric called bolting fabric containing the artwork-design portions are open, allowing flow of printing paste, while non-design areas are blocked by durable paint.
- Flexible and resilient squeegee mostly made of semi-soft rubber sheet.
- Thoroughly prepared substrate to be printed (textile fabric).
- Base blanket or cylinder (ensures positioning of the substrate), which is placed under the fabric to be printed. This gives cushion effect during printing and also absorbs the color paste flowing below the printed fabric. This should be moderately soft in all directions neither too soft nor too hard.

Integration of the aforementioned prerequisites ensures controlled transfer of the ink through the openings in the mesh onto the printing substrate. The surface of the screen must not be in contact with the substrate because it could create an unclean or damaged print due to uncontrollable substrate snap off from the screen. The contact only occurs when the squeegee applies pressure, forcing the ink through the open areas of the screen mesh in a controlled manner.

The factors controlling the amount of print paste passing through the screen are (Miles, 2003):

- The "mesh" (threads per inch) or "raster" (threads per cm) of the screen fabric; generally, a coarse mesh allows more paste to pass through than a fine one.
- The fraction of open area in the screen fabric; this depends not only on the mesh but also on the yarn diameter and the effect of subsequent treatments, such as calendaring.
- The hardness and cross-section of the squeegee blade; a hard rubber squeegee with a sharp cross-section is suitable for outlines, whereas a soft, rounded blade applies more paste and is suitable for blotches.
- The hardness of the printing table; if the top of the table is firm, a soft squeegee is probably necessary, whereas with a resilient table surface a harder squeegee is preferable.

- The viscosity of the print paste; within the constraint of the requirement for good definition, the viscosity can be varied, thinner pastes passing through the screen pores more readily than viscous ones.
- The number of squeegee strokes; from two to four strokes are usually applied.
- The angle, pressure and speed of the squeegee stroke.

All these variables should be taken into consideration, in conjunction with the nature of the design, when printing the chosen fabric.

Before printing begins, the screens must be carefully positioned on the fabric. The area to be printed by a screen (screen repeat) must fit exactly alongside the adjacent one; a slight overlap being preferable to a gap. With flat-screen printing, this is not automatically achieved (as is the case with rotary printing). The differently colored areas must be in register and, again, a small overlap is usually allowed. To achieve accurate registration, it is common practice to attach to the frame a bracket which locates against fittings, known as "stops", on a guide rail along one edge of the table.

The stops are spaced exactly one (lengthways) screen repeat apart along the whole length of the table. Two adjustable screws set the distance of the frame from the rail.

As a further aid, repeat crosses known as "pitch marks" may be incorporated at one or both sides of the screen, and the positions of the following screens checked against the first pitch mark. Often registration marks are printed along the selvedge.

Silk screen printing produces higher fidelity results with more vibrant colors which are hard to replicate using other printing techniques. It also allows for sharper, cleaner lines and more well-defined details.

The advantages of screen printing are:

- A higher quality output than digital prints.
- More durable for prints that are needed over the long-term.
- It can be used on a variety of different print materials, including glass, wood, textiles, signs, banners, electronics and much more.
- It's easy to print on specified areas of the print material.

6.5.1 DISADVANTAGES OF USING SCREEN PRINTING

- A higher initial setup cost than digital printing, and a more time-consuming process.
- Limited color ranges available as compared to digital printing.
- The amount of ink used can make the design look as if it is raised from the print material.
- It cannot be customized in the manner of digital printing.

6.5.1.1 Flat Screen

A screen consists of a frame on which a cloth is mounted. The screen-cloth is called "bolting cloth". The design to be printed is transferred onto the screen before it is considered ready for printing.

The frame of the screen is made of wood (or hollow pipe made of iron) of size 22 in x 50 in (or 27 in x 50 in). The upper and lower sides of the wooden frame are blocked by 3 in and the two other sides by 2 in. So, the actual size of the printing area is 18 in x 44 in (or for bigger screens, 21 in x 44 in).

Modern screen printing is based on the same principles, both in the textile field and in the graphic arts. The screens used in flat screen printing are made of rectangular wooden or metal frames covered with gauze fabrics with a more or less fine network of meshes. These gauze materials are covered in some areas with suitable coatings, so that the printing ink will penetrate the areas not covered by the film coat, according to the print pattern.

One complete unit of design is called a "design repeat". One screen may contain one or more "design repeats". The design contained in a screen is known as "screen repeat" and may consist of several complete design repeats. A single screen may have more than one repeat. Care should be taken so that the junction points of the repeat are not distinguishable. One repeat may have two or more colors. For each color a separate screen is required.

At first, the design is drawn on a transparent plastic paper with black ink. A separate drawing is made for each color. Four sides of each sketch are marked "+", so that different screens of the same set are (i.e., set of same repeat unit) placed in the right space.

6.5.1.2 Printing Table

The printing table is made of wood. The top of the table is slightly (about 6^{0}) inclined to the front for easier movement of the squeegee by the operator, without jerking. The length of the table for work practice varies between 50–100 m (55–110 yd) in length. The height of the table varies from 75 cm to 90 cm and width approximately 1.2–1.6 m (48–62 in). It is usually covered with a woolen felt about 6 mm (0–25 in) in thickness. If the goods to be printed are to be fastened with pins, then the felt is covered with a cotton back-grey, but if the goods are to be stuck down to the table with an adhesive, then a waterproof cover is used. Suitable waterproof coverings for tabletops of screen tables are:

- Rubber-coated materials
- Coatings based on synthetic rubbers such as "Alloprene" (chlorinated rubber) or "Neoprene"

The screen printing table may be cold or hot. For a hot table, steam pipes are provided below the table to maintain the temperature of the table around 50 to 60° C to facilitate quick drying of the printed fabric. The steam line runs throughout the length of the table. For wax-coated tables, wax becomes sticky at that particular temperature and sticks to the fabric being printed on the table.

A simple wooden screen printing table is shown in Figure 6.6. Grooves are cut at regular interval as shown in the figure to mark repeats. In commercial long tables, the registration of the design is ensured by means of a guide rail, which is fitted along the side of the screen printing table. Adjustable metal stops are attached to this rail, and are screwed in place to fit the width of each repeat. Adjustable screws or bolts

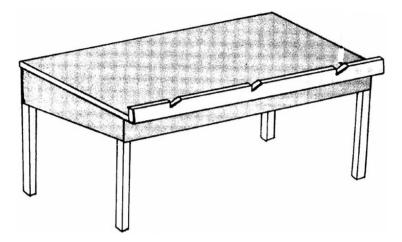


FIGURE 6.6 Screen printing table.

fastened to the base of the screen frame make contact with the guide rail. A bracket or angle iron is fitted on the end of the screen frame and makes contact with stops fastened on the guide rail. It is most important that the guide rail attached to the side of the screen printing table be aligned correctly (Clarke, 1974).

While printing, the fabric must not move or shift and should not form creases. For fine fabrics like silk, a wax table is used. The top of the table is coated with wax and the fabric is glued with wax in the hot table or by hot shoe. For normal fabrics, backgrey or Rexene is first wound on the table and the fabric to be printed is attached to it by pins. Many thermoplastic synthetic adhesives are available which work exactly like wax. After each printing operation, the table is thoroughly washed with or without detergent.

6.5.1.3 Squeegees

The tool used to press the color though the screen is called a squeegee. It consists of a straight-edged flexible blade (2) backed by a stiff wooden holder (1) as shown in Figure 6.7. In action, the squeegee traverses the inside of the screen from end to end, sweeping the color before it. As it passes over the open parts of the screen, the color is forced through the mesh and the print is made. Various types of squeegees are available. Some are made entirely of wood while others have wooden handles with rubber or metal plates inserted. Most squeegee blades are made of rubber. Squeegee blades are also made from synthetic plastics such as neoprene and polyurethane. All these materials are manufactured in the form of running strip, cut to order and sold by inch.

The length of the squeegee is approximately 40 mm (1.5 in) shorter than the internal dimensions of the screen. The type of squeegee required varies according to the material being printed and the type of table covering. For large designs, and for fabrics that absorb a good deal of color paste, a soft rounded blade is required. Patterns with fine detail that are to be printed on a flat, silk-like fabric require a sharp hard blade. Furthermore, a hard table covering requires a soft rubber squeegee, while a table with a soft underlay requires a harder blade. If the squeegee is held near the upright position, less paste will be applied than when a shallower angle is used. A more rapid movement of the squeegee or lighter pressure also results in less paste being applied. The edge of the blade must be perfectly level and clean. The edge of the squeegee must always be kept uniform and sharpened, when necessary, by sandpapering or other suitable means. Even if the squeegee is perfect, some skill is required to produce sharp, level prints – especially when fine lines are printed. The printer must draw the squeegee over the screen at the correct angle with an evenly distributed pressure. If the pressure is unevenly distributed and the stroke of the squeegee over the screen is sporadic, the resulting print will be unlevel and have poor definition. In order to make the printing independent of the varying pressure of different printers, squeegees are often weighted and provided with long handles.

In Figure 6.7, different types of squeezes are shown. The square-edged blade (A) is used for general printing on flat surfaces. With corners slightly rounded (B), the squeegee can deposit a heavy layer of paste on the substrate. A fully rounded edge (C) is generally best for textile printing. A level-edged blade (D) is useful when printing on glass, while one with a flat point (E) is ideal for imaging ceramic tiles. Bottles and round containers are generally printed upon using a squeegee that has a V-shaped blade (F). The blade is set in a wooden handle to keep it stiff and straight.

The length of a squeegee is determined by the inside width of the screen frame; it should fit more or less right across from side to side, so that the whole surface of the screen is covered in one sweep. Between the ends of the squeegee and the sides of the frame there should be a small clearance, but this need never be more than 1/2 inch (1.25 cm) (Gulrajani and Jain, 1990).

The action of printing wears down the squeegee blade, and in time the bright new edge becomes rounded. When this happens there is a noticeable change in the quality

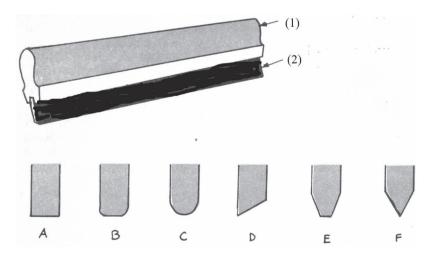


FIGURE 6.7 Squeegees for screen printing.

of prints. A rounded blade gives a thicker deposit of ink and less sharp definition of detail. Textile printers often prefer, when aiming at a saturated print, to work with a rounded squeegee blade. But if fine details are required, the blade must be kept sharp and the easiest way to do this is to grind the edge against a sheet of medium emery or garnet paper glued to a flat board.

The squeegee is to the screen printer what the brush is to the painter, and it ought to be treated with care. Never drop it or leave it resting against a sharp object, never stand it near a fire or electric iron. And always make sure that the blade is perfectly clean before putting away.

6.5.1.4 Screen Frame

The choice of frame size depends on the kind of work being printed. A frame with internal dimensions of 24 inch x 54 inch (60 cm x 135 cm) is generally preferred. A screen frame must be strong, sturdy, reasonably light in weight, reasonably cheap to make, and, above all, it must be accurately made so that it will lie flat on the printing bed. It should have dimensional stability and the smallest possible contact surface to avoid marking off, as well as haloing of the design and stains, especially in weton-wet printing. The requirements are best fulfilled by metal frames. Barth (1967) described that screen frames are of three types:

- Metal frames
- Wooden frames
- · Combined metal and wooden frames

Figure 6.8 shows various types of screen frames.

Metal frames: These are made from iron or light metal. Closed profile tubes give better results than open U-shaped or angle profile tubes. The cross-sections of the tubes can be of different shapes; square or rectangular, trapezoidal, trilateral or sectorial. Sectorial cross-sections give the best results, but square tubes with rounded edges are also used, although they are not quite so suitable because of the greater contact surface (Figures 6.8(a) and 6.8(b)).

Metal frames should be protected against rusting by a lacquer coat or preferably by galvanizing, because rust will damage the screen gauze, and cracks can be formed at the screen edges. When covering frames – especially big frames with gauze – the considerable tension required during stretching will cause bending through of the longitudinal sides, even of stable metal frames, at least to some extent. Such bending

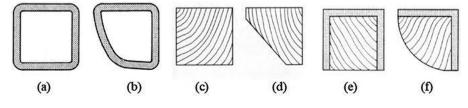


FIGURE 6.8 Screen frames.

through can be compensated by the use of "concave frames". The longitudinal sides of these frames have a corresponding outward curvature to compensate the bending through.

Wooden frames: Such frames are now only being used for special purposes such as sample prints. They tend to bend through when the gauze is fastened to the frames; warping is greatly promoted when the frames are alternately exposed to moisture and heat. Such warping of the wood is counteracted by a suitable lacquer coating or impregnation. Light, well-seasoned wood such as pinewood is used as raw material. The profile shape of the wooden ledges used for these frames can vary from square to quadrant. Depending on the size of the screens, strip boards of 4 to 8 cm height or width are linked together in the sturdiest possible manner (Figures 6.8(c) and 6.8(d)).

Combinations of wooden and metal frames: with such combinations, there is less likelihood of longitudinal distortion or warping than with wooden frames. Wooden ledges of suitable cross-sect are inserted in the conventional open U-shape or angle profiles of the metal frames and a preferably screwed onto the metal. The gauze is fastened to the wood. Suitable hard plastic can also be used in place of wood (Figures 6.8(e) and 6.8(f)).

6.5.1.5 Screen Gauze Materials

Meshed fabrics of different origin can be used to cover the screen frames, and hence named as film carriers, such as:

- Natural silk fabric (silk bolting cloth). This firm fabric is usually made of silk woven in various mesh sizes for bolting or domestic screening of wheat flour etc. or for use in screen printing, needlework or photographic enlargements.
- 2) Polyamide fibers (perlon, nylon).
- 3) Polyester fibers.
- 4) Metal filaments or threads (phosphor bronze chromium nickel steel) or glass filaments.

6.5.2 SILK GAUZE

To meet the demands made in screen printing, the bolting cloth had, of course, to be modified. A different weave type was necessary, as well as a stabilizing finish to protect the cloth against chemical and mechanical attack. Silk screen gauze is very elastic, and color lift-off is very uniform. Silk printers have been making use of this advantage for a long time to get optimum levelness – especially of grounds, borders and edge patterns – when printing shawls and neckerchiefs or scarves.

Silk gauze is given a heavy-duty finish and is normally closely woven in plain weave. It is fine and highly textured silk made with the gum still in the yarn. Coarser fabrics are given a gauze weave, or rotary weave, to impart resistance to slipping during printing.

Silk gauze is very resistant to acids and solvents. But it is very sensitive to alkali, so that its use is rather restricted. The silk will swell more or less markedly, or can even be destroyed, when printing with alkaline pastes. This swelling reduces the

size of the meshes, so that the color lift-off is uncontrollably reduced; furthermore, the strength of the silk threads is also affected. Swelling and heavy-duty wear were reduced by a special finish. Nevertheless, silk gauze should always be after-treated with diluted acetic acid during cleaning. Silk gauze is more or less heavily stained during printing. Staining with acid dyes can be easily removed with alcohol or weakly soda-alkaline soap solutions as cleaning agents. Several screens are often required when printing borders and edge patterns because these are too heavily stained. Silk gauze is less important nowadays as a result of its poor heavy-duty performance in automatic flat screen printing.

6.5.3 GAUZE FROM SYNTHETIC FILAMENTS

The introduction of automatic flat screen printing increased the performance demands made on screen gauze. It was eventually found that nylon and polyester fabrics were particularly suitable for preparing screen gauze. Conventional gauze types were completely replaced by nylon and polyester in automatic flat screen printing. Such gauze is produced in plain weave from monofilament material. Monofilament yarn is also made from polyester. Synthetic monofilament gauze is mainly supplied in the types T (textile printing) and HD (heavy duty). The type designation is given as a suffix to the gauze count. Figure 6.9 shows various types of screen gauze fabrics made from synthetic fibers.

Screen fabrics made from monofilament polyamide material are characterized by high elasticity, high breaking strength and abrasion resistance, remarkable durability, low moisture absorption, excellent color permeability, considerable resistance to alkalis, and good stability to solvents except phenol compounds. However, they are sensitive to ultra-violet radiation (direct sunlight), oxidizing agents, nitric acid, sulfuric acid and formic acid, depending on the concentration and temperature of these acids. The acid concentrations normally present in print pastes, however, are tolerated.

The polyamide gauze materials must be finished so that they are resistant to extension; they must be heat-set and stabilized for maximum dimensional stability of the screens. On account of the high elasticity of the gauze material, metal frames must be employed which are not prone to distortion.

When printing, washing and storing the screens, it must be borne in mind that the stabilized fiber will shrink in heat to some extent and re-expand on cooling.

Special types of gauzes were originally also produced, for example, with extremely fine filaments and relatively large-size meshes, resulting in good flow-through of the print paste. Additionally, the reduced fabric thickness made it possible to produce flatter color paste films. Such gauze types have now been largely replaced by corresponding special gauzes. These are obtained by calendaring monofilament gauze. This treatment produces flat fabrics without appreciably reducing the mesh openings. Figure 6.9(a) shows monofilament polyamide fabric.

Incident light is considerably scattered by polyamide gauze and also by polyester gauze. This can lead to undesirable reflections when copying (exposing) transparencies or color separations; these undesirable reflections can occur in the photosensitive layers. Outlines, screens and thin lines are particularly affected; they will become

much too thin, or can even be covered up completely, as a result of the lateral radiation when exposing the photosensitive layer to light. For this reason, colored polyamide and polyester gauze is now available which does not tend to reflect the light.

6.5.4 POLYAMIDE GAUZE

Gauze made from polyamide filament (nylon) represents the bulk of screen fabrics on account of the very favorable overall performance. The most striking feature of this material is its outstanding abrasion resistance under tension in heavy-duty work in automatic flat screen printing. Fastened and stretched polyamide screen fabrics are very resistant to impact and deformation. But they must be stretched rather tightly and uniformly on very stable screen frames, since moisture will produce a slight extension. Insufficient tension affects fitting of designs and leads to vibration of the gauze due to insufficient tension, especially in wet-in-wet printing on flat screen printing machines unless the screens are carefully lifted. As a result, parts of the print paste will be thrown back (splashed) on the printed goods.

Polyamide gauze is largely insensitive to alkalis, but even weak acids are tolerated only for a short time. However, the amounts of acid normally contained in print pastes are harmless. Depending on the temperature and concentration, polyamide screen fabrics are attacked or destroyed by sulfuric acid, nitric acid, and also by phenol, cresol, xylene and so on. Prolonged exposure to ultraviolet light will also affect the strength.

6.5.5 POLYESTER FIBER GAUZE

Polyester gauze (monofilament) has become more and more important, mainly because it is usually very resistant to acids, cold diluted alkalis and organic solvents. Figure 6.9(b) shows monofilament polyester fabric. Such gauze can be used in printing with all types of dyes and a variety of auxiliaries. Polyester gauze has a high tear resistance and a high breaking strength, but the abrasion resistance is lower than that of polyamide, although it is higher than that of silk. The elasticity is not very high, and the elongation in the wet state is also lower than that of polyamide. This dimensional stability results in a low tendency to shrink or to expand when exposed to temperature variations. Hence excellent fitting of individual motifs can be obtained when printing with polyester screens. On account of the low wet elongation, polyester gauze need not be stretched as tightly polyamide, so that frames of inferior strength can also be used without risking any distortion.

The moisture absorption of the fiber is extremely low (approx. 0.4%), so that the properties are not affected in the moist state. The fiber is not sensitive to light and is resistant to acids, diluted alkalis and oxidizing agents as well as to solvents, with the exception of a few phenol compounds. The color permeability is somewhat lower than that of polyamide fiber gauze. The number of ends per inch should be the same as in the case of silk gauze and polyamide fiber gauze.

In multifilament polyester gauze (Figure 6.9(c)), the filaments are twisted to form filament yarns. Since the filament yarns are uneven, the size and form of the mesh openings will also vary. On account of the higher volume of the yarns, multifilament polyester

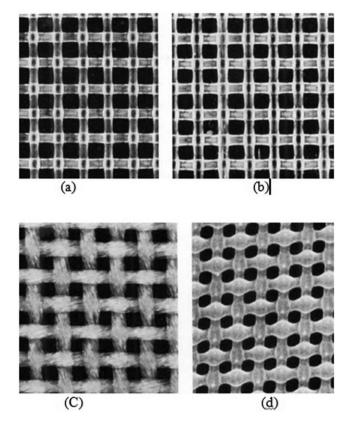


FIGURE 6.9 Screen gauze.

gauzes are produced with a fineness only up to 80 to 90 threads per running centimeter. In printing, they are well adapted to the surface of the goods. Squeegee pressure will alter the cross-section of the yarns, thus reducing the amount of color applied.

Multifilament polyester gauzes flattened by passing through calender, as shown in Figure 6.9(d), are rarely used. It is not advisable to use them for reducing the color lift-off. As a matter of fact, even the normal type involves technical drawbacks on account of the thread structure. Pigment particles can lodge between the filaments during printing. This can result in increasing the diameter of the yarns and hence in narrowing the mesh openings.

Quite frequently filaments are cut through, depending on the amount of wear to which they are subjected by the action of the squeeze. The cut ends will cause trouble by projecting into these mesh openings.

6.5.6 METAL FILAMENT GAUZE

The advantages of excellent color permeability and good resistance to chemicals, of gauze made from metal filaments, especially of gauze made from phosphor bronze

and nichrome stainless steel, are counteracted by the disadvantage of their inelasticity and the resulting risk of distortion. Screens made from such material have perfect dimensional stability, but they will hardly adapt themselves to fabrics of coarse structure. Metal gauze is used in some rotary screen printing machines; in all other types, thin nickel cylinders of more or less fine perforation are employed.

6.5.6.1 Gauze Numbering

The numbering system was formerly the only way of determining the suitability of screen fabrics, but the numbers did not convey any information on fineness and number of threads. The first silk gauze was designated 0, and every following, finer gauze, in numerical succession, was numbered 1, 2 and so on. The finest silk gauze, which was given the number 25, corresponds approximately to a screen fabric made from monofilament synthetic fibers with 77 threads or meshes per running centimeter. Multifilament gauzes, which largely correspond to the silk gauzes in respect of weaving technique, were numbered in approximately the same way. The silk screen gauze numbers 6 to 9 are suitable for blotch prints and for the printing of large areas on coarse fabrics, whereas for small areas (fittings) the number 10 to 14 can be used, depending on the type of material. For fine outlines, special effects, and screens it is better to use gauze numbers 14–16.

Metal screen fabrics are numbered differently. The numbering varies, depending upon the origin. The designations usually refer to meshes per inch. The German numbering system is particularly confusing. Up to No. 100, the Rhenish inch, or the inch applicable in the Rhineland, equivalent to 2.6 cm, is applied, while from No. 100 upwards the French inch (= 2.7 cm) is used. Goods which are exported, are classified according to the British inch (= 2.5 cm).

This system of designating metal gauzes has remained unchanged to the present date, but now the number of threads or meshes per running centimeter is given together with the number. Monofilament screen fabrics made from polyamide or polyester are usually numbered according to a uniform system. The number indicates the threads or meshes per running centimeter.

Different mesh counts are used for different applications in the screen printing process. Mesh count is a measure of how many threads of polyester (previously silk, centuries ago, hence "silk screening") cross each other per square inch of the screen. For example, a 110-mesh screen would have 110 threads crossing per square inch. The higher the mesh count, the finer the holes are in the screen.

The first factor one should keep in mind when choosing a mesh size is how detailed the image is. For example, if the image has extremely high detail, a low mesh screen simply wouldn't hold the detail. The fine lines or dots in the image would simply fall through the holes in the mesh, leaving a poor representation of the image should be. If one has a low detail image and too high mesh count, one will run into issues of not getting enough ink to lie down on the shirt.

The other important factor to keep in mind would be the thickness of the ink or paste itself. Thinner inks, such as water-based ink, generally require a higher mesh count. If too low of a mesh count is used, then the thin ink could potentially flood through the larger holes, soaking the garment with more ink than intended. Flooding the garment would make the image blurry as the ink bleeds. On the other hand, if one is trying to print with a thicker ink, such as plastisol or white inks, one will consider lower mesh counts. Too high of a mesh count one may run into an issue with inks not easily wanting to pass through the mesh, which could lead to opacity and coverage issues.

If the mesh count is fairly close, such as the difference between 155 versus 156, 196 versus 200, or 81 versus 86, the difference is so negligible that it will not matter in the final results. Since there are many variables involved in silk screen printing, it is not possible to tell exactly what mesh sizes are used for what applications.

The two most standard mesh sizes are 110 and 156. A mesh count of 110 will lay down a fairly thick layer of ink. This mesh is great for block text letters and larger spot color designs. 156 mesh will lay down a moderate amount of ink, but offers more detail capability for the image.

There are mesh counts lower than 110, and they are most often used for specialty printing. The lower mesh counts are used for glitter and shimmer inks. These inks are made special to have flakes of glitter in them to give the desired look. These flakes can get caught in the mesh of the screen if the mesh count is too high, with none going onto the shirt itself. Glitter inks have larger, more obvious flakes to them, while shimmer inks have smaller particles to give a more subtle look. A mesh size of 36 is ideal for glitter inks, though one can go up to a 64 mesh. For shimmers, an 86 mesh is recommended. Higher mesh screens, 200 mesh and above, are most often used for finer detail images and thinner inks. Graphic, discharge and waterbased inks should be printed through screens of this mesh size. The higher mesh count helps to keep the thinner inks from flooding onto the substrate. If one would like to get a softer hand feel to plastisol prints, higher mesh counts can help as well. By printing the thicker ink through the finer mesh, much less of it is laid down, allowing a thinner "plate" of ink. The results are a softer feel to the print. While plastisol prints may feel softer, one might sacrifice the opacity of the ink by using a higher mesh count (Bayer, 1974).

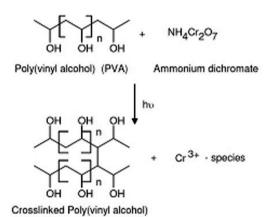
6.5.6.2 Screen Coating Lacquer

In the past, various materials have been used to coat fine mesh screens. For the purpose of screen making, dichromate as a photosensitizer and polyvinyl alcohol as a binder is found to be very effective. Polyvinyl alcohol (PVA) polymer is found to be relatively durable, water soluble, low cost, resistant to elevated temperature applications, and commercially available. In general, PVA is prepared by the partial hydrolysis of poly vinyl acetate, with 80–90% cleavage of ester group. As PVA is not water soluble at room temperature, solid polyvinyl alcohol is stirred and heated for about 2 hours to ensure the formation of a viscous solution of polyvinyl and water.

Ammonium dichromate emulsion coating is extensively used for screen fabrication, as it is cheaper and easily available, compared to potassium dichromate. The screen is coated with the polyvinyl alcohol and dichromate solution and then dried and exposed to light. The coating solutions are fairly stable when dried; the exposure of light make them insoluble by reducing part of Cr^{6-} to Cr^{3-} , and a colloidal complex $(Cr_2O_3)_x \sim (CrO_3)y$ is formed. At the same time, the coating undergoes a sol gel transformation. Then the portion which was exposed to light hardens and the unexposed part is removed by washing with water.

The basic mechanism of DC-PVA films can be explained by the photo crosslinking process of PVA when mixed with ammonium dichromate. PVA solution becomes photosensitive when an aqueous ammonium dichromate solution is added into it. The photo crosslinking of PVA with the oxidizer then begins.

The photochemical crosslinking reaction between polyvinyl alcohol and ammonium dichromate is shown in Equation 6.1. In the following reaction, the dichromate ion is reduced by light to a chromium compound (Cr III).



In this reaction, the concentration of hexavalent chromium (Cr VI) decreases and the pH of the solution increases. As the concentration of the chromium (Cr VI) is reduced, the PVA (or other alcohols) become oxidized. The reduced chromium may be attracted by hydroxyl, carboxyl and carbonyl groups of PVA chains. This reaction will lead to many crosslinked PVA configurations which are water insoluble. The light sensitivity of the coating is influenced by the quantity of dichromate to the total emulsion. Ammonium salt produces the best effects. If too much dichromate is added, the coating may become brittle. The quality of PVA also affects the quality of the pattern on the screen.

Before coating the emulsions, the screens are thoroughly cleaned, as this yields better line resolution comparable with that of photo-film masks. Control of its thickness is necessary; that the thickness variation from screen to screen is minimized, for better resolution. For this we require better viscosity control of the emulsion coating and drying technique, the tension of the screen and developing time. Exposure time is always standardized. Short exposure time does not harden the dichromate emulsions, and during developing a weak coating remains which reduces the life of the stencil and causes it to become perforated. Clean conditions are essential for all photo-chemical work. Dust particles on the screen or in the emulsion reduce its adherence to the screen mesh and develop perforation in the mask, even if all other precautions have been taken to standardize (Gurawa, 2017).

In many screen printing processes, diazo is widely used rather than ammonium dichromate because of its superior quality at high relative humidity and temperature. We can make both positive and negative masks by diazo printing.

Ferric chloride has very low toxicity, so scientists studied the properties of films of polyvinyl alcohol containing iron (III) chloride. Sodium borate acts as a cross-linking agent to bind PVA chains together. Sodium borate dissolves in water to form boric acid which then accepts a hydroxide from water to become $H_4BO_4^-$. Then $H_4BO_4^-$ reacts with PVA to form crosslinked polyvinyl alcohol structure. Sodium borate is not a photosensitive compound, so a Cds is doped to make the compound photosensitive. The doping of Cds can be done by chemical bath deposition method.

6.5.6.3 Screen Making

The making of a printing screen is a delicate and lengthy multistep process. The steps are as follows:

- 1) Design drawing
- 2) Cover the frame with gauze
- 3) Fasten and stretch the gauze
- 4) Photo-chemical method of design transfer
- 5) Light-sensitive coating: (a) chrome-gelatin or (b) chrome-PVA
- 6) Application of the light-sensitive coatings on screen
- 7) Print the color separation diapositive on the light-sensitive coating
 - a) Method of printing using large-size diapositives
 - b) Step-up method
- 8) Wash the exposed screen to remove non-hardened solution/emulsion from unexposed area from the screen; and finally, paint for improved durability of the screen

6.5.7 DESIGN DRAWING

Every print pattern is based on a drawing of a design. A design unit which is repeated at regular intervals is known as "repeat" or "fitting". A screen repeat is the dimension of the printable area of a screen, and it may consist of several pattern repeats. Each repeat may be placed side by side as well as above another in a simple manner called adjacent repeats. In other arrangements, the repeats in each line in the vertical or horizontal directions are staggered by one-half or one-third of the repeat unit; each row or column of repeat is advanced by that amount in respect of the preceding row or column.

In any case, the design drawing must be true to repeat or it must be modified in such a manner that it becomes true to repeat. This is best done by dividing the repeat rectangle into four parts which are then interchanged diagonally, so that it will be easy to detect any inaccuracies within the repeat, which can then be removed by suitable retouching or modification. The photo-chemical transfer of the print to the screen makes it necessary to copy color separations of every color occurring in the design. These separations are prepared on transparent material (paper, sheeting or film) in such a manner that the colored areas are impervious to light. This can be done by different methods, such as:

- By pointing with opaque ink or drawing sheets, films or transparent (oil) papers
- By cutting using cut film
- By direct copying
- On photographic transparent paper or film
- By using a reproduction (process) camera

When copying on unexposed photographic material (photographic transparent paper) it will be necessary to produce a negative from the tracing of the repeat, this negative being then used to make the necessary transparent (diapositive) copies.

Before color separations, we must clarify the requirements conditioned by the employed printing technique. We must, therefore, decide on the printing method (direct, discharge or resist printing), and we must know something about the precision obtainable with the printing method in question; furthermore, it is necessary to know whether overlapping designs or colors, half-tones, and so on, are required. Contours, as well as the use of dot screens will also exercise an influence.

For example, overlapping by ¹/₄ to ¹/₂ mm will be enough to prevent "blank" spaces when printing adjacent colors on accurate printing equipment, but on equipment of poor precision the overlapping is often required to be as much as 1 mm or more. This additional width is usually only provided for the paler of the adjacent colors. In the case of fine outlines, or contours, and small areas, the color separations are normally a little more "tight-fitting" because they will mostly turn out a little wider when they are printed. In overlapping designs care should be exercised to obtain good mixed shades by suitably covering up the colored areas when the individual color separations are being prepared. The same applies also to semi-tones or half-tone effects. In this case all shades which are to be reduced must be combined in a common color separation for printing the half-tone resist. For white discharges and white resists, the color separations for these effects must be impervious to light.

6.5.8 COVERING OF THE FRAME WITH GAUZE

The first step of making screens is to select suitable frames of proper type and size. A suitable gauze fabric is to be procured and carefully fixed on the screen frame. A fault-free screen is a must, otherwise a large quantity of printed fabric will be rejected. The gauze must be fastened to the frame as tight as a "drum skin". This stretching is most important, because fitting trouble will occur if the screens are not covered tightly enough or if they are stretched too tight. Silk and polyamide fiber gauzes undergo elasticity losses due to overstretching. Normal elongation values are 2% for silk, 5% for stabilized polyamide, and 3% for polyester, while metal gauzes are practically not extensible.

The gauze can be stretched by hand or with simple auxiliaries, but quicker and easier stretching is possible with special stretching devices. It will always be necessary to take the properties of the individual gauze types into account.

6.5.9 FASTENING AND STRETCHING OF THE GAUZE BY HAND

The method described by Barth (1967) (Figure 6.10) is as follows: The gauze is cut to fit the size of the screen frame, making adequate allowance for handling. Wooden frames are usually covered according to several methods, one shown in Figure 6.10 working from the center to the corners to prevent the formation of folds. The gauze is fastened in the center of the longitudinal side a, to the surface or the outside of the frame (1), stretched by hand or preferably with a pair of stretchers to the opposite side c (2), and fastened there in the same manner (3). Similarly, another part (4) of the gauze is stretched from b to d (5), working being continued alternately in direction of the corners. progressing by a few inches along each of the opposite pair of sides. This working method is chiefly for silk gauze, because sufficiently taut and even stretching is hardly possible with other gauze types.

Stretching by hand using a needle bar can be done not only for silk and polyester fiber gauze, but also for well-stabilized polyamide fiber gauze. This method is not limited to wooden frames; it can be applied to all-metal frames with equal success. Needle bars are wooden bars on which small needle boards have been fastened

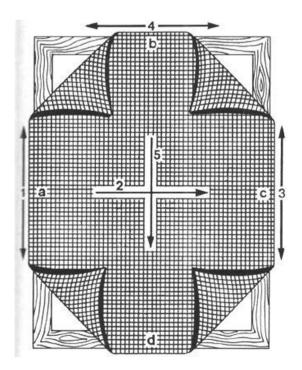


FIGURE 6.10 Screen making.



FIGURE 6.11 Needle bar for screen making.

by screws. These boards have one or preferably two rows of pins of about 3 mm length. These bars (with the screwed-on needle boards) are fastened to the outer edges of the screen frame by means of screw clamps (Figure 6.11). The frame is then covered with gauze in the manner described previously, beginning usually from the center and progressing in the directions of the corners. On one side of the screen, a part of the gauze is beaten fast to the needle bar with a brush, and then stretched to the opposite side, where it is fastened to the needles by striking it with a brush. Stretching is done on both narrow sides in the same way, and continued in stages along each pair of opposite sides in direction of the corners. In case of partly uneven tension the gauze can be lifted from the needles in those areas, and re-tightened.

The gauzes can be nailed or fastened by means of special fastening tongs or pliers, if the frame is made of wood or of metal with a wooden insert. In most cases, however, the screen fabrics are glued to the frames, especially to metal frames, by means of special adhesives. Metal frames must be cleaned first, degreased with fatdissolving agents and freed from any traces of rust which may have formed. It will also be quite useful to roughen the frame areas on which the gauze is to be glued, using a steel brush or an emery wheel.

Different kinds of adhesives can be employed – for instance, adhesive lacquers which are soluble in solvents, or adhesives which can be crosslinked, as well as thermoplastic adhesive compounds or lacquers.

Soluble adhesive lacquers are applied to the frames and allowed to dry well. The frame is then pressed against the tightly stretched gauze and the lacquer coat is moistened through the fabric by using a suitable solvent. A firm bond is obtained after a brief drying period, but this bond is not completely resistant to solvents. Crosslinking adhesives are applied through the gauze which is in contact with the frame. Bonding produced in this manner is usually resistant to solvents and to heat.

6.5.10 PHOTO-CHEMICAL METHOD OF DESIGN TRANSFER

The preparation of screens by the photo-chemical method enables an accurate reproduction of the printing design. Several methods can be used, depending on the conditions in each case. All methods have one common feature: that a light-sensitive coat is applied, usually to the outside of the screens, which is covered after drying with a diapositive of a color separation, and then exposed to light. The exposed areas become largely insoluble in water, while in the unexposed areas the coating can be easily removed by washing out with water.

6.5.11 LIGHT-SENSITIVE COATING

Several light-sensitive materials are used commercially for various purposes. But their selection is based on several factors, the most important being cost. Considering these factors, the two most popular light sensitive compounds used for screen-making are:

- 1) Chrome-gelatin solution
- 2) Chrome-polyvinyl alcohol solution

6.5.12 CHROME-GELATIN

Protein substances are used as basic materials for light-sensitive coatings, such as gelatin, fish glue, pearl glue (bone glue), albumen or polyvinyl alcohol or derivatives thereof, as well as mixtures with other polymers, which are dissolved in water and are sensitized with chromium (VI) salts.

Gelgelatinatin or (from Latin: gelatus meaning "stiff" or "frozen") is a translucent, colorless, flavorless food ingredient, commonly derived from collagen taken from animal body parts. On a commercial scale, gelatin is made from byproducts of the meat and leather industries. Most gelatin is derived from pork skins, pork and cattle bones, or split cattle hides. Gelatin made from fish byproducts avoids some of the religious objections to gelatin consumption. Gelatin, which was previously used more frequently than any other substance, is now being increasingly replaced by synthetic products which are available in a much more uniform quality.

Gelatin should be free from fats as far as possible, and should not contain any decomposition products of proteins. Graphic gelatin – gelatin for the graphic industry – will be most suitable. It is allowed to swell in water, and is then dissolved in the water-bath at a temperature not exceeding 65°C, with constant stirring. Higher temperatures should be avoided, because the gluten present in gelatin could decomposed; the chrome-gelatin coat would remain water soluble even after exposure to light, which, in turn, would cause errors during developing. Care should be taken on dissolving the gelatin that no air bubbles are formed in the solution, because otherwise the light-sensitive coatings may become porous. It is, therefore, advisable to add a defoamer, but the defoamer addition should not affect the gelling properties of the chrome gelatin.

Ammonium bichromate, potassium bichromate, or sodium bichromate can be used as sensitizers.

The photosensitivity of the light-sensitive coat is influenced by these sensitizers in the stated sequence. Ammonium salt produces the best effect. If too much bichromate is added, the coating may become brittle.

The washing-off properties of the chrome gelatin which has not been exposed to light are promoted by adding 5–10 g glycerin per kg of light-sensitive solution; but, at the same time, the drying subsequent to the coating process is also slowed down. It is, therefore, better to use a chrome gelatin solution which does not contain glycerin, and to treat the exposed screens with glycerin before they are developed.

An addition of 5 g/kg zirconium oxide as catalyst will enhance the reactivity of the chrome gelatin coating. If pigments are added, such as titanium white, adhesion

Guide Recipes (Grains per Liter) for the reparation of enforce Gerain ruste						
Substances	Recipe 1	Recipe 2	Recipe 3	Recipe 4		
Gelatin, dissolved in	170	90	80	100		
Water	450	510	580	600		
Zirconium oxide	5	-	-	5		
Dispersed with water	45	-	-	45		
Ammonia 25%		10	8	10		
Glycerin	8	-	8	-		
Defoamer	-	5	4			
Kaolin	-	90	-	-		
Titanium dioxide	-	-	80	-		
Water	160	100	-	-		
Ammonium dichromate	45	15	18	20		
Water	277	120	122	220		

TABLE 6.1

Guide Recipes (Grams per Liter) for the Preparation of Chrome Gelatin Paste

to the gauze is improved. Gelatin solutions are sensitive to attack by bacteria and should therefore not be stored for any length of time.

The chrome gelatin can be prepared in accordance with the following guiding recipes (Table 6.1), preferably in subdued daylight or in darkroom light.

Generally, the other additions are mixed with the gelatin solution in dissolved or pasted-up form, the bichromate being added last, after the mixture has been filtered through finely meshed gauze.

6.5.13 CHROME-PVA

When products are used which are based on polyvinyl alcohol, or if photosensitive lacquers based on silver halide are employed, the working instructions of the manufacturers should be closely followed, as these products can differ from each other in their composition and performance. For this reason, the following recipes for chrome/polyvinyl alcohol should be considered guide recipes which may must be modified as per commercial products.

Polyvinyl alcohol solution (10%)	910 g
Ammonium bichromate solution (22%)	90 g
	1,000 g
PVA emulsion	
Polyvinyl derivative emulsion (20%)	700 g
Ammonium dichromate	40 g
Water	260 g
	1,000 g

6.5.14 PVA Solution

The solutions and emulsions based on PVA are insensitive to bacteria, and can be stored for an almost unlimited time, provided the dichromate addition is made only just before the solution is used. The ready light-sensitive solution is then filtered through a finely meshed fabric (gauze).

The PVA light-sensitive coatings are more elastic and will adhere better to the gauze than chrome gelatin. For this reason, polyvinyl preparations are particularly suitable for subsequent lacquering on polyamide fiber and polyester fiber gauzes. The exposed areas of the light-sensitive coating are practically insoluble in water, which facilitates the production of sharp images.

6.5.15 APPLICATION OF THE LIGHT-SENSITIVE COATINGS

Coating of the gauze or of a lacquer coat which has already been applied, is best done in a darkened room, or in a darkroom, in subdued vellow or orange-colored light. The air and the equipment used must be free from dust. Chrome gelatin is usually applied lukewarm $(30-35^{\circ}C)$, while chrome/polyvinyl preparations are applied cold or at ambient temperature with an angular or hollow doctor blade or with a soft brush; a centrifugal device can also be used. It is important to ensure a homogeneous, thin coating, and to avoid streaks, drops and bubbles in the coat. The thinner the light-sensitive coating, the finer or sharper is the reproduction of the image. As the coating thickness increases, the required exposure time during the copying process should also be increased, and with it the risk that the coat is detached from the gauze or from the lacquer coat during developing on account of insufficient light penetration on exposure to light. Moreover, the gelatin and adhesive coats tend to swell quite considerably due to their high water absorptivity. When the light-sensitive coating is too thick, there is a risk of adjacent areas touching and flowing in the swelled state, thus covering open areas of the design together as well. This flowing together is irreversible after drying, so that finer details of the pattern are lost.

After the light-sensitive coating has been applied, the screens are dried in a horizontal position in a light-proof drying chamber with circulating air of maximum 28–30°C. The air stream, however, should not hit the gauze directly. If the drying temperatures are too high, the coating can become porous, and it is possible that development after exposure is rendered more difficult due to hardening caused by heat.

It is essential to allow for good drying of the light-sensitive coatings, since they will otherwise not harden sufficiently when exposed to light, and will thus remain water soluble. Moreover, the screen lacquers in subsequent lacquering will not adhere sufficiently well. Some of the hardening reinforcement lacquers are very sensitive to moisture before hardening. For this reason, it will be useful to observe a sufficiently long drying period, or even to dry for a brief period at a high temperature or with infra-red driers, as a final drying operation. The fully dried and coated screen should be processed on the same day, as far as possible.

6.5.16 METHOD OF PRINTING USING LARGE-SIZE DIAPOSITIVES

Printing on sensitized coating may be done using large-size diapositives or the step-bystep method on the light sensitive coating. In both cases, it will be necessary to ensure close contact between the diapositive of the color separation and the light-sensitive coating of the screen to prevent the occurrence of undesirable reflections which would impair the accurate reproduction of fine details of the pattern. It is also very important to illuminate the diapositives uniformly during the printing or copying process.

In the method using large-size diapositives, the color separations are copied onto the screen with diapositives the size of a screen in a single exposure operation. To obtain accurate results, it will be necessary to mark the glass plates of the copying devices, as well as the screens, and to provide for an accurate alignment of these marks when adjusting the diapositive and the screen.

Large copying equipment (Figure 6.12) is required for the method using largesize diapositives (2). Such copying equipment, which can be prepared with relatively simple means, includes a thick glass plate (1), a support block (4) and a suitable light source (6). The support block is somewhat smaller in length and width than the inside of the screen, but slightly higher than the sides of the screen frame kept on table (5). It consists of a plywood plate reinforced by traverse bars. A woolen felt or a soft foam or foam rubber plate of 10–15 mm thickness is placed on the block.

For the exposure to light, the screen (3) is placed over the support block in such a manner that the coated side faces upwards. The large-size diapositive is then fastened with a strip of transparent viscose sheet, coating facing coating. The glass plate is then placed on top, and is weighted, if necessary, by suitable weights. The soft support ensures a good contact of the diapositive with the light-sensitive surface. After these preliminary operations, the exposure to light (6) is affected with a light source which is suspended above the copying device.

Apart from this and similar copying equipment with the light source placed above the device, there are also other variations where the light source is below the copying table. There are also movable copying devices in vertical positions which can be swiveled around, and where the lamps are mounted sideways.

Vacuum copying frames are also often used. In these frames, the air is suctioned off, so that a very close contact between the diapositive and the light-sensitive coating is obtained.

The choice of the light source depends on several factors, including the technicalities connected with the reproduction, as well as the type of light-sensitive coating employed. In contrast to chrome gelatin, polyvinyl alcohol and related products

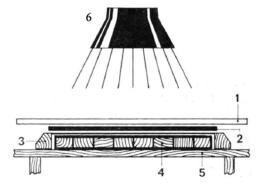


FIGURE 6.12 Light exposure machine for screen making.

require a light source which is rich in short (ultra-violet) waves. Arc lamps of 30–100 amps, especially spot light three-phase lamps, are suitable as light sources, but mercury vapor lamps and incandescent lamps, as well as fluorescent lamps and neon tubes, are also used.

To prevent undesirable reflections, the distance between a spot light lamp and the diapositive should be at least equal to the diagonal length of the diapositive. If horizontal copies are made with arc lamps, it will be necessary to provide for an ash trap placed below the arc lamp. If chrome gelatin coats are employed, even incandescent lamps of 500 watts each will be sufficient; however, they have a very low proportion of ultra-violet light, so that long exposure times will be necessary.

Powerful photoflood lamps will be better. Incandescent lamps of this type, as well as mercury vapor lamps, which require only short exposure times, develop intense heat, which can cause thermal hardening of the light-sensitive coating even in those areas which are protected against light, due to the excessive temperature increase. This can be avoided by providing for satisfactory ventilation. Fluorescent lamps have the advantage of a relatively low temperature at their surface, so that the distance between the lamps and the copying table can be reduced considerably.

Several factors are important in determining the exposure time, such as composition and thickness of the light-sensitive coating, the type of light source, its intensity and its distance from the copying table. Other factors include the transparency to light of the diapositive material, as well as the reflectance of the covering coat and of the screen gauze. The exposure time can be anything between 30 seconds and 10 minutes. It is controlled by means of light metering devices or control clocks.

The quality of the reproduction of a pattern, especially of fine details, depends not only on these factors, but also to a large extent on the degree of drying of the lightsensitive coating, and on the amount of heat developed during exposure.

6.5.17 STEP-UP METHOD

A color separation can be transferred to the screen in such a manner that several partial exposures of the light-sensitive coating are affected with a diapositive of a small pattern repeat. The diapositive or the screen is shifted by one repeat each time, and the other, already exposed areas or the not yet exposed areas of the screen, are carefully covered with material which is impervious to light. In the step-up method, it is most important to cover up the respective areas, so that no light can pass through.

6.5.18 WASHING AFTER EXPOSURE

The exposed portions become insoluble to water, but the unexposed portions remain unaffected. The screen is placed inside a water bath for 6 to 8 hours. Then the screen is placed under tap water. The soluble parts are washed out with water. Then the frame is dried. A final touch may be given with PVA solution to block the unexpected holes or to open unexpected blocks by a needle. Both sides of the screen are painted with green or any other color paint and the paint of the design portion is removed with any solvent from the other side of the screen and finally dried. The screen is now ready for printing.

6.5.18.1 Manual Screen Printing Process

At first, the design is chosen; the required numbers of screens are made or selected. The sample fabrics are printed in different color combinations called "matching". The printed samples are sent to customers for approval. The approved samples are taken in production schedule.

The bleached or dyed fabric, as the case may be, is selected and fixed on the table in creaseless condition under slight tension using adhesive or pins. In the manual screen printing process (Figure 6.13), a viscous color print paste is forced through the open areas of the screen with a flexible, synthetic rubber squeegee. The rubber blade, which is contained in a wooden or metal support, is drawn steadily across the screen at a constant angle and pressure. The screen carrying the outline portion of the design is first printed. Alternate repeats are printed with each color to avoid smudging. If the screen is too wide to allow one operator to reach all the way across it, two operators may work together, one on either side of the table. The pressures exerted by the two persons must be as similar as possible. The pegs or stops on the screen or stops on the side of the tables assist the workers in placing the screen at the proper place. Generally, the print paste is poured on the bottom side of the screen and two strokes are given with the help of squeegee to push the color through the screen onto the fabric to be printed. Then the screen is lifted and placed at an alternate peg (leaving one repeat in between). The operation is repeated up to the end, and then returned to the start to begin printing the alternate remaining repeats. Subsequently, all colors in the set are printed one after another. The printed fabric is then allowed to dry on the table.

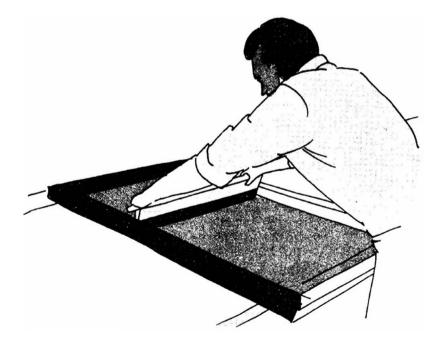


FIGURE 6.13 Manual screen printing.

The dried fabric is removed from the table and stored for a while before steaming. Steaming is carried out to fix the colors printed. Various types of steamers are in use. Boiler-fed star-agers are known to give the best results. However, some small-scale print-houses use various types of cottage steamers of varying capacities. The fabric is steamed for half-an hour to two hours depending on the steamer and the print-procedure requirements. A back-grey fabric is provided in between the layers of printed fabrics during steaming to avoid staining of the non-printed portions if they come in contact with the printed portions. Sometimes the fabric is wrapped in newspaper and steamed. The back-grey or the newspaper absorbs the excess moisture during steaming. The excess moisture, if allowed to be absorbed by the printed fabric, can result in the spreading of color from the printed areas and is liable to be rejected.

Certain dyes such as Rapid Fast colors do not require any fixing treatment. The color is developed by keeping the printed fabric in the sun for a few hours or hanging it overnight.

After fixation the printed fabric is thoroughly washed to remove the gum, residual chemicals and the unfixed dye. In small-scale industries, cement wash tanks are used. Initially a cold-water wash is given; this is followed by hot water or hot detergent wash, and a cold wash completes the operation. The fabric is finally dried in the open or on drying machines and sent for finishing. If the fabric is printed with pigments, instead of steaming, curing (dry heating) is carried out at 140–150°C for 3–5 minutes. No washing is necessary after pigment printing.

6.6 FUTURE TRENDS

Textile printing has passed several decades of its existence. We have passed from block printing and screen printing through roller printing and rotary screen methods, and finally into digital printing. All future developments will be in the field of digital printing. While no future development in the manual method of printing is expected, these methods will not be abolished and will continue to share an ever-decreasing portion of the printing market.

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7 Roller and Screen Printing Machines

7.1 INTRODUCTION

Textile printing is the process of applying color to fabric in definite patterns or designs. In properly printed fabrics the color is bonded with the fiber, so as to resist washing and friction. Textile printing is related to dyeing but in dyeing the whole fabric is uniformly covered with one color, whereas in printing one or more colors are applied in certain parts only, and in sharply defined patterns.

As the color pastes in printing are applied within a short span of time, printing can be done at a very fast rate. In printing, the color application must be done right the first time. Faults caused during printing cannot be rectified. It cannot be printed again and is liable to be rejected. To compensate this loss, printing production should be done at a very careful speed.

The primitive methods of printing like printing by painting, hand block printing and stencil printing have lost their potential, mainly because of their poor production speed. To compensate for losses due to high rejection, printers were in search of a high production machine. The outcome of those initiatives was the invention of the roller printing machine.

Engraved roller printing or roller printing is a modern continuous printing technique developed in the late 19th and early 20th centuries. The invention of roller printing is generally attributed to Thomas Bell, a Scotchman, who patented it in 1783, and who first employed it with practical success. The production rates in these machines were very high and they made hundreds of block printers jobless. Until the development of rotary screen printing, it was the only continuous technique available.

Screen printing, though slower in production, has many positive aspects which attract printers and consumers. To increase its production, flatbed screen printing machines came to the market, which may be automatic or semi-automatic.

Excluding modern digital printing machines, textile printing machines may be classified into three groups, namely:

- 1) Roller printing machines
- 2) Flatbed screen printing machines, automatic and semi-automatic
- 3) Rotary screen printing machines

Unlike dyeing machines, printing machines cannot complete the whole printing operation. Printing machines only apply color pastes onto to the fabric, which should be of short duration, followed by drying, steaming and washing to complete the printing operation. The speeds of these auxiliary machines are to be synchronized with that of the printing machine to avoid any back-ups between the two machines.

7.2 ROLLER PRINTING MACHINE

Roller printing requires a robust machine. Its construction is very heavy and its maintenance is time-consuming, intensive and demands expert operators. Figure 7.1 shows a line diagram of a roller printing machine. The pressure bowl (A) is a cast iron cylinder of a very large diameter with resilient covering (B), which locates centrally in the roller printing machine. The engraved copper rollers revolve in contact with the pressure bowl, which can accommodate 4–8 engraved roller assemblies along its circumference.

For the uniform transfer of color across the fabric width and along its length, a uniform cushion effect is to be maintained between the pressure bowl and the engraved roller. The cushion is obtained by rolling about 10–15 layers of a lapping fabric with linen warp and woolen weft around the pressure bowl. Any irregularity, including any ridge at the end of the lapping developed due to its imperfect matching with the first end, can cause a visible fault in a critical print. The cushion progressively hardens with use and requires change from time to time.

Generally speaking, the finer and more delicate the design to be printed the smaller is the amount of lapping required, and the harder or more compact in texture it must it be. On the other hand, for heavy designs, deeply engraved, a larger quantity of a soft, thick, openly woven quality lapping is necessary, especially in cases where the color is required to penetrate through to the back of the cloth or conversely, in other cases, where the great pressure of the printing rollers against the bowl that it is necessary to obtain a good impression of the pattern on a hard lapping would force all the colors (except the last) of a multicolor pattern too deeply into the body of the

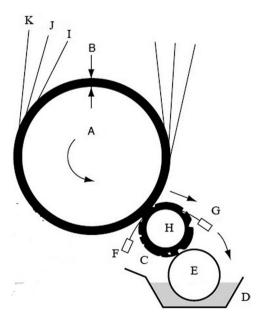


FIGURE 7.1 Line diagram of a roller printing machine.

cloth, and thus detract from their brilliancy, or "face", as it is technically termed. The durability of any quality of lapping is dependent upon many factors, but, so far as it depends upon the skill of the printer, it is a question of the manner in which it is wound upon the pressure bowl. If it is wound on too loosely, the enormous pressure put upon it during printing causes the several thicknesses to slide about over each other continuously, with the result that the constant grinding action thus set up rapidly wears them away, until eventually the lapping "breaks" or is torn asunder, and at once becomes utterly useless. As all good work depends, amongst other things, upon the lapping being of uniform elasticity and density throughout, and of a smooth, even, unbroken surface, it is of the utmost importance to guard against these qualities being destroyed by the passage of hard substances between the lapping and the rollers. Even a small nail or other solid body falling into the machine from the floor above, or during repairs, is sufficient to cause a vast amount of damage to both rollers and lapping – damage which frequently entails several hours of skilled labor to repair (Knecht, 1912).

Once all rollers (one roller per color) are engraved, it is loaded on the printing machine. On a multicolor roller printing machine, the printing rollers (C) along with their respective auxiliary equipment (namely color box (D), furnishing roller (E), color doctor or cleaning doctor (F) and lint doctor (G)) are arranged around the circumference of the pressure bowl (A) with minimum separation of the rollers.

The heavy copper cylinder (roller) (C) is engraved on its surface with the print design by carving the design into the copper. Copper is a soft metal, so once the design is engraved, the roller is electroplated with chrome for durability. Each engraved cylinder (C) is mounted on a steel mandrel (H). The machine must be of robust construction because pressures of several tons are applied, and each mandrel is driven by a single large crown wheel.

As the copper roller rotates, a furnishing roller (E) being partly immersed in a color box (D), transfers print paste (color) into the engraving as well as on the surface of the copper roller. The surface color is almost immediately removed by the steel blade known as the color doctor or cleaning doctor (F) as the roller moves forward. This doctor blade must be precisely ground, sharpened and set, at the optimum angle and tension, to leave the surface perfectly clean. Improper position of the color doctor tor blade may damage the surface of the copper roller. The doctor blade is to be sharpened from time to time when the cleaning of the roller surface is unsatisfactory. Engraved areas retain the color in parallel grooves and the doctor blade is "carried" on the crests between the grooves.

The sharpening or "getting up" of the cleaning doctor blade edge is possibly the most difficult and most important part of the machine printer's work; though an apparently simple operation, it demands for its proper performance an amount of skill only to be acquired by long practice, and an unerring judgment as to the kind of edge required for different classes of engraving. No definite rule can be laid down for the production of the "edge" best suited to a given style of work, for its quality depends not only upon the weight and scale of the engraving, but also upon the thickness and hardness of the doctor blade (Knecht, 1912).

After transferring its color to the cloth to be printed and before returning to the furnishing roller, the engraved roller is cleaned by a brass blade known as the lint

doctor (G). This removes any loose fibers that may have stuck to the surface of the roller. If not removed, these loose fibers could get trapped under the color doctor or cleaning doctor blade, where they could cause a color streak to be printed. Without the lint doctor, this color would be carried into next printing roller and cause rapid contamination; although some color contamination is unavoidable because the lint doctor will push a little color into the empty engraving.

Setting and maintaining the correct registration –fitting each color of the design relative to the others – requires an arrangement for separately rotating each roller a small distance while the drive to all the rollers is engaged. The original box-wheel device was elegantly simple but introduced a serious hazard to the printer's hands as it required the insertion of a rod, or tommy key, into a hole in a wheel rotating near the meshing drive gears. A safer device has been described by Gleadow (1981), who has also given a more detailed account of engraved roller printing. The main iron cylinder or central bowl (A) is fitted with a large gear. This gear fits into and drives each print roller. The main cylinder gear drives all of these parts.

To protect the lapping from color paste that had spread beyond the fabric edges or that passed through the printed fabric, an endless printing blanket (I) must be used. The blanket should be washed and dried continuously before returning to the point of printing. In addition, a back-grey (J) is used, between the blanket and cloth to be printed, to absorb color paste and to give greater resilience, if the resilience provided by the blanket is not enough. Back-grey is able to hold the excess color satisfactorily (for example, in fine grooves in a neoprene surface). In the printing of lightweight or knitted fabrics the woven back-grey is often "combined" with the fabric to be printed (K), using small amounts of a suitable adhesive. This helps to maintain dimensional stability of the fabric to be printed under the tension applied during printing.

Printing occurs as the fabric swipes print paste from the print roller and passes through the pinch point between the roller and the main cylinder. After color transfers by all the printing rollers, the printed fabric is separated from the back-grey and blanket and carried on to the drying section of the machine, avoiding any contact of the print face until it is somewhat dried. The printed fabric cannot be stored as such after printing and is to be dried continuously at a speed similar to that of printing.

It is necessary to correct the pattern fit from time to time during printing, because each roller will have a different effective circumference if there are significant differences in the area engraved or the pressure applied. Thus, the fabric will be stretched or allowed to relax to a minute degree between rollers and the fit of the design will gradually be lost. As already noted, combining with a back-grey can improve stability.

Good pattern fitting also requires a perfectly rigid fit of the engraved cylinder on its mandrel. To this end, the cylinders and mandrels are tapered and a forcing jack is required to mount and to remove the mandrel. In addition, a key, or "tab", on the inside of the cylinder engages in a slot along the mandrel.

7.2.1 ROLLER ENGRAVING

The print design development and color separation methods are identical to those used for the preparation of printing screens.

The printing designs are transferred to the copper rollers by photoengraving. Each roller, which (as in all methods) has previously been turned to size, polished and cleaned, is given an even coating with a photosensitive polymer solution (using a safe light). The coated rollers are exposed to light when the non-design portions get hardened, while the unexposed photosensitive lacquer in the design portion remains water soluble and washed out after exposure. The rollers are then put in chemical etching bath to remove copper from the areas that will hold color paste.

The essential steps in the process are as follows:

- 1) A master copy of the design is drawn, in outline, and a copy is made for each color.
- 2) Color separations are made by blocking out with opaque paint all the areas except those of one color.
- 3) The process is repeated for each copper roller assigned for each separate color in the design. At the same time, adjustments must be made for any overlap of colors required or allowance for color spread. These separations can now be made by electronic color scanners with appropriate computer software.
- 4) The negative color separations are converted into positive images (diapositives) on stable photographic film, and at the same time the ground lines are introduced by exposing through a grid of lines the required spacing. At the same time an outline around the solid areas must be obtained by using suitable spacers.
- 5) A step-and-repeat machine is used to produce a full-size positive film for each color that will cover the complete roller surface.
- 6) The complete set of films is assembled and checked by transmitted light to ensure perfect register.
- 7) Each film is accurately positioned and fixed and the image is transferred while the roller rotates under a suitable light. Within those areas that are exposed to light the polymer coating is altered chemically and becomes insoluble and acid resistant.
- 8) Unchanged polymer is washed off from the unexposed areas.
- 9) Etching is carried out in a bath of acid or iron (III) chloride solution, until it is clear that the adjacent V-shaped grooves have almost met each other (small pieces of polymer float off at this point). The number of grooves per inch, the scale, corresponds to the grid spacing and determines the depth of engraving obtained and the amount of print paste held. A scale of 55 gives a depth of about 0.11 mm (0.005 in) and may be suitable for a smooth-surfaced synthetic fiber fabric, whereas a scale of 35 gives a depth of 0.20 mm (0.008 in) and would be more suitable for a cotton fabric.

As a rule, a combination of line and stipple (dots) is employed for engraving gradated effects on copper rollers. Very light line engraving is not suitable, for the most delicate tones and heavy stipple engraving cannot be made to give an even shade over an extended space of solid color. But using the two styles together, very good effects are easily possible. For example, in expressing the idea of a flower in light and shade,

the darker parts of it and those in shadow would be engraved in line, to print as solid patches of color. From these, lines of diminishing thickness would be made to radiate, according to the shape of the petals, and finally dots (or stipple) of various sizes and depths, and at constantly increasing distances from each other, would be added between and beyond the radiating lines, to complete the scheme of gradation. Rollers engraved in this way, when printed in conjunction with superposed colors, yield wonderfully delicate effects of shading, but it is questionable whether the amount of work they represent is justified by the effect obtained. Artistically speaking, flat effects based on conventional lines with gradation suggested rather than realized and unmarred by fussy detail generally give more satisfaction.

7.2.2 Advantages

The advantages of roller printing are:

- 1) The roller printing machine is robust and very durable. A properly maintained roller printing machine may run 40–50 years.
- Roller printing is especially suited for printing large batches. Speeds can amount to approximately 100 meters per minute. Moreover, roller printing can be used for very fine printing.

For small batches, however, it is uneconomical. The set-up or changing times for printing between various batches are considerably high. The complete production process for each batch is quite high. The efficiency (cost-effectiveness) in machine utilization can drop to 50%. A long changing time is necessary for adjusting and preparing the machines for a new design.

3) Another advantage is the crush effect. Applying several colors in one drawing is achieved by using several printing rollers. Each printing roller applies one color. During the printing process, each color will be "crushed" by the following rollers as many times as there are colors left to be applied. Consequently, the color will be pushed more and more through the fabric to be printed. Many mixed colors may be obtained.

7.2.3 DISADVANTAGES

The disadvantages of roller printing are:

- A major disadvantage of engraved-roller printing is the limit to the fabric width that can be printed. The application of pressure to the mandrel ends inevitably produces some bending and the fabric edges tend to be printed more heavily than the middle.
- 2) In roller printing, it is essential to apply the light colors before the darker ones because traces of the preceding color can be carried forward into the following color. After a long run, such mixing of color may be unacceptable and the machine may have to be stopped for thorough cleaning.
- 3) Engraving the printing rollers is an expensive operation, which raises the price of the roller printing technique considerably.

- 4) Another disadvantage of engraved-roller printing is that the sequence of colors printed cannot be chosen arbitrarily, because of the color contamination problem mentioned earlier. The pale colors should be placed early in the order, with the stronger ones at the end. Sometimes it is necessary to start by printing a dark color (for instance, a black outline) to obtain the required depth when one color falls on another. In such a case a plain roller may be inserted after the dark one, and a colorless paste used with it to reduce the contamination of the next color.
- 5) Another disadvantage is the time lost in pattern changing, due to the need to handle and difficulty in accessing the heavy rollers and associated accessories.
- 6) Effective printing time is often less than 50% of working time, and short runs reduce this dramatically. Roller weight was reduced by using cast-iron cylinders with an electrodeposited copper plating, and damage to roller surfaces is reduced by chromium plating.
- 7) Unlike screen printing, deep colors are difficult to obtain. There may be a reduction in color strength of up to 50%.
- 8) This method is not economical for short runs of fabric.
- 9) It is difficult to produce blotch designs by this method unless printing is carried out by the discharge style.

7.2.4 DEFECTS OF ROLLER PRINTING

Various defects that occur during roller printing are listed as follows.

7.2.4.1 Scumming

Scumming is a term applied to the effect produced by the insufficient cleaning of the unengraved smooth surface of the printing roller. As a result, the whole surface of the cloth is soiled by a film of one or more colors. Scumming may arise from any one of the following causes:

- (a) A rough doctor edges.
- (b) A badly adjusted doctor, the edge of which does not rest upon the roller sufficiently sharply to scrape off the superfluous color.
- (c) A badly faced roller that is, one with a rough surface which retains enough color, after passing under the doctor, to soil the piece of cloth in those parts which ought to remain unprinted by it.
- (d) Defective color, which either obstinately resists the cleaning action of the doctor or abrades the polished surface of the roller, or destroys the smoothness of the doctor edge by acting upon it chemically or physically. Strong basic colors, colors containing much acid, badly ground pigment colors and those too, containing a large amount of solid matter or strong alkali, are all liable to act detrimentally in one or other of these ways, and their preparation, therefore, demands the utmost care. In the case of printing pastes made up with energetic oxidizing or reducing agents, and with strong alkaline dyes, it is frequently necessary to prepare the cloth

with some substance capable of neutralizing the action of the thin film of color paste, which always remains on the roller, even when the machine and color are in the best possible condition. Re-polishing of the roller, re-sharpening of the doctor or modifying the composition of the color and re-straining it are all remedies for "scumming" that are applied, according to the circumstances under which they occur.

7.2.4.2 Scratches

These may be caused in several ways, but they are usually due to gritty particles (and/or metal) in the color, which cut into the surface of the roller deeply enough to show themselves when the goods are fully developed. Scratches are repaired by burnishing.

7.2.4.3 Snapper

Large, ugly-looking double stripes of color running up the piece are caused by some foreign substance getting under the doctor edge and lifting it off the roller, thus permitting a large amount of color to pass and to transfer to the cloth in the form of a smudgy stripe. "Snappers" may be either long or short, depending on whether the obstruction gets jammed between the roller and doctor or works itself loose almost immediately; in either case it is advisable to stop the machine, to wash both doctor and roller, and to send the color to be strained afresh. One of the most common causes of "snappers" is loose threads from the cloth escaping under the "lint doctor" and then being carried up with the color under the "cleaning doctor", which they lift and create the defect. Bits of dried color, pieces of starch that have not been mixed improperly and other hard bodies are all likely to give rise to "snappers" if they are allowed to remain in the printing color.

7.2.4.4 Lift

These are much like small "snappers", but they usually occur at regular intervals on the cloth, although they are sometimes veritable snappers, caused by the passage of a minute particle of grit under the doctor. When they recur at regular distances, corresponding to the circumference of the roller, they will invariably be found to be caused by a particle of steel that has become embedded in the roller, and which, by projecting a little, lifts the "doctor", every time it passes under it, and so allows a small quantity of color to remain upon the smooth, unengraved surface of the roller – color which, of course, is transferred to the cloth.

7.2.4.5 Streaks

Streaks consist of fine lines or series of fine lines running along the piece in a direction more or less parallel to its selvedge, and they may result either from a scratch on the roller or from a snip in the doctor. Both scratches and snips are mainly caused by grit in the color, and not infrequently by the steel filings that have escaped removal when the doctor edge was sharpened. A "doctor streak" is easily distinguished from a scratch in the roller by its wavy appearance, which is due to the "traverse" motion of the doctor; streaks arising from scratches in the roller are always straight, unless it happens that the offending particle of grit sticks on the doctor, and is carried to and fro with it, thus cutting an undulating line on the roller. As a rule, a scratch of this latter description forms a broken line or "streak", whereas a snip in the doctor gives a continuous line throughout. Streaks can only be remedied by either polishing the roller or re-sharpening the cleaning doctor.

7.2.4.6 Scrimp

These and "doubled edges" are simply creases in the cloth which pass through the machine, and, in preventing the color from reaching the underlying parts of the cloth, show up as white places in the finished goods. As a rule, good "scrimp rails" of corrugated brass are all that are necessary to smooth out and stretch the cloth, but occasionally fine creases that have been "dried in" on the drying machines after bleaching, resist all attempts at removal in this way, and the only thing to be done in such cases is to wet out the cloth and re-dry it, either over the ordinary drying cans or on a stentering machine.

7.2.4.7 Uneven Printing

Uneven distribution of color takes place under many different conditions and manifests itself in various ways, all of which may be accounted for by some defect in the cloth, the rollers, the color or the working of the machine. If light, granular looking, irregularly shaped patches are developed during the operations of steaming or drying, their occurrence may be put down in most cases to the presence of lime left in the cloth during the bleaching. Lime stains occur at irregular intervals, and are easily identified.

The high fixed cost of copper rollers, expense of engraving process, long maintenance time during color and design change, and possible distortion of fabric during printing have led to its reduced use, now being less than 5% of the worldwide textile printing market. The fine design detail possible with this technique has always been its main advantage.

7.3 SEMI-AUTOMATIC SCREEN PRINTING MACHINE

In manual screen printing, alternate repeats are normally printed along the full length of the table and then the intermediate repeats are filled in. This allows time for the print paste to penetrate into the fabric and partially dry before the frame falls on the next printed area. Once all repeats are printed by the first screen, the second screen is introduced to print the second color. The manual process has been semi-automated by mounting the screen in a carriage and driving the squeegee mechanically across the screen. In these machines manufactured by M/s Zimmer, the rod squeegee is rolled across the screen by means of a moving electromagnet under the blanket. Long tables, typically 20–60 m long, are used, and some provision is usually made for drying the printed fabric. Semi-automated flat-screen printing is still very popular where the scale of production is not large, or where capital investment is limited. In both manual and semi-automatic flat-screen printing all colors are printed one after another allowing time for drying, which means that the situation approaches "wet-on-dry" printing. Hence, sharper results can be achieved than is possible by printing all the colors in more rapid succession ("wet-on-wet").

The production rates of manual and semi-automatic screen printing are very low. In order to increase the speed of flatbed screen printing, it was necessary to devise a method of printing all the colors simultaneously. Unfortunately, flatbed screens are not suitable for a truly continuous printing process, and in all automatic flat-screen printing machines the color is applied through the screens when the fabric is stationary.

7.4 AUTOMATIC SCREEN PRINTING MACHINE

In a typical automatic flat-screen machine, all the screens for a specific design (one screen for each color) are positioned accurately along the top of a long endless belt, known as a blanket. A machine intended to print traditional furnishing designs might have space for 15 or more screens. The width of the gap between the areas printed by any two adjacent screens may not be a whole number of lengthways design repeats. This need not necessarily be the same as the lengthways screen repeat, as there may be several design repeats per screen repeat; for example, where there are three design repeats per screen repeat, the gap between adjacent screens need only be one third of a screen repeat.

The endless blanket is coated with thermoplastic adhesive. Such adhesives, often based on acrylic copolymers, can withstand the washing necessary to remove excess print paste without becoming detached from the blanket. Their permanence is limited; however, replacement being required after perhaps two weeks' printing, and permanent thermoplastic adhesives have proved more satisfactory. These adhesives are coated on to the blanket and are only tacky when heated. Heat can be applied either directly to the adhesive layer or to the fabric in order to achieve the required bond. Such thermoplastic adhesives often remain serviceable during the printing of several hundred thousand meters of fabric.

When the fabric comes in contact with the blanket with the help of a hot metal at the entry end, the adhesive gets tacky and the fabric get stuck to the blanket. The fabric moves along with the blanket in an intermittent fashion, one screen-repeat distance at a time. All the colors in the design are printed simultaneously while the fabric is stationary; then the screens are lifted and the fabric and blanket move on. When the fabric approaches the turning point of the blanket, it comes in contact with another hot metal blade. The adhesive again becomes tacky and the fabric is pulled off and passes into a dryer. The soiled blanket is washed and dried during its return passage on the underside of the machine.

7.4.1 SQUEEGEE SYSTEMS

In manual screen printing, the printing paste may be spread across the screen either along the length, or across the width. The latter has been used more, possibly because this was the tradition for manual printing narrow fabrics, but it also has the advantage that no pressure is exerted on already printed areas at the end of the stroke. One, two or more passes of the squeegee can be made as required. The two most popular squeegee systems are described as follows.

7.4.1.1 Double-Blade Squeegee

This system is illustrated in Figure 7.2. A pair of parallel rubber-blade squeegees is driven across the screen with the print paste in the gap between them. Only the rear squeegee makes contact with the screen, the leading squeegee being raised slightly above it. When the next stroke is made, the leading squeegee for the first pass becomes the rear one for the reverse direction. Figures 7.2(a), 7.2(b) and 7.2(c) display the double blade squeeze in the Stork (Holland) screen machine for the movement of the squeeze back and forth along with the color paste.

The double-blade arrangement is simpler to construct than one utilizing a single squeegee that must be lifted over the pool of print paste at the end of each stroke, although this type is found in some modern semi-automated machines.

7.4.1.2 Magnetic-Rod Squeegee

A completely different approach was adopted by Zimmer, who invented a rolling-rod squeegee moved by an electromagnet, driven intermittently under the blanket. This type of squeegee is used in Zimmer flat- and rotary-screen printing machines, except that the electromagnet is stationary in the latter case. In fully automatic flat-screen machines the rod rolls in the lengthwise direction and only one passage is usually all that is required for adequate cover and uniformity. The diameter of the rod is usually small enough to allow print paste to flow over and round it at the end of a pass. It is clear that screen distortion and wear are less where rolling rods, rather than rubber-blade squeegees, are used.

7.4.2 INTERMITTENT MOVEMENT OF THE BLANKET

The biggest problem of flatbed screen printing machine is the intermittent motion of the blanket; the blanket should be stopped while the screens carry out printing operation (i.e., the flow of print paste into the screen followed by the distribution of the paste throughout the design area of the screen). Once the printing operation ends,

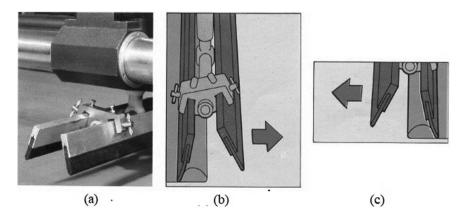


FIGURE 7.2 Double blade squeeze.

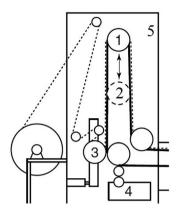


FIGURE 7.3 Compensator.

the blanket start moving for one screen repeat unit and stops again. High precision is required to maintain this movement accurately.

Buser, a Swiss manufacturer, has introduced an ingenious method of overcoming these difficulties which enables a blanket to move continuously on the return passage under the machine and in the feed-in unit. Guide drums at both ends act as compensators to allow the simultaneous, intermittent and continuous running of the blanket.

It was discovered at the development stage that controlled movement of the blanket could not be provided simply by a motor-driven roller at one end of the machine. The blanket tended to slip and overrun, and a more positive control of the movement was required. Stretching of the long rubber-coated, laminated neoprene blanket also introduced inaccuracies. Some early machines incorporated a continuous metal strip along the edges of the blanket to reduce its extensibility and provide accurate edge location, but modern machines more often employ a series of electromagnetically or hydraulically operated clamps which grip the edges and move the blanket precisely one repeat distance without stretching it. The drive for the forward movement is usually hydraulic.

Figure 7.3 shows a compensator to deal with the blanket movement. The continuous movement of the blanket is made stationary intermittently by moving the blanket up and down with the help of a roller moving up and down in two positions 1 and 2. When the blanket is required to be stationary, the roller moves upward, the rubber blanket is pulled up and its forward movement stops. After a specified time, the roller is brought down to position 2, the blanket relaxes and due to its endless nature, it is pulled forward for the specific length and then the roller automatically starts moving up, stopping forward movement of blanket. The fabric to be printed (shown as dotted line) is pressed with the blanket by the pressure roller 3 (Miles, 2003).

7.4.3 DISCONTINUITY OF GUMMING AND WASHING

When water-based gums are being used, a line of excess gum is likely to be produced each time the blanket stops moving, which in extreme cases may affect the levelness of the print. The device (4) is used for continuous application of adhesive to the blanket (Figure 7.3). The blanket, on its return passage, will also receive an irregular degree of washing.

7.4.4 CONTROL OF FABRIC SPEED THROUGH THE DRYER

After the fabric has been printed it passes through the dryer, often being supported on a conveyor belt. Some machines also allow for the fabric to be supported between the end of the blanket and the entry to the dryer, particularly if the entry point is much higher than the blanket. Here also the intermittent movement may cause problems of variable stretching and over-drying. Ideally the fabric should move through the dryer at a constant speed equal to the average linear velocity of the blanket, but this is not always possible. The limits between which the fabric can be lifted off the blanket are the end of the last screen and the end of the top linear surface of the blanket. One technique (Figure 7.4) often employed to maintain the fabric within two limit switches A and B. The movement of the fabric is stopped by a limit switch controlled by light beam "A" when it makes a specific angle between the dryer and the conveyor belt. When the fabric reaches the light beam B the drive starts again. Alternatively, a single diagonal beam can be used (Miles, 2003).

7.4.5 PRODUCTION RATE

The production rate depends primarily on the time interval during which the fabric is stationary. The speed at which the blanket is advanced is much less important, as the blanket is in movement for considerably less time. Speed of advance must be restricted, as at high speed the system would have so much forward inertia that there would be a tendency for the fabric to overrun the blanket. The other factors that play an important role in the determination of the overall production rate are listed to follow.

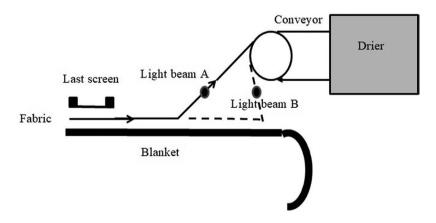


FIGURE 7.4 Arrangement for intermittent movement of fabric to drier.

7.4.5.1 Number of Squeegee Passes

Sometimes more than one pass of the squeegee is required to achieve uniformity and adequate penetration, especially in blotch areas. This applies particularly to thick fabrics and those with irregular surfaces. In some machines the squeegees can be used to make a stroke while the screens are in the raised position (known as a "flood stroke"). This fills the mesh in the printing areas of the screen with paste before the screen touches the fabric, and more color is applied with the second stroke when the screen is lowered.

7.4.5.2 Repeat Size

Where the squeegee movement is widthwise, the greater is the lengthwise repeat and the blanket moves forward further at each pass; consequently, the printing speed is greater. The effect is less marked if the squeegee movement is lengthwise, as the squeegee will take longer to move along the screen where the repeat distances are large.

7.4.5.3 Efficiency of the Dryer

If the dryer is short, or if the temperature in the dryer is too low, the printing speed will have to be reduced in order to ensure that the printed fabric is adequately dried. This is particularly critical for designs in which a high proportion of the total area is printed (high percentage cover).

7.4 6 PRINTING FAULTS

Some faults in automatic flat-screen prints are due to poor registration (misfitting of the colors in the design); others are associated with screen frames falling on wet areas of the printed fabric.

7.4.6.1 Registration

It has already been pointed out that accurate movement of the blanket exactly one screen-repeat distance, each time it advances, is essential for the correct registration of the colors in the design, and that inadequate adhesion of the fabric to the blanket will cause local misfitting. Another cause is screen distortion due to excessive drag exerted by the squeegee. This is especially likely where rubber-blade squeegees are used and the design contains large repeats.

7.4.6.2 Frame Marks

When printing consecutive screen repeats, the screen frame inevitably falls on the part of the area most recently printed and may leave an impression. This is a particularly difficult problem for blotch screens where large amounts of print paste are applied. The problem is reduced in hand screen and semi-automatic screen printing by printing alternate screen repeats and then moving back to fill in the gaps, but this is obviously not possible in automatic machines, since in these the movement of the blanket is always in the same direction. On the other hand, it is a more serious problem in fully automatic screen printing as the printing speed is much higher, so that there is less time for intermediate drying or penetration of the fabric.

One technique used to avoid this fault is known as off-contact printing. The screen frame is lowered to a point only just above the blanket, the gap being so small that,

as the squeegee passes and stretches the screen fabric, the printing area of the screen makes contact with the fabric being printed.

A related problem is the crushing of colors by succeeding screens, which is most serious when the screens are close together and the printing speed is high. Offcontact printing obviously reduces the problem and the screens should be spaced out as much as possible. If necessary, the printing speed is reduced. Printing a blotch as the final color is also normal, to avoid this effect.

7.4.6.3 Splashing

When screens are lifted straight upward after printing with the screen remaining horizontal, print paste on the fabric in the space below the screen can often remain in contact with the screen momentarily. As a result, a little amount of paste is lifted and splashes back onto the fabric. This can be avoided, or at least reduced, by lifting the screens on one side just before the other. Inevitably, however, this may slow down the overall printing speed a little.

7.5 ROTARY SCREEN PRINTING MACHINE

Rotary screen printing is a continuous method of printing in which perforated cylindrical screens are used to apply color. Color is forced from the interior of the screen onto the fabric. Fully continuous printing is best achieved using cylindrical (rotary) screens and many attempts were made to form flat wire mesh screens into cylinders, despite the necessity of a soldered seam. When printing through a cylindrical screen with a seam, a line will show across the fabric once every cylinder circumference, unless the seam can be hidden within the design. This was the approach used in the screens manufactured by A.J.C. de O Barros for the Aljaba machine, first introduced in 1954 (Barros, 1966).

Wire-mesh screens are too open for printing purposes, and on the early Aljaba screens electrodeposited copper partially filled the holes. This process was later discarded, to be replaced by the use of an outer seamless woven nylon sleeve. Later still, in fact after the closure of the Aljaba Company, W. Sword introduced a new version of the wire-mesh screen, the Durascreen, in which the holes in the mesh were partially filled with a flexible polymer by electrophoretic coating. The same process can also be used on electroformed nickel screens, extending their life considerably, since the flexible polymer coating reduces the risk of creasing (Miles, 2003).

In the UK, the switch from copper roller printing was initially slow but then accelerated, the technique's share falling from 90% in 1960 to only 6.6% in 1992. In the same period, the output from rotary-screen printing grew from perhaps 1% of the total to 82.8%. Thus, the machine introduced in 1785 dominated the industry for some 160 years, but is now fast disappearing. The use of copper rollers is still important in the gravure method of printing in color on paper (Miles, 2003).

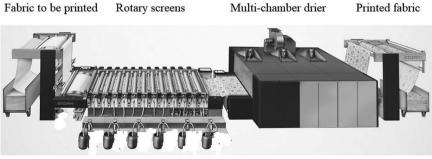
The invention of seamless screens of electrodeposited nickel was the really significant step which heralded the rapid expansion of rotary-screen printing. Peter Zimmer (Austria) introduced the galvano screen in 1961, and Stork (Holland) the lacquer screen in 1963. These screens soon proved to be superior, in many respects, to Aljaba screens. Between 1964 and the end of 1972, Stork sold 600 rotary machines throughout the world. The main features of the machine are (blog: https://textilehelp.org/):

- 1) Each screen is independently driven; printing paste is fed by special pumps individually to the different screens.
- 2) The print paste level inside the rotary screen is automatically and constantly controlled.
- 3) The transfer of the printing paste through the perforations of the screen onto the cloth is governed by specially designed squeegee blades.
- 4) The pressure of the squeegee inside the screen as well as the individual pressure and positioning of the different rotary screens can be controlled at will.
- 5) It is also possible to lift the screen automatically whenever the machine stops so that no stop marks are produced.
- 6) At the time of starting the machine again, the screens are lowered and start printing.
- 7) All screens fit in perfectly, independent of the movement of the fabric or the blankets so that a perfect fitting of the design is obtained at all times.
- 8) The speed of the machine can be adjusted from 10 to 100 m per minute.

7.5.1 CONSTRUCTION

- 1) The printing machine is provided with a feed arrangement, a selvedge alignment unit and a continuous gluing unit for gumming down the fabric.
- 2) The print paste is pumped into the screen as required and its level is regulated by automatic level controls.
- 3) For cleaning, each rotary screen can be dismantled and washed. Change of pattern can be achieved in about 3 minutes per screen.
- 4) A high efficiency washing and drying unit for the blanket is provided below the printing table. The washing unit consists of circular brushes with constant water feed and works only when the printing blanket is moving.
- 5) The drying unit uses hot air, the temperature of which is thermostatically controlled.

Figure 7.5 shows a schematic diagram of a rotary screen printing machine.



Containers carrying printing paste

FIGURE 7.5 Schematic diagram of a rotary screen printing machine.

7.5.2 SETTING-UP OF ROLLERS

The walls of seamless nickel screens are only about 0.1 mm thick. But those are strong enough to rotate freely provided they are put under lengthways tension. Light aluminum alloy end-rings are fitted to the ends of the screen; the plane of the roller and ring is set accurately at right angles to the axis of rotation of the screen. Notches in the end-rings fit into the mountings (heads) on both sides of the blanket and a turn of the screen locks it firmly in position. Tension is then applied by moving the head furthest from the pump outward. The height of the heads can be adjusted so that the bottom of the screen is either just in contact with the blanket or higher up to allow for the thickness of the material being printed. When all the screens are in position, squeegee assemblies and level controls are fitted, adjusted, and the flexible color pipes connected.

When starting to print a multicolored pattern the screens are adjusted while running in order to achieve registration of all the colors in the design. Several meters of fabric are wasted as a result. This problem has been overcome by the German machine makers MBK, who have introduced a laser screen registration system for accurate alignment of rotary screens prior to printing. A red helium/neon laser beam shines down the length of the machine, and the screens are adjusted until the beam shines through the pitch marks (Miles, 2003).

7.5.3 BLANKET AND SCREEN DRIVES

Some rotary screens are driven from both sides to avoid the danger of twisting and buckling. Correct fitting should be ensured even during speed changes, if there is a direct link between the blanket and screen drives, provided that the blanket does not slip on the driving rollers. The shorter blankets of rotary machines and their continuous motion substantially reduce the problems of extension and sideways movement often experienced with flatbed machine blankets. The blankets should have low extensibility. The fitting of patterns during an extended printing run is sometimes less than satisfactory, especially with wide fabrics or when printing pile fabrics or carpets. One explanation, put forward by Peter Zimmer, is that these materials exert a considerable drag on the screens so that they are pulled around slightly in advance of their correct position. Eventually, at a seam perhaps, the screens will spring back and the pattern registration will be affected. Zimmer claims to be able to overcome this problem by running the screens at a slightly slower speed than that of the blanket. The company M/s Stork has also introduced this facility into their most recent machine, which features independent speed control for each screen (Miles, 2003).

7.5.4 WORKING

- The fabric to be printed is placed under the printing section of the machine. Fabric should be under uniform tension to avoid any defect.
- 2) As the screen moves over the fabric, the printing paste is applied by a squeeze which forces the paste through the screen to the fabric.
- 3) After printing, the fabric goes to the drying section for drying using an oven. Finally, finishing, curing and washing is done.

- 4) The printing is usually affected on a conveyor blanket significantly shorter than the one used for flatbed printing.
- 5) In all, up to 24 colors can be printed using one screen for each color and it is possible to obtain speeds up to 100 meters per minute without any defect.

During a working shift of about 8 hours, it is possible to obtain a production of about 15,000 to 20,000 meters of flawless fabric.

7.5.4.1 Types of Rotary Screens

Nickel has been found to be the most suitable metal because of its high tensile strength, flexibility and good resistance to most of the chemicals used in textile printing. But nickel rotary screens are costly. Most of the rotary screen printers have their own nickel shell manufacturing unit so that they need not depend upon others for their requirements of nickel screen.

Rotary screens broadly are of two types:

- 1) Lacquer screen
- 2) Galvano screen

7.5.4.2 Lacquer Screen

Lacquer screens were developed by M/s Stork (Holland) in 1963 and then used by several manufacturers. These screens have uniformly spaced hexagonal holes arranged in lines parallel with the axis of rotation of the cylinder and offset in alternate lines, as in a honeycomb, for maximum strength. The walls of the holes are larger on the outside of the wall than on the inside. The open area, measured on the inside of the screen, varies between 9 and 13% of the total for the rotary screens used for textile printing.

The standard internal circumference of cylindrical nickel screens for printing textiles is 640.0–640.1 mm. A wide range of screen diameters are available in the market. However, this dimension depends solely on the diameter of the mandrel on which the screens are electroformed. But even the largest screens (1018 mm) will not provide as large a repeat as a large flat screen or a carpet loom. Peter Zimmer (Austria) solved the problem of large repeats by using a system of intermittent raising and lowering of screens. A particular color in the pattern might then be printed in sections by two or three screens. The design areas do not fill the complete circumference of the screens, the remaining blank portions being provided so that when the screens are in their raised positions print paste will not drip through them.

Lacquer screens are manufactured by electro-deposition of nickel onto a millengraved mandrel. The mandrel is a cylindrical steel roller which is coated with a thin layer of copper by electro-deposition and engraved with the required hexagons using a milling machine. The mill is a small, hardened steel cylinder with the hexagonal design standing out from the surface. It is pressed against the polished copper and moves along the length slowly while the mandrel and mill are rotated, producing a spiral pattern with no seam. The hexagon-shaped recesses are then filled with a polymer which acts as an electrical insulator, after which the copper surface is protected by nickel (or chromium) plating followed by a further filling in of the recesses up to the outer plating level. Nickel-plated mandrel is made inactive by coating with a thin layer of oxide with chromic acid, in order to prevent it from fusing to the nickel screen. It is then immersed in the nickel-plating bath where it becomes the cathode, while the anode consists of nickel lumps held in nylon bags contained in titanium baskets along the sides of the bath. The composition of the plating bath is patented; it may be nickel compounds like nickel sulfate or nickel sulfamate. Other components may be boric acid and an organic compound such as saccharin, which helps to reduce stress in the electrodeposited layer. When the nickel layer is about 0.1 mm thick the mandrel is removed from the bath and hosed down, and the nickel screen detached from the mandrel.

As the thickness of the nickel layer builds up it gradually bridges across the insulator and eventually the holes are blocked. This means that it is not possible to produce screens finer than 100 mesh (holes per linear inch) by this technique, and the finer the mesh the thinner is the wall. The most popular screen meshes are "60 mesh" for blotches and motifs and "80 mesh" for outlines and synthetic fabrics.

For the production of finer-mesh "electroformed screens" the screens are removed from the mandrel and then re-immersed in the plating bath – the so-called "electroless" process. Stork introduced lacquer screens known as PentaScreens, and more recently, NovaScreens.

The 125 mesh PentaScreen has a percentage open area similar to the original 60 mesh screen, and the 185 mesh the equivalent to the 80 mesh screen. The profile of each hole from inside to outside is rather different, being narrowest in the center of the wall, like that of an hourglass. With the new screens it is possible to print a line 0.12 mm thick, which is half the minimum width obtainable previously.

NovaScreens are a combination of high mesh counts and holes that are larger than in equivalent PentaScreens. This favors half-tones, and also allows printing with pastes with high pigment loadings, such as whites and metallics. NovaScreens are slightly thicker than PentaScreens, which makes them less subject to creasing.

The design is introduced onto the rotary screens by a method similar to that used for flat screens. However, the shape of the screens necessitates modifications in the details. A full-size (full-out) positive is usually prepared for rotary screens to avoid the need for multiple exposures of the screen on a step-and-repeat machine.

Stork introduced the annular squeegee for coating screens by hand with photosensitive polymer, starting at the bottom and moving upwards. Modern screen coating units, however, apply one thick layer of highly viscous emulsion, starting at the top and moving down. Melamine formaldehyde resin, polyvinyl alcohol and other polymers that promote good adhesion to nickel are used as the lacquers.

The coated and dried screen is placed on an inflatable rubber tube and the fullsize positive wrapped round it. The film is carefully positioned on the screen with the aid of the reference lines, using a sliding pointer attached to the exposure machine. This allows the other positives to be aligned correctly on their respective screens. Special care is taken that the junction is accurate, and in this respect greater precision is achieved if the join is nonlinear, as sideways slippage is thus avoided. The rubber tube is then inflated to ensure good contact between screen and positive and the assembly is rotated while the screen is exposed to an ultraviolet light source.

7.5.4.3 Galvano Screens

The other type of rotary nickel screen, the galvano screen by Peter Zimmer, is manufactured on a very different principle. The design is introduced at the same time as the nickel is electrodeposited. This means that the non-design areas are solid nickel instead of a uniform mesh filled with a thin layer of lacquer. They are, therefore, stronger and less susceptible to pinholes. A mandrel similar to that used for the manufacture of lacquer screens can be used for the preparation of galvano screens, but Peter Zimmer designed a thin, inflatable nickel tube, known as a matrix, to replace the mandrel. The matrix (or mandrel) is first coated with photosensitive polymer. A full-size negative of the color separation is required. This is wrapped round the hollow matrix together with a second film on which the required grid pattern is reproduced, and the matrix is inflated to provide close contact. The coated matrix is then exposed and washed in the normal way. At this stage the non-design areas and the supporting mesh in the design areas are free from polymer. Besides defining the design areas, the polymer also acts as a dielectric resist (insulator). The matrix is then mounted in a nickel-plating bath and the nickel screen built up in the same ways as for the lacquer screens. Bridging of the insulator is a more serious problem with galvano screens, and a nominal 80 mesh screen is the finest that can be reliably manufactured.

The lacquer screens are most suitable for narrow fabrics and fine patterns, while the galvano screens are beneficial for wide-width printing due to their higher strength, particularly in rigorous conditions such as those encountered in carpet printing. In these cases, the wall thickness is 0.35–0.4 mm, instead of the 0.08–0.1 mm used for textiles, and the mesh is much coarser.

7.5.5 HALF-TONE PRINTING

Half-tone printing (that is, a gradation of tones within one colored area) is a common feature in copper roller printing, but not easy to produce by screen printing. Half-tone illustrations for screen printing on paper are prepared with the aid of a cross-screen grid which breaks up continuous tones into rows of dots of different sizes, large dots for dark areas and small dots for paler areas. When half-tone positives produced in this way are used to prepare printing screens, interference patterns, known as moiré patterns, are likely to occur unless the angle of the positive relative to the printing-screen mesh is carefully adjusted (Miles, 2003).

7.5.6 LASER ENGRAVING

Laser light is highly monochromatic, polarized, coherent and powerful. The use of high-powered lasers for engraving screens is a development from their use for engraving rubber-covered flexographic printing rollers. Initially the process was restricted to lacquer-type rotary screens, carbon dioxide (infrared) lasers being used to burn away the lacquer. A thin, even coating of a non-photosensitive lacquer is applied to the screen, usually starting at the bottom of the cylinder.

The polyester mesh of flat screens would be burned away along with the lacquer by a carbon dioxide laser, and so a photosensitive lacquer is exposed to a computercontrolled argon ion laser (blue-green).

A typical rotary-screen laser engraving machine consists of 1,000-watt class 4 industrial lasers, sufficiently powerful to allow the machine to be employed for stripping all the lacquer off used screens so that they can be used again.

The laser requires supplies of nitrogen and helium as well as of carbon dioxide, and the infrared beam (10.6 µm) is passed from the generator down the length of the engraving unit. It is deflected at right angles by a mirror and focused by a lens onto the screen. Care is taken to remove all the degraded lacquer with a powerful suction and filter unit, so as to avoid contamination of the optical system. The coated screen, having been mounted in the engraving unit, must be held precisely in position while it is being engraved. A moving hardened steel guide ring with a diameter slightly larger than the screen runs in three roller bearings, which are mounted on the same carriage as the engraving head. When a screen is being loaded or unloaded the guide ring is concentric with the screen position. For engraving, the guide ring is moved off-center, away from the engraving lens. This brings the ring into contact with the screen under light pressure. As the screen is rotated the ring turns at the same speed, so there is very little friction between screen and ring, but it is sufficient to hold the screen securely in position. During engraving the ring moves with the carriage, in front of the beam (Miles, 2003).

7.5.7 MERITS/DRAWBACKS OF ROTARY SCREEN

The advantages of rotary screen printing are:

- 1) Highest production as compared to roller printing or automatic flatbed printing machine.
- 2) As many as 24 colors can be printed by this machine but 8 to 10 colors can be printed easily.
- 3) No joint marks in rotary printing.
- 4) Half tone effects and vertical lines can be produced successfully by this method.
- 5) The prints produced are free from smudging effect.

The disadvantages of rotary screen printing include:

- 1) The method is not economical for short runs of the fabric.
- 2) The cost of engraving of the screens is very high.
- 3) The size of repeat of the design is limited to about 65 cm.

In rotary-screen printing, continuous rotation of a cylindrical screen while in contact with the fabric ensures genuinely continuous printing. Print paste is fed into the inside of the screen, and during printing is forced out through the design areas with the aid of a stationary squeegee. Machines using rod or roller squeegees, such as those manufactured by Peter Zimmer (Austria) and Mitter, have been very successful in printing wider substrates, such as carpets. Rotary-screen machines have also been used to print paper for the transfer printing process (Miles, 2003).

7.5.8 SQUEEZE SYSTEMS

The squeeze systems in rotary screen printing are broadly of two types, namely:

- 1) Thin metal squeeze introduced by M/s Stork which again may be of one of the following two types:
 - a) Short squeeze
 - b) Long squeeze
 - With thin metal squeeze, the squeeze will bend more with increase in pressure. But due to rigidity of the plate, the area of contact and the transfer of color paste will not increase.
 - Figure 7.6 shows thin metal squeeze used in rotary screen printing short squeeze (Figure 7.6(a)) and long squeeze (Figure 7.6(b)).
- 2) With magnetic rod squeeze introduced by M/s Zimmer, color transfer can be changed by changing the rod. With a larger rod, magnetic force, and thereby, the penetration of color will be higher. One defect of this system is that a very small color pool can be maintained behind the squeeze because the squeeze rods are very small in size: 4 mm to 15 mm in diameter. Figure 7.7 shows rod squeeze used in rotary screen printing: small rod (Figure 7.7(a)) and large rod (Figure 7.7(b)).

In further developments, metal blade and magnetic-rod squeegees supported by air sacks (such as the Stork Airflow) are being more widely used for better control of squeeze pressure.

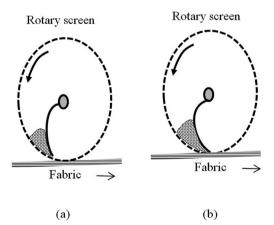


FIGURE 7.6 Thin metal squeezes for rotary screen: (a) short blade; (b) long blade.

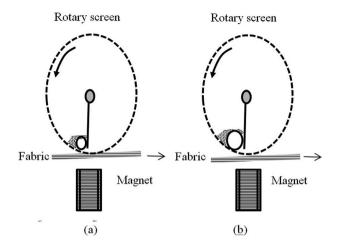


FIGURE 7.7 Magnetic rod squeeze: (a) small rod; (b) big rod.

TABLE 7.1 A Comparison of Three Types of Squeezes

Properties	Thin metal squeeze	Magnetic squeeze	Rubber squeeze
1. Penetration	Moderate	Good	Good
2. Evenness	Good	Excellent	Good
3. Relation between penetration and color transfer	Almost independent	Independent	Related
4. Control of color transfer while the machine is running	Not possible	Not possible	Possible
5. Workability with viscous paste	Moderate	Good	Good
6. Wiping off excess color paste	Moderate	Moderate	Excellent
7. Versatility	Moderate	Moderate	Excellent
8. Squeeze lift	Good	Excellent	Moderate

The wiping off the excess color paste can be best achieved by the rubber squeeze, but they are subject to wear and tear due to abrasion. The grinding of the rubber squeeze should be done after printing of about 1,00,000 meters of fabric.

The comparison of three types of squeezes is shown in Table 7.1.

7.5.9 SCREEN VARIABLES

Lomas and Short (1999) investigated the effects on print paste consumption of altering screen printing variables in rotary- and flat-screen printing. An analysis of fabric consumption factors for a 100% coverage screen on a number of different substrates is reported. Average factors were calculated for each substrate and the uptake variations brought about by altering squeegee size, magnet pressure, mesh size, machine speed and print fall-on recorded. Paste viscosity remained constant throughout the investigation. The fabric factors, together with screen open area percentages available from the laser engraver, are used to predict the amounts of paste required to print a designated length of fabric. A laboratory Zimmer magnetic rod printer was used under controlled conditions to draw comparisons with the bulk printing results.

7.5.9.1 Sustainable Production

Joost Smits, Managing Director Textile at Stork Prints, stated that activities to reduce the impact of the printing process can be grouped into five distinct categories:

- 1) More sustainable consumables like screens
- 2) Greater process efficiency
- 3) Longer equipment lifespan
- 4) Adherence to strict legislation
- 5) Fundamental R&D into sustainability-related issues

Stork screens are also of a special shape and size so there's less mechanical force required to push the printing paste through onto the substrate. A major advantage of this unique feature is that considerably less nickel is deposited on the textile being printed because there is less wear and tear. The screens also last longer as a result.

An average printing line has a nominal power rating of approximately 75 kW, most of which is required for the drying process. A relatively high temperature must be maintained inside the drying chamber, and the various vapors emitted as the textile dries must be extracted. Stork drying systems use a radial extraction technique which removes moisture while leaving more warmth in the chamber. This uses approximately 25% less energy, and also means printers can produce more quickly because the process is faster.

7.5.9.2 Calculation of Predicted Consumptions

The amount of paste required to print a specific fabric with a given screen was calculated using the formula (Equation 7.1):

Amount of paste (kg) =
$$(lw \times FO) + c(1)$$
 [Equation 7.1]

Where l = fabric length, km w = fabric width, m F = consumption factor O = screen open area, % c = constant of 10 kg (to account for screen and pump wastage).

Thus, for example, 145 kg paste would be required to print a 2 km length of 1.5 m wide plain cotton fabric using a 60% coverage screen.

Once reliable consumption factors were established the information was stored in the computerized records on the paste autoweigh system. This was done when entering recipes for a new design and consisted of entering the calculated consumption factor, followed by the open area percentage for each screen. A paste consumption factor was then given for each screen before the initial print run and this removed the possibility of inaccurate estimates for paste consumption.

7.5.9.3 Evaluation of the Accurate Paste Autoweigh System

This was done when entering recipes for a new design and consisted of entering the calculated consumption factor, followed by the open area percentage for each screen. A paste consumption factor was then given for each screen before the initial print run and this removed the possibility of inaccurate estimates for paste consumption. As there are many influencing variables, an accuracy of $\pm 20\%$ in the predicted amounts was deemed a success. Results indicated that the initial trials were successful in producing predicted consumption values similar to the actual quantities of paste used, and usually to within $\pm 15\%$.

A variable, the amount of "fall on" or overprint, became noticeable. If a color falls on an area of the design already printed with another screen, the amount of paste used will be lower, as the free space in the fabric able to accommodate the print paste is already occupied.

The print paste used was a pigment paste of low shade depth, produced on the Autoweigh system at a regulated viscosity of 8.5 Pa s. The magnet pressure on the machine was varied, on a scale of 2–6. The speed control ranged from 10 to 100% with the maximum setting of magnet bar speed being approximately 16 m/ min. One squeegee stroke was used for all the trials.

The variables chosen for evaluation were as follows:

- (a) Magnet bar (squeegee) size
- (b) Screen mesh count
- (c) Magnetic pressure (force)
- (d) Machine speed
- (e) Fall-on effects (50 and 100%)

The results of the open area consumption trials suggested that certain variables had an effect on paste usage whilst others had little or no effect. In particular, the level of the magnet pressure appeared to have no bearing on consumption.

Variations caused by higher or lower machine speeds were difficult to assess, as all padded (100% coverage) designs tend to be run between 35 and 45 m/min. However, a small number of designs which ran at speeds close to 50 m/min resulted in a decrease in consumption of between 10 and 20% compared to the average for that fabric. This indicates that the time dependent loss in paste uptake due to increasing speed exceeds the effect of a reduction in viscosity due to an increase in shearing force.

As the printing speed rarely dropped below 35 m/min it was not possible to sufficiently test the theory of Ferber and Hilden that a change in speed at low speeds had a greater influence on consumption than at high speeds.

Assessment of the influence of mesh size involved similar problems, as the majority of 100% coverage screens. used were 125 mesh Penta screens. A limited number of 155 mesh screens were used, resulting in a small drop in consumption of 10–15%. No noticeable difference was recorded in the 60 mesh screens.

The size of the magnet bar also affected the paste consumption. Most of the print runs were carried out using a 13 mm diameter roller squeegee, yet those run with a 10 mm bar resulted in reduced consumption of up to 25%. Similarly, a 15 mm bar created increased consumption of up to 25%. In other words, the angle of the squeegee bar to the screen and its impact on the downward force on the paste wedge had a major influence on the level of paste application.

The figures recorded for paste consumption in the commercial print trials only gave a general indication as to the effect of different variables on paste consumption, as there were noticeable exceptions to the above generalized observations. These variations were attributed to a number of factors, including:

- (a) Amount of fall-on in the design
- (b) Number of samples taken
- (c) Fabric construction variations (particularly in the nonwoven fabric)
- (d) Fabric absorbency variations (only a small number of fabric runs recorded a low consumption that could be attributed to poor absorbency)
- (e) Amount of paste remaining in the color supply system at the end of the run

The above parameters are to be varied for a successful print.

The high fabric consumption factor (1.0) recorded on the polyester/viscose fabric can be attributed to the fabric thickness and very good absorbency. The latter is due to the hydrophilic nature of the viscose component. The greater percentage reduction in paste uptake of the more compact woven fabrics, compared with that of the more open knitted polyester structure, suggests that a greater number of interstitial spaces within the former were fully occupied or contained more paste than those contained within the latter.

Some conclusions drawn by Lomas and Short (1999) are as follows:

- Increasing the squeeze bar size from 8 to 13 mm resulted in the greatest variation in paste consumption, an increase of 36% from the standard.
- An increase in the screen mesh count from 77 (threads/cm) to 90 resulted in a 13% reduction in paste consumption. This suggests that the greater shearing force created by a finer mesh with smaller holes did not result in an increase in consumption.
- Altering the magnet pressure or squeegee force had no influence on paste consumption. This also appeared to be the case during the production trials.
- There is no doubt that fall ons, or overprints, have a significant effect on paste consumption, yet their effects are very difficult to quantify as every design is different.
- It proved difficult to assess accurately the paste consumption throughout the bulk trials, as the number of influencing factors outside the direct control of the investigation was many. However, it was apparent that an increase in machine speed resulted in a reduction in consumption, whilst an increase in squeegee size brought about an increase in consumption.

7.6 FIXATION AND AFTER-TREATMENT METHODS

In a typical textile process, color paste is applied batch-wise or continuously on textile fabrics using tools or machines. Screens and blocks are used in batch-wise printing, while copper roller, flatbed and rotary screen printing machines as well as inkjet printing machines are popular for continuous printing of textiles.

After printing by any of the above tools or machines, the colors in the printed portions are wet and sticky due to the presence of thickeners and water. The printed fabric should be dried in open width condition. Otherwise, the paste will stick irregularly to various portions of the printed fabric, spoiling the fabric. In manual printing with wooden block or flat screen, the fabric is allowed to dry on the printing table, either by hot steam pipes fixed under the printing table or by hanging the fabric in open air or under a ceiling fan.

All continuous printing machines run under high speed and due to high production rate, the printed fabric cannot be dried without the help of a drying machine. Several types of drying machines are in use, namely:

- 1) Roller drier
- 2) Conveyor drier
- 3) Loop drier

After printing and drying, the colorants (dyes or pigment) are stuck to the fabric superficially. If a typical textile print is washed soon after printing and drying, a substantial part of the colorant is washed out. An appropriate fixation step is, therefore, necessary. Complete fixation can rarely be achieved. Hence, the unfixed dye, thickening agents and auxiliary chemicals are to be removed thoroughly by soaping and washing until the wash liquor is colorless.

The efficiency with which these processes of fixation and washing are carried out is vitally important to both the quality and the cost of the prints. The proportion of faults in the final product that are introduced at this stage can be disastrously high.

When water-soluble dyes are used the necessity for fixation is obvious enough, but even the ubiquitous, simple pigment print shows poor fastness to washing if the fixation process is skimped or omitted. Since the pigments used contain significant amounts of dispersing agent, and since the polymeric binder is also a dispersion with its own dispersing agent, the printed deposit is readily redispersed in water after a short drying process. When the printed fabric is kept under a specified high temperature for a specified time, the binder gets polymerized and forms a continuous film that incorporates the pigment particles inside the film and adheres satisfactorily to the fiber surfaces. At the same time, crosslinking of the binder molecules is completed if appropriate monomers or agents have been incorporated, and the required pH and temperature achieved.

After printing, colorants along with thickeners and chemicals remain on the surface of the printed fabric and unless it is handled carefully the color paste may stain unprinted portions which may cause rejection of the printed materials. Three steps of after-treatment of printed material after printing are as follows:

- 1) Careful drying, preferably in open width condition.
- 2) Fixation by steaming in case of printing with dyes or dry heat fixation or curing in case of printing with pigment.
- 3) Washing and soaping to remove unfixed dyes, thickeners and other auxiliaries from the printed fabric so that no incidence of color bleeding occurs during washing by the user. In case of pigment printing, the water-insoluble pigment particles are embedded in film formed by binder molecules. There is neither any free pigment particles nor any thickener on the surface of the printed fabric. Hence, no washing or soaping after curing or fixation is necessary in case of pigment printed fabric.

7.6.1 DRYING

It is possible to use any controllable means of raising the fabric temperature:

- Convection in hot air
- Conduction on cylinders
- Radiation
- Steaming

The first and second means are commonly used.

7.6.1.1 Curing Machine for Pigment Print

The conventional roller baker or "curing" oven or roller drier (Figure 7.8) consists of two rows of rollers (one above another). The lower row of rollers is in forward position with respect to the top row in such a way that vertically each roller in the bottom row is in between two rollers of the top row. The fabric in open width is threaded above the top rollers and below the bottom rollers alternately and moves

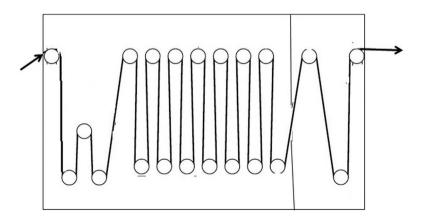


FIGURE 7.8 Drying cum curing machine for pigment printed fabric.

under tension. The chamber may be used as a drier or curing chamber by circulating hot air in the chamber. A similar chamber may be used for "roller steaming" by circulating steam in the chamber with suitable and necessary modifications required for the steamer. The number of fabric transport rollers and the synchronized speed of the rollers decide the exposure time of the printed fabric. The number of rollers should be such that the fabric remains in the chamber for a reasonable time. Shorter times are required at high temperatures, but the risks of discoloration and the chances of inadequate treatment are high. Times of 3-5 minutes at temperatures in the range 140-160°C have been generally preferred. The rate of heat transfer in baking is low and times of 20-60 seconds are required to bring the fabric to a temperature close to that of the air. Treatment times of 2 minutes or less, therefore, allow little latitude, and any variation in moisture content of the entering fabric can lead to significant differences in the fixation. Thus when drying and fixation are to done in a single unit, the control of the conditions is critical. Generally drying is done at a temperature below 100°C to avoid bleeding of color outside the design portions, while curing is done at much higher temperatures of $140-150^{\circ}$ C. A single stage process appears attractive, but is likely to use more energy than a two-stage process because the large volume of fresh air required for drying and not required for baking will be unnecessarily heated, unless humidity control is practiced (limiting fresh air inlet). Fabrics that cannot be handled on such machines include almost all knitted fabrics.

7.6.1.2 Drier for Roller Printing Machine

In roller printing machine, the printed fabric is dried continuously by running over a set of hollow rollers or cylinders internally heated by steam. Cylinder driers are preferred because the drives are similar to those of the roller printing machines. Figure 7.9 shows a schematic diagram of a cylinder drier attached to a roller printing machine. The number, diameter and the temperature of the cylinder surface as well as the arrangement of the cylinders vary widely from manufacturer to manufacturer A second cylinder drier is also synchronized with the roller printing machine if backgrey is to be dried before washing.

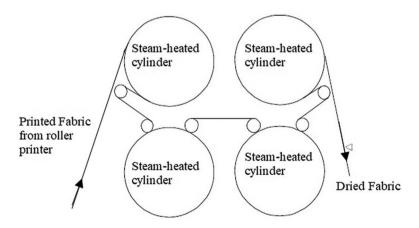


FIGURE 7.9 Steam cylinder drier for roller printed fabric.

7.6.1.3 Drier for Rotary Screen Printing Machine

In rotary screen printing machines a drying cum curing chamber (Figure 7.10) is used, similar to that used for the curing of pigment printed fabric described previously.

7.6.2 FIXATION OF PRINTS

Fixation of fabrics printed with dyes may be done by one of the following methods:

- Fixation with saturated steam
- Fixation with high temperature steam
- Fixation with high temperature and high pressure steam
- Wet fixation

In case of pigment printing, the final reaction product is water. Hence, it cannot be fixed with steam. Pigment-printed fabric can be fixed only with dry heat.

During steaming the dyes and chemicals absorb a certain amount of moisture from steam causing swelling of the fiber as well as of thickener film. A temporary dyebath is created in which the dyes get dissolved, get diffused inside the fibers and interact with fiber. To accelerate swelling and penetration, several printing auxiliaries are incorporated in the printing paste. In case of synthetic fibers, swelling takes place only at high temperature and/or high pressure. Vat, indigosol, azoic and

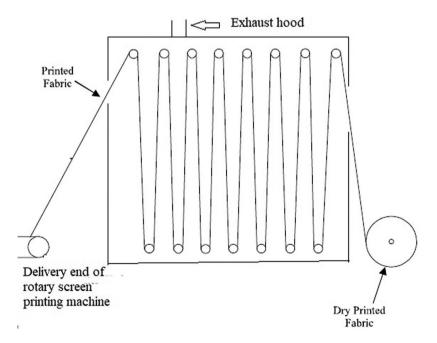


FIGURE 7.10 Drying and curing chamber for rotary screen printing machine.

reactive dyes can be fixed by steaming under atmospheric pressure, while disperse dyes on polyester require high temperature and high pressure.

7.6.2.1 Dry Heat Fixation

Usually pigment, reactive and disperse dyes are fixed by this process. Baking chambers or hot air stenters with high temperature heating systems are used for this purpose. Fixation takes place for pigments at 130–150°C for 5–3 minutes, for reactive at 150°C for 5 minutes, and for disperse dyes at 180–200°C for 30 seconds.

7.6.2.2 Wet Fixation

The wet fixation method is followed for different types for dyes such as solubilized vat dyes, oxidation of vat dyes, alkali fixation of reactive dyes and two-phase printing of vat and reactive dyes.

7.6.2.3 Steam Fixation

Steam fixation of printed fabric is a relatively costly process as steam consumption is quite high.

In pressure steaming the fixation is done for 20–30 minutes at 0.5 to 2 atmospheric pressure, while fixation by high temperature steaming is done at 180–200°C for 50–30 seconds, respectively. Pressure steaming is a discontinuous process and not suitable for high rates of production.

High temperature steaming fixes reactive dyes on cotton and reactive/disperse or metal complex on synthetic fibers in 30 to 60 seconds only. Reactive dyes fixed by high temperature steaming give better color yields than by thermo-fixation processes.

7.6.3 STEAMERS

The fabrics printed with dyes are usually fixed by steaming processes. The moisture and heat carried by steam favors the transfer of dye molecules from the thickener film to the fiber within a reasonable time.

In ancient days printed fabric were hung on poles and left in a room with a warm and humid atmosphere for some days, allowing the processes of diffusion and chemical reaction to occur. As the process was very time-consuming, it was named as "ageing" and the name prevailed for a long time. The term has been retained in use for various steaming treatments, especially for short processes and machines, namely "rapid ager" and "flash ageing". The terms steaming and ageing (with steam) are synonymous – the two terms can be used interchangeably.

The time and conditions for fixation in steam varies with the properties of the dyes and fibers used. The time ranges from 10 seconds to 60 minutes in steam and the temperature from 100 to 200°C. Technical and economic factors have encouraged the use of higher temperatures and shorter times, and the change from batch-wise to continuous processes. A constant feature in the design of all printing steamers, as distinct from steamers for other textile processes, is the need to prevent the markingoff of printed color on to pale-colored areas (Miles, 2003).

7.6.3.1 Batch Steamers

For expensive fabrics and small quantities, there are obvious advantages in using low capacity steamers that can be quickly raised to their working temperature and that produce no creasing, stretching or other damage to the fabric. Batch steamers also show advantages when color yields are improved by steaming at above-atmospheric pressure or for extended times, as in the case of deep colors on polyester fabrics.

A star ager or bell steamer (as popularly known) consists of a cylindrical pressure vessel, mounted vertically and closed at the top (like a bell) with a door that can be swung into position at its base. As steam is lighter than air, with this arrangement the bell-shaped cylinder remains filled with steam. The star frame can be raised into the steam, or the bell lowered onto the star frame. Less air is taken in with the fabric, and the air is more easily displaced by steam than in any other possible arrangement.

A star-shaped carrier frame is used to put printed fabric hanging spirally on the hooks fixed on a circular plate. The hooks are fixed on the bottom of the carrier plate. The printed fabrics are hooked along the selvages with a space of about 1 cm between the fabric "layers". An interleaved back-grey is used to eliminate all risk of marking-off, as the weight of the fabric and the uniformity of winding are unlikely to be adequate to prevent adjacent layers from touching. The capacity of the star ager is up to 500 meters.

The steam supply should be air-free and, ideally, dry but saturated. If there is significant superheat in the steam, a humidifier is used to increase its relative humidity. Wet steam is undesirable because splashes and drops of water inevitably cause local bleeding of dye or auxiliary chemicals.

The older-style cottage steamers were often larger vessels into which the printed fabric on a carrier was wheeled horizontally. Substantial flow of steam is required to displace air from such a steamer.

Times of at least 10 minutes are usually allowed for fixation in batch steamers in order to ensure optimum fixation and therefore keep the staining hazards in washing-off at a minimum. Saturated steam at 1.5–3 atmospheric pressure gives good color yields on triacetate, acrylic and polyester fiber fabrics.

7.6.3.2 Continuous Steamers

There are several disadvantages of the star ager, namely:

- Longer times for loading and unloading printed fabric from hooks.
- There are poor controls on the process.
- It is not possible to check the fabric in between.
- There is tremendous loss of steam and energy.
- All other disadvantages of batch processes.

7.6.3.3 Festoon Steamer

Continuous processes are advantageous, in general, over batch processes. One method of making steaming a continuous process is to loop the printed fabric over several rotating rods (Figure 7.11). The rods move forward leading to the continuous transport of printed fabric in festoon steamers. Long loops are formed on rods,

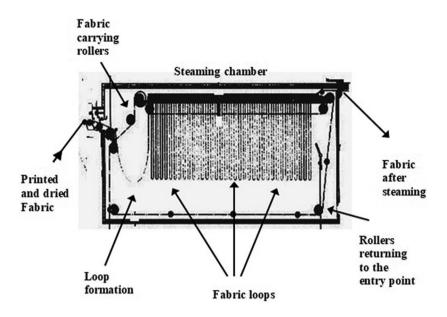


FIGURE 7.11 Schematic diagram of a loop or festoon steamer.

touching only the unprinted face, which are moved slowly along a track near the top of a large steam chamber, constructed in brick or steel. The rods may be slowly rotated to avoid bar marks due to non-uniform accessibility to steam. With loops (festoons) of up to 5 meters in length, long steaming times or high throughput velocities can be achieved without the tension and mark-off problems associated with top and bottom carrying rollers. Several ingenious mechanisms for the formation of festoons of equal length are available. At the end of the steaming period, the fabric is withdrawn at the same high speed as at the entry point. A fabric content of 800 meters allows an overall throughput speed of 80 m/min with a 10 minute steaming time. Capacity can be doubled by introducing two layers of fabric, with an intermediate back-grey, if the printed area is not large. The larger the steamer dimensions and the more densely it is packed with fabric, the more difficult it will be to maintain uniform steaming conditions.

It is now considered essential to have fan-assisted circulation of steam. In older designs a flow of steam through a water tank at the base, which reduces the superheat of injected steam, to exhaust ducts in the heated roof was used to help maintain uniformity and provide a valuable cooling effect.

In most early festoon steamers, the fabric entry and exit were through slots in the roof, provided with heated roller seals. The seals could never be perfect and escaping steam, absorbed by the print, increased the mark-off from the printed surface to the sealing roller. A doctor blade was therefore required to clean the roller surface before it again contacted the fabric. In modern equipment the fabric entry and exit ports are usually positioned in or near the base of the steam chamber, which reduces the sealing problem significantly (as steam is lighter than air).

The steamers made by Stork and Babcock have steam circulation arrangements. Steam is collected from the bottom of the steamer and passed through radiators. Water is sprayed when needed, and forced through ducts to the top of the steamer, whence it passes down the folds to the bottom.

The festoon steamers are increasingly being produced as universal steamers, so that any temperature between 100 and 200°C may be employed. Many knitted fabrics can be satisfactorily handled in festoon steamers, provided the loops are not too long; the term "universal steamer" can in fact be justified.

Where the steaming time required is short (up to 2 minutes), more compact machines with fabric-carrying rollers have been used. The term "Mather and Platt Roller Ager" was often applied to such steamers, in which the fabric path resembled that in a roller curing oven. With the increasingly important screen prints, which usually have more surface color than engraved-roller prints, marking-off via the rollers became more probable.

7.6.3.4 Washing

As discussed earlier, fabric printed with pigment colors does not contain any unwanted substances and hence, after-washing is not required. However, textile fabrics are also printed with classes of dyes. In those printing processes, various chemicals and thickeners are used, which are to be finally removed in order to make the printed fabric soft and resilient. Depending on the class of dye, a good portion of dye remains unfixed and is to be removed thoroughly. The removal should be done very carefully in long liquor so that the released dye is not redeposited in other portions of the printed fabric.

The washing-off of printed fabric is a multi-stage process, namely cold wash, hot wash, neutralization, treatment with soap or detergent, reduction clearing and so on. Small-scale cottage printers carry out these unit operations in batches in small vessels made of steel or cemented tanks. For large batches produced by printing machines, washing must be done continuously.

In batch dyeing machines washing after dyeing or printing is carried out in the same machine after changing the treatment liquor. In continuous dyeing machines, each unit performs a specific job and a continuous open width washing range is necessary for removal of dyes and chemicals after dyeing and printing.

Continuous open width washers probably started as a single-dip saturator and quickly evolved into a multi-dip box in which the fabric passes alternately between the top and bottom rollers (in tight-strand machines) with the latter being immersed in washing liquor. The top rollers are driven usually by chains or V-belts in a bank of five or six, which make up a compartment or unit. The bottom rollers are free wheels. Both the top and bottom rollers should be of largest practicable diameter, for instance, around 12–13 cm, and the distance between them should be kept to a minimum to minimize fabric creasing or curling. In the era of cheap energy, these open vertical boxes dominated the market. Each rinse box in the range was flooded with plenty of fresh hot water. As energy availability decreased and cost increased in the 1970s, tremendous interest developed in decreasing energy costs for continuous washing. Counter-flow lines were added to existing ranges, partitions were added between the bottom rollers inside the box to increase the counter

flow effect and makeshift tops were attached to the open boxes to reduce heat loss (Roy Choudhury, 1996).

In the counter-current system, as the fabric runs through the washing compartments from entry to exit, clean water is passed through the plant from the back to the front. This means the cleanest fabric comes in contact with the cleanest washing liquor. By applying this counter-current principle, it is possible to save water and energy.

The standard range consists of a series of compartments, separated by mangle nips which draw the fabric through the machine and limit the carry forward of liquor, which determines the washing efficiency. The effectiveness of washing also depends on the number of units in the range and on the efficiency of impurity interchange between fabric and wash water.

The use of water may be minimized by feeding fresh water at the last chamber, flows from the last to the last but one chamber and so on; the flow of water is opposite to the flow of fabric. Each successive immersion of the fabric is in cleaner liquor, whereas the liquor becomes increasingly contaminated as it approaches the discharge point close to the fabric entrance. The fabric path in the washing compartment is vertical between the upper and lower rows of guide rollers, with only the lower ones submerged.

Several techniques are adopted by the machine manufacturers for promotion of fabric-liquor interchange and for providing mechanical action on the fabric, such as (Roy Choudhury, 1996):

- 1) Fluted or wavy bottom rollers, which not only agitate the wash liquor in the box, but also tend to force liquor through the fabric.
- 2) Passing the fabric between corrugated formers, which distort the liquor movement; for example, the Gaston County Agitator.
- 3) Passing the fabric round a 30-cm diameter perforated cylinder immersed in wash liquor, as in the Kuster Vibrotex machine. The axle of the cylinder is vibrated and it causes vigorous radial oscillations in the wash box. Such a machine is intended for fairly open-structured fabrics, especially knitted fabrics.
- 4) Passing the fabric round a perforated drum containing an inner fluted roll or a roll fitted with baffles, independently controlled. The rotation of the inner roll induces a pulsating action on the fabric. The outer roll is free rotating and is taken round by the fabric.

7.7 FUTURE TRENDS

Screen printing has been around for more than 200 years. Many industry specialists concur that the approach of advanced silk screen printing will influence a few businesses where screen printing has major industry hold or market share. Computerized printing is more cost-effective, but offers restricted substrate assortment, which is why for substantial printing jobs organizations will keep on utilizing screen printing in the coming years regardless of technology shifts.

Technological advancements have augmented the popularity of screen printing for clothing companies and emerging clothing startups who want to pursue a flourishing career by utilizing silk screen printing. Many companies have and will continue to create lifestyle brands through consistent utilization of screen printing to increase financial returns.

It is a prominent fact that screen printing comprises a large portion of the market, producing substantial returns that contribute towards escalated employment and significant return on investment for printing firms. This is likely to continue in the coming years; why? It is because screen printing plays a tremendous role in myriad domains for the production of diverse products (Sunrise, 2016).

Masselink (2020) discussed the future of rotary screen printing of fabric. Back in the late 1980s, when digital textile printing was being developed, estimating the consequences of these innovations was not yet possible. However, it was soon thought that digital textile printing would push rotary screen printing into the background and eventually even replace it.

Now, almost 30 years later, the rotary screen printing is still very much alive and kicking, despite digital printing continuing to develop rapidly. Can rotary screen printing keep up with this development? And what are the expectations now? How long will rotary screen printing last?

The first digital textile printing machine was introduced by SPGPrints (at that time called STORK) on the ITMA in 1991. At the beginning of the 21st century, when the printing speed of digital textile printing became faster, rotary screen printing was expected to become outdated within a few years. Opinions differed about exactly how long this would take, but most predictions agreed on a period of 10 to 15 years. After that, digital textile printing would have taken over the market entirely.

Today's reality proves the opposite. The digital share of printed textiles is less than 10%. Besides that, it can be very clearly seen that the business for screens is still growing as the overall worldwide printed volume continues to grow. There was indeed a decline in certain countries, especially in areas where digital strongly influenced textile printing, such as in Italy. However, in other countries – for example in Bangladesh – the rotary screen printing is still very prominent. These geographical differences are strongly related to printing volumes.

The reason that in the early 1990s the rotary screen printing volume was expected to be largely extinguished around the year 2000 was mainly due to the expected speed improvements and price decline of digital. However, not everything has become cheaper with digital printing and developments to make fast and reliable digital printers were taking much longer than anticipated. Large orders, for example, are still cheaper to print with rotary screen printing. Especially if the quality guaranteed by digital printing is not necessary, rotary screen printing is often the cheaper choice. Additionally, rotary screen printing is still developing as well, reducing engraving costs and screen prices and therefore enabling cheaper and more efficient solutions.

Developments in rotary screen printing are one of the reasons that digital technologies have still not taken its place. Rotary screen printing continues to respond to the modern market, keeping it relevant. The reverse is also true: The fact that new developments are still being made shows that rotary screen printing is far from a thing of the past. SPGPrints are still developing new screens.

After all, new screens and technologies are not developed within a few months; a lot of time and investments are necessary. New screens are developed every so often.

In the 1970s, for example, Penta technology was developed as a logical evolution next to the standard screens. After that, NovaScreens were developed in the 90s. Quite recently, in 2019, OrtaScreensTM were added to the long list of screen developments.

In order to stay up to date in both the digital and rotary markets, it was important that rotary screen printing was able to approach the image quality performance of digital textile printing. The new OrtaScreensTM respond to the digital development by enabling more detail and sharper lines in rotary screen printing. OrtaScreensTM can do this with an innovative orthogonal raster of holes. The development of this technology alone took more than 2 years.

Nowadays, a lot of printing companies use both digital and conventional printing machines. This leads to a higher expectation of quality. After all, the final customer only appreciates the quality of the final product, and they do not care whether it is printed with a digital or rotary printer.

While the end consumer mainly focuses on the quality of the final product, digital printing often allows achieving a higher quality for these consumers. Nevertheless, printing companies still invest in rotary screen printers. There are a few reasons for this.

First of all, there are the economic reasons. As a digital printing company, it is generally difficult to compete with companies that use rotary screen printing. That's because rotary screen printing enables printing larger volumes faster and cheaper. That is why long print runs are still being printed with rotary screen printing. Also, striving for the highest quality with digital printing is an expensive investment, especially if this high quality is not an absolute necessity. Take, for example, lowend fashion with few colors. It is much cheaper to make this with rotary screen printing, especially because mass production is much cheaper and faster with rotary technologies.

Besides the economic reasons, companies still invest in rotary machines because there are some technical differences between the two types of printing. For example, some textiles can't be printed digitally. These will have to be printed conventionally. This also applies if dyes have to penetrate the fiber completely; if the print has to be identical on both sides of the fabric, then digital printing is not possible. Another technological difference is that certain applications, such as pigment printing, are quite expensive in digital textile printing because of the high ink consumption in combination with a costly production method for the inks. This makes the production process very expensive, while you want to produce a cheap product. That is why rotary screen printing is more suitable for these dyes.

Because of these differences, the tendency that prevails nowadays is that the two technologies can best be used side by side. That is why many companies nowadays invest in digital but also want at least one machine to enable rotary screen printing.

There are instances in which digital developments have put some distance between rotary screen printing and digital textile printing.

- The industries where high quality is very important: Digital can give the highest quality.
- The industries where a high production rate with competitive pricing is required: Rotary can give the largest volume to the lowest prices.

- The designs that profit from flexibility and reruns (fashion, sportswear): Digital offers higher flexibility and perfect matching reruns.
- Time to market: Digital requires less preparation time.

Digital textile printing provides a lot of flexibility, since it does not need preparation but can start almost instantly; furthermore, it allows changing designs on the same fabric in a split second.

Nevertheless, the prediction that digital textile printing would completely replace conventional rotary screen printing did not come true. That expectation has changed over the years: Conventional printing is not expected to disappear in the foreseeable future. There is a common understanding in the industry that both technologies will remain present, as they are to a large extent complementary.

One of the reasons for this is that nowadays more than 4 seasons are acknowledged in fashion, which means that collections are being replaced faster. The lifespan of clothing is getting shorter and shorter, which makes digital textile printing the most suitable. But the price gap still plays a major role here and therefore still the majority of fashion is printed with rotary. Customers are not always willing to pay the added value of higher quality that digital textile printing offers.

There are still several production conditions that justify the choice of digital textile printing. For example, digital textile printing is optimal for printing volumes that are too small for rotary screen printing. Exclusivity and higher quality go hand in hand.

Several factors influence the choice between rotary and digital. The volume and price per meter is a decisive factor when choosing between a rotary screen printer or a digital textile printer. Many companies use both technologies.

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8 Digital Printing

8.1 INTRODUCTION

A very important transformation began 30 years ago and is taking place in the textile industry: the digital revolution. Traditionally, rotary screen printing had been the most popular traditional textile printing machine.

At present, the textile industry produces the majority of its 34 billion square yards of printed textile fabric by screen printing. However, as we move into the digital age, developments in digital printing of paper are being adapted more and more for the textile market. Inkjet textile printing is growing while growth in analog textile printing remains stagnant. As digital print technologies improve, offering faster production and more cost-effective print runs, digital printing will grow to become the technology that provides the majority of the world's printed textiles.

Digital technology is the fastest growing method of printing textiles, according to a report in the latest issue of Textile Value Chain (2021). Between 2000 and 2005 digitally printed textile output rose by 300% to 70 million square meters.

Although digital methods still account for less than 1% of the global market for printed textiles, their share is likely to expand to as much as 10% by the early part of the 2020s. Screen printing still dominates the textile printing market with 80% of global output. However, this share is expected to fall as digital printing gains more of a foothold in the market.

One reason for the expected growth in digital printing is that more textile manufacturers are able to provide "prepared for print" (PFP) fabrics to digital printers. But much of the increase will be due to improvements in digital printing equipment, such as print-heads and ink dispersion techniques. Growth will also stem from advances in pigment-based inks.

The inkjet textile printing technology has been rapidly accepted in the past few years. The history of applying inkjet to textile printing is rather long, as an alternative convenient method to conventional printing technology. It was expected to be suitable for quick delivery, short-run production and photographic print with multilevel tone reproduction, which is difficult to achieve with existing analog technology. Some advanced users have already used inkjet for years to manufacture a wide variety of products, mainly for short-run production or sample-making. Recently, however, improved reliability of inkjet printers, along with the introduction of digital technology in design process, has made this technology a realistic option to be utilized for mass production. Market expectation for more productive inkjet textile printer has also contributed to this new trend. Digital textile printing is quite different from traditional textile printing in nature. Hence, digital textile printing is often termed "the next generation printing" (Mahapatra, 2021).

Although rotary screen printing offers many benefits, there are also many drawbacks such as low machine efficiency due to pattern changes and correcting printing problems (40% downtime). Short print runs are not easily accommodated by rotary screen printing. Traditional analog printing involves a lengthy and expensive sampling process in addition to the machine efficiency problem. The design is converted into screen files and screens are engraved. Once the screens are ready, colors are matched and patterns are "struck-off" on the print machine. With an average strike-off time of 5 ± 6 hours and screen engraving turnaround of 2 to 3 days, the total time from design origination to finished product can be several weeks.

Digital textile printing can offer solutions for these run-size and time problems. Digital printing reduces the turnaround time between design origination and finished product. Digital printers do not require a lengthy setup time between patterns and can print continuously. In addition, digital printing also provides the elimination of screen cost in sampling and offers profitable short-run production. Printing without screens eliminates the registration problems and more importantly provides mass customization.

In the early 1970s, Milliken of Spartanburg, South Carolina, USA, developed a digital carpet printer, which launched in 1975 as the Milliken Millitron. This device fires continuous streams of dye from an array of nozzles along the full print width. Targeted streams of air deflect drops that do not contribute to the image are recycled. Undeflected drops continue on to strike a web of white carpet. Milliken advanced this technology from its early 10 dpi resolution to over 70 dpi. In 1976, Zimmer announced its carpet printer. Today, most printed commercial carpeting is digitally printed.

Digital printing is considered to be quite a new technology. Originally it was developed for printing on paper. The first patent for an inkjet printing system was received by Lord Kelvin in 1867. Furthermore, the earliest use of inkjet printing machines on textile fibers occurred in early 1970s, but this was confined to the carpet industry owing to the relatively low pattern definition of which the machines were then capable. In the 1980s it became possible to produce digital laser versions of electrophotography transfers for t-shirts and other garments and accessories (Ujiie, 2006).

In 1968, the first patent of Inkjet printing technology was used. In the carpet industry, inkjet printing machines have been in use since the 1970s. By the 1990s, for paper printing, inkjet printers became readily available.

Digital textile printing started in the late 1980s as a possible replacement for analog screen printing, however, it was not until the early 1990s when it caught the imagination of the textile industry. It was a revolutionary change from what the fashion world had experienced until then.

Digital textile printing is one of the most remarkable achievements in the printing field of the textile industry. It changed the whole scenario of the printing industry and presented a big challenge to the traditional printing methods prevailing for the last few centuries. Digital printing enables unlimited color sampling, as well as excellent print fastness.

Inkjet printing is a technique in which materials, in a liquid phase, are transferred onto a substrate. This is done in a controlled way, via a non-contact process with the application of an external signal to the printhead. Inkjet is a technique of digital printing that enables printing on various textile substrates and is conducted without any contact between the substrate and ink (Le, 1998). Inkjet printers spray liquid ink through microscopic nozzles onto paper. Laser printers, on the other hand, have a drum unit that fuses (or melts) toner powder onto paper with heat. So, one printer type uses ink, the other uses powder.

In the early 1980s, Dr. Sweet from Stanford University (USA) introduced the concept where he, with the help of a pressure wave pattern, reached a uniform size and distance among drops, which contributed to a faster development of inkjet printers with a continuous flow of printing ink (Le, 1998).

Nevertheless, the use of inkjet printers substantially increased only with the rise of desktop publishing, especially due to demand for high-quality color prints. Inkjet printers, as the name implies, use ink to print text, graphics, and images onto various types of paper. These printers are most common in homes and small offices, though many commercial printing companies use industrial inkjet printers to produce highquality brochures, flyers and other pieces.

Printing on textile substrates also requires some adaptation of the traditional printing technologies in terms of fixating the ink on the target surface. The need comes from the fact that fabric must be resistant to washing and exposure to elements. Thus, there are two methods for digital printing on textiles (Bowles and Isaac, 2009):

- Indirect inkjet heat-transfer printing
- Direct inkjet printing.

Indirect inkjet heat-transfer printing (see Chapter 4, section 4.10), also known as transfer printing, in essence uses a special transfer paper with a layer of plastic or polymer coating to print the image. Then that the image can be transferred to the fabric by applying heat to the transfer paper; printed face of the paper in contact of the fabric surface to be printed. As a result of heat application, the plastic layer will be transferred to the fabric surface along with the printed image. For the direct inkjet printing, the color fixation is also done by applying the high temperature to the target surface. It can be done by the means of steam in a steamer device or by the means of heat in the oven. The particular heating approach is chosen based on the chemical components that were used for printing. Current trends in printer hardware show the development and implementation of print engines using piezo, drop-on-demand or continuous inkjet technology (King, 2009).

8.2 HISTORY OF DIGITAL PRINTING

Ujile described (www.HitoshiUjile.com) the history of digital printing at the "CREATE = Colour Research for European Advanced Technology Employment" conference on October 20th, 2008, summarized as follows:

- 1878: The principal mechanism (Lord Rayleigh)
- 1960s: First inkjet system (Continuous Inkjet System)
- 1972: Piezoelectric D.O.D. heads by Clevite Corp in Ohio
- 1975/76: Millitron Printing System by Milliken (carpet and upholstery fabrics)
- 1979: Thermal D.O.D. inkjet heads (HP and Canon bubble jet)

- 1995/96: Seiren Viscotex System (production inkjet printing on cloth)
- 1995/96: Encad TX 1500 series (thermal D.O.D. heads)
- 1998/99: Large format sampling printer (Mimaki TX series)
- 2003: Production printers (Mimaki, Reggiani, Robustelli, Konica/Minolta, Osiris, Miyakoshi/Kyocera, Tencate)

8.3 MARKET OF INKJET PRINTED TEXTILES

In recent years, inkjet printers have become very popular in the field of printing on textile substrates. Digital textile printing is a printing method for textiles and garments that uses industrial inkjet technology to print colorants onto fabric. As an alternative option to traditional screen printing, printing textiles and garments with industrial inkjet systems offers many advantages for single pieces, midto small-run cycle production, and long-runs as an alternative option to screen printed fabric.

At the 1995 event of ITMA, digital inkjet printing was first shown on continuous rolls of textile fabrics. The industrial benchmark for digital textile printing was set at the ITMA in 2003 with the introduction of high-grade industrial inkjet printers. Since then, technology has been evolving when it comes to digital inkjet printers where one can print on a variety of media including different fabrics. Designs and color options are limitless with these new generation printing machines.

With shorter run lengths, individual designs and fast fashion, there have been major changes in the textile printing market globally. In the developed printing markets, inkjet printing technology is widely used, as it reduces the overall cost of samples. Small scale textile printing productions such as banners or flags along with the sportswear industry are adopting wide-format inkjet printers. In the technology of inkjet printing, specific ink and chemical requirements should be satisfied with the reliable performance of the printer platform. Physical and chemical specifications of ink are precise and they are different from the normal printing pastes. The normal printing pastes lack the ability to contain the majority of chemicals that are required to yield vibrant colors. The operating and firing performance must be kept in mind while developing the ink for textile inkjet printers along with the chemical compatibility of materials that are used during the manufacture of printheads (ColorJet Team, 2020).

Various marketing organizations are regularly carrying out surveys of the present market of digitally printed textile materials and projected future markets. According to Verified Market Research, the Global Digital Textile Printing Market was valued at USD \$1,670.3 million in 2018 and is projected to reach USD \$4,727.6 million by 2026, growing at a CAGR (compound annual growth rate) of 14.16% from 2019 to 2026 (www.marketsandmarkets.com/).

The Global Digital Textile Printing Market report provides a holistic evaluation of the market for the forecast period. The report comprises various segments as well as an analysis of the trends and factors that are playing a substantial role in the market. These market dynamics involve the drivers, restraints, opportunities and challenges through which the impact of these factors in the market is outlined. The drivers and restraints are intrinsic factors whereas opportunities and challenges are extrinsic factors of the market. The Global Digital Textile Printing Market study provides an outlook on the development of the market in terms of revenue throughout the prognosis period.

Equally significant, as far as Digital Textile Printing Machinery was concerned, according to Persistence Market Research: The global market for digital textile printing equipment was expected to attain a value of USD \$2.25 billion by the end of 2028, growing at a CAGR of 14.9% during the forecast period (www.fespa.com/).

A market study by Smithers Pira projected the digital textile printing market to grow at 20.1% annually through 2019. Experts have also predicted that global digital textile printing production will be around 1.6 billion square meters annually by 2019. As many as 650 million square meters of fabric was digitally printed until the second quarter of 2014 (Fibre2Fashion, 2015).

Estimates for total output of Indian digital textile printing are in the region of 85 million square meters, approximately 7% of the current digital market – still very small, considering India is the second largest textile printing market, which currently prints 17.5% of the global 31 billion square meters of the traditional textile prints. The real unknown factor, which could significantly increase digital textile print production penetration, is the possible future market penetration of the fixed-printhead-array digital textile machines (so-called "single-pass" types), which have the capability to match the millions of square meters printed per year by rotary screen machines (Provost, 2016).

8.4 SCREEN PRINTING VERSUS DIGITAL PRINTING

A collection of printed fabrics for men's shirts was designed and printed by both inkjet and screen printing methods. The colors for designs were inkjet printed on cotton fabrics with pigments and ultraviolet-cured. These prints represented the target colors for subsequent flat-screen printing, which was performed using pigment printing pastes and thermal curing (Mikuž et al., 2010).

For an exact transfer of colors of the inkjet-printed standard into the screen printing process, a computer recipe prediction method was used. A comparison of colorimetric parameters of fabrics printed with both printing techniques shows minimal and acceptable differences in the CIELab color values. A comparison of color fastness properties proves that very good color fastness is achieved on the pigment-printed fabrics produced with both printing techniques. The flat-bed screen-printed fabrics show better color fastness to washing, perspiration and rubbing, while inkjet-printed fabrics show better color fastness to drycleaning and light. The fabrics printed with both printing techniques have high rigidity and non-elastic properties. The mechanical and physical parameters are strongly dependent upon the amount of the dry substance of the printing media applied on the cotton fabrics show better air permeability than flat screen-printed fabrics.

8.4.1 MERITS/DRAWBACKS OF INKJET PRINTING

The merits and drawbacks of screen printing and digital printing are discussed next.

8.4.1.1 Advantages of Screen Printing

When it comes to screen printing, one of the major benefits is that it's an effective solution for bulk printing, as it is extremely cost-efficient. Other benefits include:

- A higher quality output than digital prints.
- More durable prints that are needed over the long-term.
- Can be used on a variety of different print materials, including glass, wood, textiles, signs, banners, electronics, and much more.
- It's easy to print on specified areas of the print material.

8.4.1.2 Disadvantages of Using Screen Printing

- One of the main disadvantages of screen printing is that it has a much higher initial setup cost than digital printing and takes more time.
- Limited color ranges available.
- The amount of ink used can make the design look as if it is raised from the print material.
- It cannot be customized in the manner of digital printing.

8.4.1.3 Advantages of Digital Printing

The advantages of digital printing are:

- No engraving no screen no repeat limitation.
- Low cost set up and speed of turn around.
- Transfers photographic images accurately.
- Quick response to the market.
- Cost-effective short to medium runs (up to 500 m).
- Minimal environmental wastes.
- Personalization and mass customization prints can be customized in a variety of ways.
- Designs sit flat on the print material and do not bulge out from the surface.
- Flexibility in new design style (photographic, extreme tonal/extremely fine, unlimited use of color, simulation, graphic, digital effect).
- New business model.

8.4.1.4 Drawbacks of Digital Printing

- The range of printable fabrics is more limited than with screen printing.
- The prints are not so durable.
- The color white cannot usually be reproduced within the print.
- Due to fixed pricing, bulk printing does not offer scaled cost reductions.

The benefits of digital printing as reported by www.pigmentinc.com (accessed on 23.11.21) are:

8.4.1.5 Sustainability

- Low energy consumption (electricity, water).
- Minimum environmental impact.

8.4.1.6 Less Investment, Higher Savings

- Sampling costs dramatically reduced.
- No more engraving departments.
- No more cost and stock of screens.
- No more color kitchens.
- No set up costs.

8.4.1.7 Manpower Flexibility

- Easy training.
- Reduced labor costs.
- Quicker response to customer needs.

Digital inkjet textile printing does not use screens or rollers as is the case with conventional textile printing. Hence, all the costs related to screen making or roller engraving, paste making, strike-off, downtime and wastage do not exist. For short lengths of fabrics, the conventional textile printing process is not economical due to its high preparatory costs, high costs of engraving and screen making, high wastage of fabric, and high cost for ink or paste preparation, the number labors involved and cost therein as well as cost and time spent on the preparation stages. Design sampling or proofing is a costly process in conventional textile printing. Nowadays, the length of fabric printed for each design has decreased and the demand for a greater number of designs in the market has increased.

On the other hand, digital inkjet textile printing is not preferred for long lengths of printed fabrics as several obstacles are faced. Even though less labor is needed in digital inkjet textile printing, it requires high-tech talented personnel to operate the printer. The inkjet printheads are quite expansive. Their maintenance is more stringent and costly as compared to the conventional textile printing machines. The digital inkjet textile printers are, therefore, installed in a very clean place equipped with humidifier, air filter and conditioner to ensure the stability of printer.

The inks used in digital inkjet textile printing are very delicate and should maintain stringent quality standards. The prices of such inks are, therefore, much higher than the traditional print pastes.

Patterns printed by a digital inkjet textile printer have better fineness than by the conventional textile printer. It is possible to have photo-like accuracy, which provides more possibilities for the designer. It is possible for a digital inkjet textile printer to print any number of color-ways. All the technical data of digital inkjet textile printing images (including color match) are stored in the computer to ensure the consistency of printed sample and bulk production. Customers can access the manufacturer through

the internet. Digital inkjet textile printing brings the possibility to realize personalized ecommerce consumption of textile printing. Customers can send their own designs, personal data and requirements to the manufacturer via the internet. Products will be delivered to customers within a short period. But in bulk production, textiles printed by a conventional textile printer have more stable quality than digital inkjet printers.

8.4.2 MASS CUSTOMIZATION

In the 21st century, consumers show a high preference for personalized products. People are not satisfied with the standardized service provided by mass production. Companies need to predict customers' demand and desire accurately to sustain market competitiveness. Digital inkjet textile printing is an emerging technology and has a large potential to fulfill market demand and impact company strategy. Mass customization can be realized by adapting digital inkjet printing technology in the textile printing industry, and influencing soft goods supply chain gradually. Digital inkjet textile printing methods have brought an unprecedented personalized experience to textile printing and dyeing industry.

The concepts of digital inkjet printing are close to life with the combination of art and technology. Digital inkjet printing technology links design and production together, and achieves the feasibility of unlimited images printed on fabrics. In addition, business and production processes of textile printing can be automated by applying digital inkjet textile printing (Fralix, 2006; Fang, 2011).

The future of fashion, according to Epson (Arthur, 2017), is all about customization – from the prints and colors we choose to wear, to indeed the size and shape that best suits us. Tie together digital printing, a bit of artificial intelligence and some robotics on the end, and it's a vision that's not too far off, which is precisely what the technology company is hoping to help make possible on all accounts.

Other benefits of digital printing include that it enables higher quality, more unique designs at scale, greater variety of rich colors and more. It's literally possible to take a picture on your iPhone today and print it onto a textile at photo-realistic quality straight away (Arthur, 2017).

8.5 POPULAR INKJET PRINTER MANUFACTURERS

Some Common Brands of Digital Textile Printing Machine are (RMG Bangladesh, 2021):

•	Durst Alpha	Italy
	Zimmer Machine	Germany
•	Atexco Machine	China
•	Reggiani	Italy
•	MS	Italy
•	Homer Digital Printer	China
•	Mimaki	Japan
	Encon	Ionon

Epson Japan

8.6 BASIC CONCEPTS OF INKJET PRINTING

The textile printing production is initiated by a design concept. Before a design concept is put into real production, proofing is an important link that manufacturers need to go through. Designers will first draw the pattern with CAD software. For digital inkjet textile printing, the digital file can be input to the printer. Digital inkjet printers will print samples for a designer to proof directly. However, the digital file used in conventional textile printing needs to be edited first. The color needs to be separated to make a sample screen. The sampling department will mix color paste to print samples after the screen has been prepared. After this process, samples are compared with the original. If the pattern or colors require re-modifying, the process will be repeated. With the digital inkiet textile printing method, the image of the sample can be modified directly on the computer and then a new sample can be printed, saving a lot of time. Due to screen making, color paste mixing, and other processes, conventional textile printing takes longer for sampling time than digital inkjet textile printing. This leads digital inkjet textile printing to be more advantageous for short run production. However, conventional textile printing has a significant advantage in mass production. A rotary screen printer can print over 1,000 square meters per hour, and a commercial digital inkjet textile printer can print only in the range of 2 to 150 square meters per hour (Wang, 2017).

8.7 PRINCIPLES OF INKJET PRINTING

Inkjet technology creates printed documents with streams of ink drops that are deflected to the substrate (paper or textile) based on information in digital files. It does not require an image carrier, or plate, and it does not require equipment like a Xerographic device or a printing press. The same information can be printed throughout a print job or variable information can be printed based on the requirements of the application.

Inkjet printers may be classified as being based on:

- (a) A selectively deflected charged-drop (continuous drop production) principle; or
- (b) A drop-on-demand (DOD) method, in which drops are produced at will by some impulse system. In a drop-on-demand inkjet processes, drops of ink are only generated if the information to be printed requires them.

The print medium or ink may be liquid or melted solid. The ink may be applied at atmospheric pressure, even a slightly negative pressure or under pressurized condition (0.2-30 atm, 0.02-3.00 MPa).

8.7.1 CONTINUOUS INKJET PRINTING (CIJ) PROCESS

In continuous inkjet printing (CIJ) ink is squirted through nozzles at a constant speed by applying a constant pressure. The jet of ink is naturally unstable and breaks up into droplets shortly after leaving the nozzle. The drops are left to go to the medium or deflected to a gutter for recirculation depending on the image being printed. The deflection is usually achieved by electrically charging the drops and applying an electric field to control the trajectory. The name "continuous" originates in the fact that drops are ejected at all times.

The operation of CIJ is based on a physical phenomenon called Rayleigh instability (Plateau-Rayleigh instability) that explains the behavior of a stream of fluid with respect to the droplet size under the influence of surface tension. It is possible to break a stream of liquid into a continuous stream of fine droplets. If they are charged, the direction of the inkjet can be controlled when droplets are passing through the electromagnetic field. In continuous inkjet, the jet of ink generated by each nozzle breaks up into droplets shortly after exiting the nozzle. Without any other intervention, the breakup would occur randomly and would result in droplets of variable sizes. This is usually corrected by providing a periodic excitation to the nozzle in the time domain that translates into a spatial perturbation in the jet of fluid. The combination of the jet velocity and frequency of the excitation determines the droplet size, which can be controlled to very high accuracy (Freire, 2006).

A pump sends ink drops through a nozzle at the rate of over a million per second, which can produce an image of nearly the same quality as a continuous tone image such as a photograph. There are three types of continuous jet technologies (http://agpcptech.weebly.com/uploads/1/2/4/2/12423472/unit_v.pdf):

- · Charged drops for printing
- Uncharged drops for printing
- Electronic deflection

8.7.1.1 Charged Drops for Printing

Drops of ink are given a charge and are deflected to the substrate to produce the image. The ink drops that are uncharged are recycled through the system to be reused.

8.7.1.2 Uncharged Drops for Printing

This type of technology also applies a charge to the ink drops except that the uncharged drops are used for the actual printing and the charged drops are recycled.

8.7.1.3 Electronic Deflection

This type of technology applies a charge to all the ink drops and the application of the drops is determined by deflection, which is controlled electronically.

In the traditional continuous ink jet approach, a piezoelectric transducer is coupled to the printhead to provide the periodic excitation. The oscillations are therefore mechanical in nature. After leaving the nozzle, the drops are electrically charged by an amount that depends on the image to be printed. The drops then pass through an electric field to enable their deflection (Freire, 2006). There are two ways of deflecting the drops in piezoelectric-driven CIJ:

- Binary-deflection
- Multi-deflection

8.7.1.4 Binary-Deflection CIJ

Figure 8.1 shows an example of a binary deflection process, where the drop has one of two charge states (namely uncharged for conveyance to the paper and charged for deflection in an electrical field). In this system, inks are forced at a very high pressure and high frequency through a nozzle. The emerging stream of ink is broken into small droplets. These droplets can be selectively charged and deflected by passing through high voltage plates. Drop selection is achieved by deflecting the desired drops for the image to the substrate and collecting the unwanted drops for recycle. In this system, the ink is electrically conductive and as the ink passes through the charged plates, current flows into the ink column. As the drops form, they will have a net charge opposite to the charge on the plates.

There are two possible techniques for obtaining designs. In one technique, the charged droplets are deflected onto the substrate in a predetermined manner and the uncharged droplets are collected in feedback and recycled. This is known as the

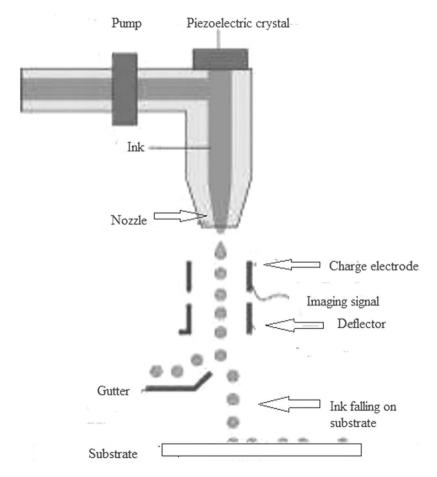


FIGURE 8.1 Binary-deflection piezoelectric-driven CIJ.

"Raster-Scan method". In the second technique, known as the "Binary continuous inkjet system", the uncharged droplets will be unaffected by the deflection plates, which carry a charge opposite that of the charging plates. The un-deflected drops then strike the substrate to form the image. Drops carrying a charge are deflected to a gutter by the deflection plates for recycling.

Besides these, the multi-deflection continuous inkjet has also been used for textile printing. This differs from the binary system in that the dye drops are given a variable charge that gives different deflection as the drops pass through the deflection plates. This allows multiple positions on the substrate to be printed from a single jet. This technology has found application in printers for industrial marketing and served as the basis for t-shirt printers. The uncharged droplets are ejected directly to the substrate, while the charged droplets are recycled into the printing system (Majnarić, 2015).

8.7.1.5 Multi-Deflection CIJ

In the multi-deflection process, the droplets receive different electrical charges and are diverted onto the substrate at different angles. The uncharged droplets return to a gutter to be re-circulated. This differs from the binary system in that the dye drops are given a variable charge that gives different deflection as the drops pass through the deflection plates. This allows multiple positions on the substrate to be printed from a single jet. This technology has found application in printers for industrial marketing and served as the basis for t-shirt printers.

A line diagram of a multi-deflection inkjet printer is shown in Figure 8.2. The various components of the machine are shown numerically, which are described as follows: (1) ink pump, (2) nozzle, (3) deflector, (4) charging system, (5) gutter, (6) digital input signal, (7) substrate and (8) direction of substrate movement.

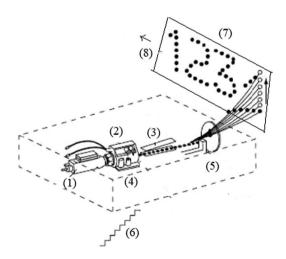


FIGURE 8.2 Multi-deflection piezoelectric-driven CIJ.

In Continuous Ink Jet, there is a system called the Hertz printing method, which was presented in 1966 by Hertz and Samuelsson (1986). In this method, the density of printed ink per pixel is variable. This is achieved by generating very small drops (of the order of 3 pl) at speeds of about 40 m/s with excitation frequencies of over 1 MHz. The drops not intended to reach the medium are charged and deflected to a gutter (Freire, 2006).

There is another CIJ printing method known as a Microdot CIJ printing, in which drops of different diameters are produced, but only the smaller drops are selectively charged and deflected to the substrate (Hertz and Samuelsson, 1986).

Generally, we can say that droplets in this process have large diameter (approximately 40 μ m) and that is the reason why the print resolution is relatively low. This process is generally used in industrial applications, but it is not dominant in inkjet process in textile printing.

8.7.2 DROP-ON-DEMAND (DOD) INKJET TECHNOLOGY

The drop-on-demand (DOD) inkjet process was invented by Siemens in 1977. The first drop-on-demand technique was the thermal drop-on-demand ink jet technique. Except thermal, the other two techniques that fall into the same drop-on-demand category are piezoelectric (Kyser and Sears, 1976; Stemme, 1973; Zoltan, 1972) and electrostatic (Silverbrook, 1998). The difference between these techniques is the way they generate a pressure pulse, because in this type of inkjet printing system, droplets are ejected from the nozzles by pressure pulse created only when it is necessary (Kyser, and Sears, 1976; Stemme, 1973; Zoltan, 1972). In the thermal inkjet process, a drop can be generated by heat transfer, while in the piezoelectric process, a drop is generated by changing the chamber volume in a nozzle channel, and in the electrostatic ink jet method, the droplet's ejection through the nozzles is induced by electrostatic forces.

A drop-on-demand inkjet printer is a type of labeling system whose printing heads eject discontinuous droplets onto the printing substrate to produce the image by means of the heat-induced explosion of ink bubbles (e.g., in bubble jet printers and thermal inkjets).

In the drop-on-demand printing technique, the ink in the tiny print cartridge chamber is first heated until it evaporates. This allows the formation of ink bubbles that later expand and inject small drops of ink on the printing surface through a nozzle. Each nozzle is individually controlled.

8.7.2.1 Advantages

The advantages of drop-on-demand inkjet printers are as follows:

- The main advantage of drop-on-demand inkjet printers is that they can directly print over the surface of an item, making labels unnecessary.
- Low cost. Since drop-on-demand inkjet printers can directly print over an item, the costs that would otherwise be incurred in manufacturing labels is eliminated.
- Large character printing. Because of the relatively large diameter of the nozzles, drop-on-demand inkjet printers can print particularly large size fonts.

- High printing quality. With drop-on-demand inkjet printing, the resultant printed image or text is clean and readily legible.
- High quality printing on sensitive and uneven surfaces.
- Compatibility with special inks. Drop-on-demand inkjet printers are compatible with special inks of different colors for use on porous surfaces (e.g., paper, cardboard, wood) and smooth, impermeable surfaces (e.g., plastic, metal, glass).

8.7.2.2 Drop-on-Demand Inkjet Printer versus Traditional Label Printer

The main difference between drop-on-demand inkjet printers and traditional label printers is that the former can directly print over the surface of an item, while the latter are used to print labels that must afterwards be applied to a surface.

In this sense, drop-on-demand inkjet printers can significantly reduce the costs and time associated with marking, as they do not require the manufacturing and application of labels. Instead, both processes are combined and carried out at once.

Drop-on-demand is a type of inkjet technology in which the ink drops are formed and then applied as a response to a digital signal. There are two types of drop-ondemand printer systems: piezoelectric and thermal inkjet.

8.7.2.3 Piezoelectric DOD Inkjet Printer

The most common technology used for printing on textiles is the piezoelectric dropon-demand (DOD) inkjet technology (Bowles and Isaac, 2009). It is based on the approach that a stream of ink droplets is projected on a substrate in order to form a pattern. The precision of droplet placement is achieved using an electromagnetic field (Kipphan, 2001). In piezo ink jet systems, the drop is generated as a result of a change of volume within the ink chamber due to piezoelectric effects, which leads to the drop of ink being ejected from the nozzle system. A piezoelectric crystal is given an electric charge, which produces a pressure pulse in the imaging head. This produces the emission of an ink droplet onto the substrate. In piezoelectric DOD, the computer imposes an electrical potential across a piezoelectric material, which causes a contraction in the direction of the electric field and an expansion in the perpendicular direction. The expansion causes a drop of ink to be ejected. The applied potential returns to its normal dimensions and the ink chamber is filled from an ink reservoir by capillary action. The replenishment rate can be 14,000 cycles per second. The drop size is somewhat smaller, but it gives good resolution (2880 dpi). They also have superior printhead life.

Figure 8.3 shows a schematic diagram of a piezoelectric DOD inkjet printing machine. It shows ejection of ink drops by mechanical displacement in the ink channel (Novaković and Kašiković, 2013). The numbers in the figure represent the following: (1) ink, (2) piezoelectric ceramic, (3) imaging signal, (4) nozzle and (5) substrate.

Piezo element is typically made of lead zirconate titanate (PZT). The piezo transducer could be attached to a membrane that forms an ink chamber wall or could actually constitute the chamber itself. In both cases, the volume of the chamber is reduced, and the ink droplet is ejected from the nozzle (Freire, 2006).

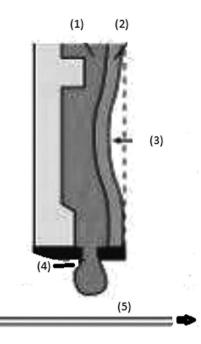


FIGURE 8.3 Piezoelectric-based DOD inkjet printing technology.

There are a couple of other alternatives for the inkjet technology: thermal DOD and continuous flow printing. However, it is the piezoelectric DOD technology that is primarily used for digital printing on textiles at the moment.

8.7.2.4 Thermal DOD Inkjet Printer

There are two types of printer systems using thermal inkjet technology:

- Liquid thermal/bubble jet
- Solid inkjet

8.7.2.5 Liquid Thermal/Bubble Jet

Heat produced from an electrical resistor vaporizes the moisture in the ink, which causes an ink bubble to form. The expanding bubble creates pressure inside the ink nozzle, which propels the ink to the substrate. The ink bubble then contracts, which lowers the pressure, causing more ink to be drawn into the printing head. The entire process occurs very rapidly in the printing device. In fact, the process is repeated thousands of times per second, producing high quality results.

With thermal drop-on-demand inkjet, unlike piezo drop-on-demand, ejection of an ink drop is generated by heating and vaporization within the inkjet system as shown in Figure 8.4. The numbers in the figure represent the following: (1) ink, (2) heating unit, (3) imaging signal, (4) nozzle and (5) substrate.

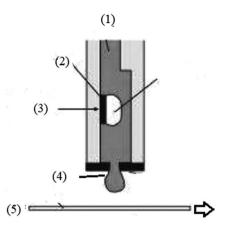


FIGURE 8.4 Thermal-based DOD inkjet printing technology.

The droplets are formed within a few microseconds, where the temperature is rapidly raised to 300–400°C (in order to evaporate the ink) using resistive element. High temperature and resulting ink evaporation create a bubble which forces the ink out of the nozzles (Le, 1998). After droplets are ejected, an ink chamber is filled with fresh ink and the process can be repeated. The printheads made for this inkjet process type are not expensive and the very important thing is that they have the ability to create small-size droplets, although there are certain limitations on the use of fluids in ink formulation. The fluids not only have to be able to vaporize (aqueous solution), but they must also withstand ultra-high temperatures (Soleimani-Gorgani, 2015).

The thermal inkjet process has several configurations of drop ejectors. The most popular are "roof-shooter" (Hewlett Packard, Lexmark and Olivetti) and "side-shooter" types (Canon and Xerox) – depending on the heater position, although in some printing machines we can find "back-shooter", multi heater, double heater, suspended heater and movable member drop generator design.

This process is not so widespread as piezo inkjet process, where only several companies manufacture this machine type (Canon, HP, Olivetti, Lexmark, Xerox). Firms like Canon, HP, Lexmark and Memjet produce very high quality thermal printheads. Canon has developed a specific type of thermal printhead, known as "bubble jet". As well, Canon mastered a technique of printhead manufacturing known as Full-Photolithography Inkjet Nozzle Engineering (FINE). This patented process enables the manufacturing of high-density printheads with exceptional precision. Typical thermal printheads have a maximum of only 600 nozzles. However, Canon produced printheads for image PROGRAF printers with a total of 15,360 nozzles. Unfortunately, Canon did not find still adequate solutions for textile printing. HP invested significant funds in improving their thermal heads. One of the effects of these high R&D investments is the development of advanced inkjet printing machines like HP Latex Series, HP Latex Inks and HP Thermal Inkjet. These technology provide durable, odorless prints, sharp, vivid image quality, application versatility and high productivity (Kašiković et al., 2016).

8.7.2.6 Solid Inkjet

A solid inkjet printer is also known as a "phase change inkjet printer". The ink begins as a solid and is heated to convert it to a liquid state. The ink is propelled as it drops onto the substrate from the impulses of a piezoelectric crystal. Once the ink droplets reach the substrate, another phase change occurs as the ink is cooled and returns to a solid form instantly. The print quality is excellent and the printers are capable of printing on almost any type of paper and transparency substrates (http://agpcptech. weebly.com/uploads/1/2/4/2/12423472/unit_v.pdf).

8.7.2.7 Valve Jet

As the name suggests, this involves the use of valves. Solenoid valves are used to control the flow of ink in an air stream that carries the drops to the substrate. Resolution is limited to 25 psi and thus not quite suitable for apparel. However, these machines have been used for printing billboards, banners, and even draperies, carpets and wall hangings.

8.7.2.8 Electrostatic DOD Inkjet Printer

Electrostatic head printers are faster than piezo and thermal inkjet technologies and capable of variable printing. They offer the best transfer of chemistry to the media because the toner consists of metallic particles that become physically fused to the substrate surface. Electrostatic printing prevents the absorption, density loss and colorant related stability problems found in other inkjet types (Marshall et al., 1998). As the name implies, electrostatic printers use electrostatic attraction of particles to create an image. Material handling through electrostatic droplet manipulation technique, with high precision, is of paramount importance, and is a powerful technique that has received interest in recent years, like protein crystallization, drug discovery, printed electronics, solar cells and so on (Marshall et al., 1998).

The inkjet printer, commonly used to print computer-generated text and graphics, also employs electrostatics. A nozzle makes a fine spray of tiny ink droplets, which are then given an electrostatic charge. Electrostatic printing uses positively charged toner and inks that attract and stick to negatively charged paper. In electrostatic drop-on-demand ink jet printing process (Figure 8.5), an electrical field between the nozzles and the substrate is generated. The ink drops are produced by sending image-dependent control impulses to the nozzles. These impulses cause an ink drop to be released and routed through the electrical field onto the substrate (Kipphan, 2001). The numbers in the figure represent the following (Kašiković et al., 2016): (1) ink, (2) switching element, (3) imaging signal, (4) meniscus, (5) substrate and (6) electrical field.

The steps to be followed are:

- Tiny droplets of ink are electrically charged as they are forced out of a very fine nozzle;
- The droplets pass between metal plates across which a voltage can be applied so that one plate is negative and the other plate is positive;

- The charged droplets of ink are attracted towards the plate with the opposite charge and away from the plate with the same charge. This means that they are deflected as they pass between the plates;
- The size and direction of the voltage applied across the plates is controlled so that each droplet in turn is deflected to a particular place on the paper;
- Each droplet of ink produces a tiny dot on the substrate and many such dots, each in exactly the right place, produce the printed characters.

Newly developed micromachining technologies enable the production of high resolution, electrostatically driven head. In research by Rahman et al. (2010), the focus of the analysis and investigation was to study the behavior of droplet ejection from hydrophilic to electrostatic system. Different hydrophilic type inkjet nozzle heads were compared and the behavior of the meniscus and the required extraction force analyzed. Jetting and drop-on-demand behavior was also investigated. It was also found that the latter could eject drop more precisely and synchrony with the pulsation are verified by printing conductive lines on PET substrate. It was analyzed that when the pulsed voltage magnitude and width are further increased on heads, the induced electric stress becomes great enough to produce a cone-jet. As a result, the liquid at the tip of meniscus, subjected to the most intensive normal electric stress, can be ejected directly out from the apex, thus causing a dripping mode. If the electric stress is small, some liquid on the meniscus surface will still be removed to the apex of the meniscus by the tangential electric stress, but no jet is created due to the lack of sufficient electric stress. Thus, a voltage pulse of greater amplitude can move the liquid on the surface of the meniscus and force it to form a much finer jet. From these results, the hydrophilic needle type inkjet nozzle allowed to eject precisely controlled very fine droplets and to print very

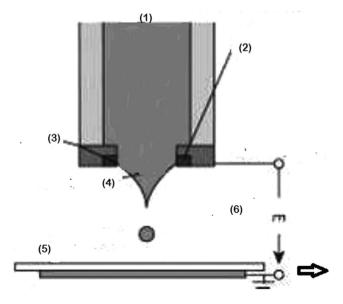


FIGURE 8.5 Electrostatic DOD inkjet printing technology.

	Carpet	Textiles	Paper
Definition (d.p. i.)	12–20	80-100	150-400
Substrate speed (m/min)	5-15	25-60	50-200
Firing frequency (kHz)	$5-20 \times 10^{2}$	1–4	3-20
Pulse length (ms)	$1 - 10 \times 10^{3}$	100-500	10-100
Volume per drop (pl)	$1-5 \times 10^{6}$	$1-5 \times 10^{3}$	100-500

TABLE 8.1Comparison of Inkjet Requirements for Different Substrates

fine line width at 6kV. This has advantages of small size, low power consumption, long lifetime and precise dropping of drops at high printing speeds. This study will help develop the liquid ejection technique to facilitate the application of the inkjet printing technology for electronic devices (Rahman et al., 2010).

The requirements on the characteristics of the ink drop producing mechanism are shown in Table 8.1 (Dawson, 1992), and these have greatly affected the various solutions achieved in machines that have eventually been produced commercially.

As most inkjet printers were devised for paper printing, the terms encountered in, for example, technical specifications are more related to those used in reprographic industries than those used by textile printers. Thus, reference is made to toners and inks rather than dyes, pigment and print pastes. Similarly print resolution and speed are defined in dots per inch (dpi) and characters per seconds (cps) or even pages per minutes, rather than mesh/raster and yards/meters per minutes. The various market sectors into which jet printing may be introduced place widely different technical requirements on the characteristics of the ink drop producing mechanism, and these have greatly affected the various solutions achieved in machines that have eventually been produced commercially.

8.8 SUBSTRATE PRETREATMENT

When inkjet printers were first introduced on paper, it was found that print definition can be improved by incorporating a 20 mm thick layer of colloidal silica onto the paper surface. Paper pretreatment for inkjet printing has been well covered by patents, particularly in Japan.

Among the suggested methods are coating with products possessing a "microcracked" surface such as diatomaceous earths, treatment with cationic polymers and with super absorbents, to improve dye uptake. When attempting to print on textiles using a sufficiently high pick-up to achieve adequate penetration, it is difficult to achieve smart as in case of paper. Since textiles are jet printed with relatively low viscous paste (at most a few hundred centipoise), there is a tendency of the liquor to wick laterally along the individual yarns in the fabric. Thus, on woven material, each drop of liquor tends to give a star-shaped spot as wetting occurs in the warp and weft directions. This may be partially overcome by printing with thickening agents with highly pseudo-plastic flow or by pre-padding the fabric to be printed with such a thickener. Control of the spreading of the ink may also be achieved by pre-coating the fabric, particularly with products that increase the surface area available for liquor adsorption (Dawson, 1992).

All textile substrates destined for coloration, whether by dyeing or printing, require preparation to make them clean and receptive to aqueous treatments. This is the case whether the fibers involved are natural or synthetic, although natural fiber substrates require a more thorough and expensive processing route. For example, a typical sequence for woven cotton fabric is as follows:

```
Singe > desize > scour > bleach > mercerize > dry > weft-straighten > batch
```

The order of these processes may vary slightly and some of the processes can be combined. It is during the hot alkaline scouring stage that the hydrophobic outer layer of the cotton fibers is removed. Mercerization with concentrated caustic soda solution improves dye yield and luster for cotton fabrics. A less severe causticization process is used for viscose rayon and lyocell fabrics.

The first step in digital textile printing is to pretreat the fabric with liquid solutions that prepare it to accept the dye and better absorb the color. Then it is fed through the printer, which sprays the dye onto the textile with tiny droplets. The final step is fixing the fabric, a process that ensures the permanency of the design. Depending on the type of textile and type of dye, fixing may involve steam, dry heat, or pressure. Sometimes it requires a combination of two or more of those.

Cotton, viscose rayon and lyocell fabrics are normally jet printed with reactive dyes by the two-phase method; the fabric is pre-treated with thickener and alkali, while the ink contains the dye. The pre-treatment liquor is normally applied with the aid of a pad mangle, though it could be screen printed. In either case the fabric must be dried to about $5 \pm 7\%$ moisture content before printing.

The main constituents of the aqueous liquor are usually thickener, alkali and urea, for example:

100 g/L medium viscosity sodium alginate,
100 g/L urea,
20–30 g/L sodium carbonate.
Pad (approx. 75% pick-up) and dry at low temperature, 100–120°C.

The pre-treatment for acid dyes on wool and silk is quite different. The three main constituents are thickener, urea and an acid or latent acid (a substance that breaks down during fixation of the print to release acid). A tentative recipe is as follows:

150 g/L guar gum thickener, e.g., Meyprogum NP 8 (8% solution)
100 g/L urea
50 g/L ammonium tartrate solution
Pad (approx. 75% pick-up) and dry at low temperature, 100°C or below
Pre-treatment for polyester printed with disperse dye ink
10 g/L Cibatex AR (Ciba)
100 g/L sodium alginate medium viscosity, e.g., 6% Lamitex M5
Pad (70% pick-up) and dry.

Some pigment systems for inkjet printing require a fabric pre-treatment. The binder may be applied to the fabric and dried before it is printed instead of being included in the ink. Another system involves pre-treating fabric with a solution containing multivalent metal salts (e.g., magnesium nitrate). The ink contains pigments that are coated (or encapsulated) with resins (e.g., styrene acrylic resins) and colored by oilsoluble dyes.

8.9 TYPES OF DIGITAL TEXTILE PRINTER

Two types of printing structures which represent distinct methods of handling materials are:

- Batch process to place the fabric on a flatbed, either as a cut length or ready-made into a garment (e.g., SHIMA SEIKI's Flatbed Textile Printer SIP-160F3)
- 2) Continuous process by supply the fabric by pulling through from the roll (e.g., HP's Latex 335 Roll-to-roll Textile Printer)

For holding fabrics in place, the flatbed printer is equipped with an even surface with a vacuum device, which offers suction beneath the bed. This sort of printer is mainly utilized for printing cut-pieces of fabric individually (Ayau, 2018). It is possible to print patterns along the length or as a "placement" print in a particular location and on a ready-made item, like a t-shirt.

The other type of printer is the roll-to-roll printer, an entry-level printer exploiting a series of pinch rollers, grit rollers and a small motor for moving the fabric (Ayau, 2018). It is called "roll-to-roll" since, to move through the printer, a fabric roll releases a fabric length that is then printed and wound onto another roll, prepared to be stored, transported and used to continuously supply the fabric by pulling through from the roll.

8.9.1 DTG AND DTF PRINTING

Although both terms are used to describe printing on textiles, "DTG" printing and "DTF" are slightly different in meaning. Direct-to-garment (DTG) printing involves printing on textiles and garments using specialized or modified inkjet technology. Direct-to-fabric (DTF) printing involves spraying ink directly on a roll of fabric.

DTG printing is a process of printing on textiles using specialized aqueous inkjet technology. DTG printers typically have a platen designed to hold the garment in a fixed position, and the printer inks are jetted or sprayed onto the textile by the printhead. DTG typically requires that the garment be pre-treated with a PTM, or pre-treatment machine, allowing for the following:

- Stronger bond between garment fibers and the pigmented inks
- Lays down loose fibers to provide for a smoother substrate
- Chemically reacts with the inks to promote drying and curing

Since this is a digital process, the print is sharper and has a higher resolution, or dpi, than traditional printing methods such as screen printing. However, unlike screen printing, there is no long setup or clean-up process, and DTG has the ability to print just one single shirt for minimal cost.

Depending on the type of fabric, various inks can be used for DTG and DTF printing:

- Pigment ink is used for cotton fabrics.
- · Acid dyes work primarily with nylon and silks.
- Reactive dyes provide the best results on cotton and other viscose materials.
- Disperse dyes (sublimation) are almost exclusively used with polyester.

8.10 COLOR SIMULATION ON PAPER

Javoršek and Javoršek (2011) carried out research to establish whether a print on textile made with a digital printer produced by Mimaki (Mimaki Engineering Co, Ltd, Japan) can be simulated with a print on paper with an inkjet (Canon Image Prograf W8400) and laser printer (Canon Image Press C1+).

The following chemicals were used for cotton impregnation by Javoršek and Javoršek (2011):

- 50 g urea, 99% p.a. (Fluka, Switzerland)
- 15 g sodium bicarbonate, 99.7% p.a. (Fluka)
- 60 g Ludigol (1:5) (BASF, Germany)
- 400 g CHT alginate EHV 3 (4%) (Bezema, Switzerland)
- 475 g cold deionised water

After the impregnation, a steam fixation was performed for 8 min at 102°C.

The research results demonstrated that most colors (color difference up to 6) could be fairly successfully simulated on a Canon laser or inkjet printer, whereas slightly better results are acquired with an inkjet printer. The experimental prints on paper are cost and time saving, as the pre- and after-treatment of the textile substrate are, in comparison with paper, obligatory.

On the basis of simulated prints, a customer can decide on the color appropriateness for a selected pattern. The aim of the research was to establish whether longterm and expensive pre- and after-treatments can be avoided with the help of an appropriate development of printer profiles. The latter would be conducted through a print simulation on paper printed with a Canon laser or inkjet printer. Printing smaller collections and unique textile products requires higher flexibility of printers and, consequently, faster prepress and printing of color designs. With a broader use of design software, the expectations of textile and fashion designers, as well as of managers, are on the increase. In most cases, customers insist that the color pattern or shade on the textile substrate be exactly the same as on paper. However, the imaging process of final prints on the textile substrate is more complex, which results in deviations among the color shades on paper, computer screen and the textile substrate. By introducing color management into the field of digital textile printing, the time required for prepress could be shortened and the use of material could be reduced, which would lower the printing process costs.

Because of the high price of printing colors used in digital textile printing and the costs connected with the pre- and after-treatment of printed fabrics, an appropriate preparation of color patterns and simulated prints is of even greater importance. A print simulation in textile printing can be observed on a screen (i.e., soft proof) or conducted on another printer (i.e., hard proof), which enables – with appropriately built profiles for any device and their correct use – a simulation of particular color patterns on a different output device. In the investigation by Javoršek and Javoršek (2011), they focused on hard proofing, as soft copies are self-luminous, while hard copies are reflection images (Fairchild, 2005), the same as the original that they tried to simulate. Moreover, soft proofing excludes the feel and substance of a hard copy. In their investigation, the matching between the original (1,872 colors) and hard copy (simulation of 1872 colors) was investigated using the color difference equations CMC (1:1).

8.11 IMAGE QUALITY

The effects of printing direction, weave structure and finishing on image quality of lines inkjet printed on polyester woven fabric were investigated. The image quality for lines printed in the filling and warp directions are usually different due to asymmetric fabric structure. When ink drops impact yarns running transversely to the printing direction, wicking in the transverse direction may occur and reduce image quality. Due to the filling yarns floating over the warp yarns, line image quality parameters for 5-harness filling-faced satin polyester fabric are inferior to those for the plain and twill weaves used in this study. Applying acrylic resin finish to polyester fabrics can reduce the effects of the fabric structure and improve line image quality.

However, finishing with polyurethane resin does not improve line image quality. Ink type can greatly affect line image quality. Using the alcohol-based ink, the image quality is good, even for unfinished fabrics because alcohol-based ink is very volatile and the solvent evaporates before significant wicking occurs (Park et al., 2006).

8.12 COMPONENTS OF INKJET PRINTERS

Inkjet has three basic components, all of which need to work well in order to produce an acceptable output. These pieces are the printhead, the ink and the medium.

8.12.1 PRINTHEAD

The printhead is a component in a printer that houses ink cartridges. The printhead is the engine of an inkjet printer that puts ink to paper. A printhead is the element which puts the ink to the page to form the text or image being printed. The printheads are separate from the ink tanks and can either be replaceable or built into the printer itself.

Instead of using a membrane to build pressure and force ink out onto paper, heat is used to boil the ink and create an air bubble of ink vapor. The air bubble is then exploded as it is forced through the printhead's nozzle. Once the ink is expelled, the chamber rapidly cools down and the process repeats. Essentially the printhead contains an ink chamber, with a piezo electric actuator, made of a material such as Lead Zirconium Titanium (PZT). When an external electrical charge is applied to PZT it changes shape, forcing a drop of ink from the ink chamber and out through the nozzle.

Piezo-ceramic materials are ideally suited for small, electrically addressable systems (Kipphan, 2001), but depending of their deformation, piezo inkjet printing technology could be classified as bend (Tektroni, Epson, Biofluidix printheads), push (Hitachi, Dataproducts, Epson, Biofluidix printheads), shear (Tektronix, Sharp, Xaar printheads), and squeeze (Microdrop, Microfab printheads). Common characteristics for all these modes are that the printheads are heat resistant; spacing of droplets can be controlled by angling the line of nozzles along the printhead; and the most important feature is that the speed, size, and shape of the droplets can be controlled by adjusting the waveform of voltage applied to the nozzles.

A lot of companies produce piezo inkjet printing systems. For example: Brother, Epson, Fujifilm Dimatix, Konica Minolta, Kyocera, Panasonic, Ricoh, SII Printek, Toshiba Tec, Trident, Xaar and Xerox. This technique could be used in a very wide range of applications – not only for textile products.

With this system we have adaptable configurations to provide higher speeds and print quality, consistent drop velocity and drop volume, wide range of ink capability, high accuracy jetting, long-life printheads and more. Various printheads like Epson DX5 Series printhead, Fujifilm Polaris PQ-512/15 AAA, Fujifilm Dimatix StarFire SG1024, StarFire SG-1024/M-C, Konica Minolta 512, Konica Minolta 1024i Series, Kyocera KJ4B-QA and Ricoh GEN5 are available in the market (Kašiković et al., 2016).

Most printheads used in the textile industry are derived from the printheads created for and used in the graphic printing market. These types of printheads are perfectly suitable for printing on flat and even materials but are not ideal for the typical three-dimensional structures of textile fabrics. Nonetheless, this type of printhead is widely used in the textile industry.

Quite often, this causes problems such as printhead damage, high repairing costs and a lower printing quality which required a suitable solution. So, what is this suitable solution? How do you minimize printhead damage in digital textile printing?

The main frustration among textile printers has been frequent printhead damage due to their close position to the substrate. Printheads used in textile printing are based on the ones used in the graphical market. Within this market, only flat materials must be printed upon and the printheads are positioned close to the material. Because of the close position to the substrate, printhead damage occurs with thicker fabrics, resulting in high costs for textile printers.

With this technology, printers are offered both precision and a significantly greater jetting distance than other printheads. The nozzle plates in the Archer+ print bar are situated at least 4 mm away from the substrate surface, compared with the typical 1.5 mm nozzle-fabric distance offered by other printheads. This longer jetting distance greatly reduces the risk of head strikes and reduces replacement costs. Because of its high jetting frequencies, small drop size and high resolution, the Archer+ technology assures fine line details, blotches and tonal curves.

Printhead damage occurs easily when they are positioned close to the substrate and come in contact with the fabric. This shortens the lifespan of the printheads, and repairing printhead damage costs a lot of money. In most cases, the warranty from printer manufacturers and printhead manufacturers does not apply to printhead damage from the outside (Notermans, 2021).

8.12.2 COLOR CARTRIDGE

In printer the colors are filled in cartridges. In modern inkjet printing machine there are 8–16 cartridges fixed. About 6–8 colors are used in a printer. In some modern machines like Mimaki Tx2–1600, 10–12 colors are present. These colors are filled in the cartridge. These colors create the multi-color effect on the fabric. Every cartridge has 2,000–2,500 nozzles. Every cartridge has the capacity of about 300–500 ml. Every nozzle sprays the color drops and the volume per droplet of ink is 150–200 Pico liters (1 × 10⁻¹² L). Cycle time is limited to approximately 10,000 drops per second in the fabric. The cartridge function is fully controlled by a computer. High quality ink cartridges should be free from air, gas and dust.

All inks for the Dupont ArtistriTM 2020 are supplied in one- or two-liter cartridges. A plastic cartridge surrounds and protects a bag inside where the ink resides. Prior to filling the bag, the ink goes through a degassing process. Dissolved air in the ink is removed to improve the jetting performance of the printhead. Dissolved air in the ink can escape during the printhead's jetting process (this is called rectified diffusion) and cause it to misfire or misdirect the drop. The problem is similar with all piezo inkjet technologies and, if ink is not degassed, the printhead will have to be operated at lower firing frequencies, negatively affecting productivity of the printer (Raymond, 2006).

8.12.3 COLORANTS FOR INKJET PRINTING

Both dyes and pigments are used for inkjet printing which are:

- Dyes: soluble in water, water-organic solvent mixtures or soluble only in organic solvents or oils.
- Pigments: mostly organic and a few inorganics such as carbon black.

8.12.3.1 Merits/Drawbacks of Dyes and Pigments

The merits and drawbacks of both types of inks were discussed by Fryberg (2005):

8.12.3.1.1 Advantages of Dye-Based Inks

- High color brilliance
- Large color gamut
- Wide choice
- Higher penetration into layers
- Higher stability of inks
- Good abrasion resistance
- Good transparency
- Easy ink formulation

8.12.3.1.2 Disadvantages of Dye-Based Inks

- Lower permanency
- Prone to diffusion

8.12.3.1.3 Advantages of Pigment-Based Inks

- Good light stability
- No diffusion
- Good water fastness
- No interaction with the layer
- Suitable for printing on uncoated surfaces.

8.12.3.1.4 Disadvantages of Pigment-Based Inks

- Difficulty in ink formulation
- Poor ink stability
- Low color brilliance
- Prone to abrasion
- Prone to nozzle clogging
- Higher costs.

8.12.3.1.5 Desirable Properties of Dyes

The dyes selected for inkjet printing ink should have the following properties (Fryberg, 2005):

- High aqueous solubility (> 20%), low crystallization tendency
- No or poor diffusion irrespective of media used
- Good thermal and chemical stability, no kogation in thermal printers
- Should provide large color gamut, alone or in mixture
- No influence of physical properties by change in viscosity or surface tension
- High light fastness in all media, even in higher humidity, no catalytic fading
- No gas fading, no diffusion under humid conditions
- Purity: single compound, salt-free, no surfactant, no calcium ion
- Toxicity: registration required, eco-friendly, Ames negative, no skin sensation

(Kogation means gradual and inevitable degradation of the printhead of a heat-based inkjet printer from residual ink and/or impure water.)

8.13 CLASSIFICATION OF INK COLORANT

To choose a colorant type, fiber content and the fabric's ultimate use should be considered, along with a pretreatment that is compatible with the fabric and colorant. Textile printing inks are of five main types, which are formulated for compatibility with the inkjet process. Inks must be matched to fabrics according to fabric structure, use and fiber content.

There are two kinds of inks used to print on textiles: dye and pigments (Lee, 2018). Dyes are susceptible to being dissolved in water or fluid and used for coloring

textiles along with other materials which are permeable to fluids. On the other hand, pigments don't dissolve but rather are suspended in a carrier fluid as tiny particles (Lee, 2018). Inkjet formulation components differ in their detail but in general contain a colorant, solvent (carrier), water, surfactant, acid or alkali (Cie, 2015).

8.13.1 REACTIVE DYES INKS

Reactive inks can be utilized on the widest variety of fiber contents, including cellulosic, protein and synthetic nylon. They are most efficient for printing on fabrics that are derived from plants and are cellulose-based – like cotton, linen, rayon, hemp or jute – in which they create bright shades with remarkable colorfastness to washing and light (Lee, 2018).

They are referred to as reactive inks because they permeate the fabric and react with the fiber and the pretreatment chemicals under alkaline conditions to build a covalent chemical bond between the ink and fiber (Hawkyard, 2006; Lee, 2018). Pretreatment of fabrics is required before they are printed, and steaming, washing, and drying are needed after printing (Lee, 2018).

8.13.2 ACID DYES INKS

Acids are used to produce and apply acid dyes, which are renowned for printing not just protein fibers, such as wool and silk, but also nylon (Cie, 2015). They are anionic dyes soluble in water and have no reaction with the fiber for structuring covalent bonds, but rather, they penetrate to the spaces inside the fiber that are charged positively. Often, the shades obtained are deeper and brighter as compared to those of reactive dyes (Cie, 2015). To avoid wicking of the ink on the fabric, a pretreatment is needed. For fixing the dye, steaming after printing and drying is to be carried out (Chen et al., 2002; Yang and Li, 2003).

8.13.3 DISPERSE DYES INKS

Synthetic fibers like polyester, lycra and spandex that have low water-absorption attract disperse dyes as finely dispersed particles. Disperse dye inks are produced in two types by ink manufacturers; for transfer printing and direct printing onto the substrate (Hawkyard, 2006). The inks for transfer printing are a special kind of disperse dye, which is first printed on paper and then transferred to fabrics by using a heat press (Kan and Yuen, 2012). Disperse dye-based inks for inkjet printing have specific properties for fastness and can be printed on the substrate directly. High temperature steaming is required after printing and drying so that the dyes are fixed and give satisfactory print quality and colorfastness (Fan et al., 2008; Lee, 2018).

8.13.4 PIGMENTS INKS

Pigments are capable of being applied to fiber types or blends that do not have compatibility with dyes: cellulose fibers, protein fibers and nylon (Cie, 2015). Pigments are not soluble in water, and particles are unable to interact with fibers; they are instead mechanically held or fixed to the surface of fibers by using a polymeric binder as an additional component in the ink (Hawkyard, 2006). The binder forms a film or glue when cured after printing and holds the pigment particles on the fabric in place (Cie, 2015).

Applying pigment ink does not require pretreatment or washing after pigment fixation (Kan and Yuen, 2012; King, 2013). But still, pretreatment can improve the ink receptiveness, color intensity and color gamut of fabrics (Ding et al., 2019; Lim and Chapman, 2019).

In general, dye-containing inks are more stable than inks containing pigments, since the ink is thermodynamically stable (all components are dissolved in one solution), while in pigment inks, the system is only kinetically stable (Lin, 2004, King, 2013).

For all different types of inks, there are two very important properties: cohesion and adhesion. Cohesion describes the ink's ability to hold together; adhesion refers to its power to stick to a different material – for example, a substrate (Adams, 2004; Fromm, 1984). These two properties are common from the point of view of the physico-chemical nature of the pigment particles especially because their disperse ability is defined by the amount of energy required to distribute the individual pigment particles in a continuous medium so that each pigment particle is completely surrounded by the medium, and no longer makes contact with other pigment particles (Oyarzun, 2000).

8.13.5 NATURAL DYES

The potential use of a series of four natural dyes – annatto, cutch, pomegranate fruit rind and golden dock – for the production of environmentally friendly cotton prints through the formulation of suitable printing techniques was investigated by Savvidis et al. (2014).

The physical and rheological properties (pH, surface tension, conductivity and viscosity) of the water-based inks prepared were measured over a period of 90 days for fastness with evaluation of ink stability. The inks were used for the digital printing of cotton fabrics. The printed samples (directly and after fixation) were subjected to the standard wash, rub and light fastness tests commonly performed for printed textile fabrics.

The wash and rub fastness are relatively low, but they improve after fixation and are comparable with the wash and rub fastness of some low-molecular-weight direct dyes on cotton. Light fastness remains low before and after fixation. However, the results were promising, and this paves the way for the production of environmentally friendly inkjet inks to be used for the digital printing of cotton for niche markets through the formulation of suitable printing techniques.

8.14 INK COMPOSITION

One of the most important components of inkjet printing technology is color ink, which has an important influence on printing quality and reliability (Le, 1998). Color rheology and its chemical characteristics substantially influence the shape and size of drops and, consequently, directly influence the shape and size of the elementary dots on the print. Therefore, printing inks developed simultaneously with the development of printers. In consequence, various inks intended for different purposes and demands are used in digital textile printing; for example, reactive, acid, disperse dyes and pigments (Petrinic et al., 2001).

The ink used in digital inkjet textile printing is mainly produced on water-based dye (reactive, disperse and acid dyes) or pigments. Dye-based ink composed of four basic colors CMYK (cyan, magenta, yellow and black) plus 24 different kinds of special colors (such as golden, orange, red and blue) is widely used presently (Yang and Li, 2003).

The diameter of the nozzle is normally small, and the resolution requirement is high. That is why the viscosity, surface tension, purity, concentration, impurities content (salt) of the ink must be precisely controlled. The requirements for different nozzles are different relating to these parameters. This means a specific digital inkjet textile printer is required to use a specified brand of ink to ensure the normal operation of the device. The specialized inks are costly; this is responsible for the high cost of digital inkjet textile printing. Ciba Specialty Chemicals, Canon and DuPont applied plenty of patents for the inks used in digital inkjet textile printing (Yang and Li, 2003). These ink recipes are core secrets. The ink used in digital inkjet paper printing has been developed maturely, but the development of ink for use in digital inkjet textile printing is still at its initial stage. Although several large world class companies have launched proprietary series of inks, the quality of the ink needs to be improved to adapt to different nozzles

In spite of the widespread popularity use of pigments, reactive dyes still occupy a significant place in textile printing – especially when using thermal bubble inkjets. Reactive dyes are used for printing on cotton fabrics and their blends, as well as linen and silk. Prior to printing, a chemical pretreatment of a textile substrate is required, as, because of its viscosity and stability, the ink does not contain chemicals required for binding of dyes with fibers. After printing and finishing of the substrate, a chemical bond between the reactive dye and fibers is formed. Hence, color prints have excellent wet fastness.

The production process for inkjet printing of cotton fabrics with reactive dyes is different from conventional printing processes (Fan et al., 2002). In conventional reactive dye printing, the dye is applied along with alkali and all necessary chemicals in the form of a print paste. The print is then heat treated or steamed to fix the dye on the cotton, and finally washed to remove any unreacted dye, chemicals and thickener (Rudolph, 2002). But in inkjet printing of cotton fabrics, the fabrics need a certain pretreatment before digital printing due to the purity and specific conductivity requirements of the ink in the process.

Hence, it is impossible to combine the ink and pretreatment chemicals (Bohringer, 2000). As a result, most fabrics used in inkjet printing will require a pretreated coating to prevent the colors from bleeding on the fabric (Tincher et al., 1998). However, commercially pretreated cotton fabrics available on the market for inkjet printing are padded with pretreatment paste. For commercial reasons, the contents of this paste are not disclosed, resulting in very high prices for these fabrics.

Previous studies revealed that the pretreatment paste used for printing cotton fabrics with reactive dye contains alginate, alkali and urea (Perkins, 1999). A comprehensive study of the content of the pretreatment pastes together with the duration of steaming time showed that varying the amount of chemicals in the pretreatment paste and the steaming time duration could significantly affect the final color yield of inkjet-printed cottons (Yuen et al., 2003).

A further study (Yuen et al., 2004) revealed that the final color yield was not only influenced by each individual factor (i.e., amount of alginate, amount of alkali, amount of urea, duration of steaming time), but also by the interaction effects of these factors.

Yuen et al. (2005) analyzed the interaction effects of each factor on the final color yield of inkjet-printed cottons using an experimental design technique. The factor that has the greatest effect on the final color yield can be determined by examining the data with the graphic capabilities of a bar chart, called the Pareto chart. In this chart, the factor with the greatest effect is placed in the upper position, with the rest of the effects, in descending order, in the lower positions (Montgomery, 2001). Four different colors – cyan, magenta, yellow and black – were considered, and the influences of these factors on the four colors were studied.

From the Pareto chart analysis, the amount of urea used in the pretreatment paste is located at the highest position compared with all the other factors in each color. This implies that it is a dominant factor with respect to the color yields of the four different colors. The interaction plot of cyan shows that the final color yield of the inkjet-printed cotton attains maximum color yield with 20 g of urea in the pretreatment paste. However, for magenta, yellow and black, when the amount of urea in the pretreatment paste is more than 10 g, the color yield of the inkjet-printed fabric decreases. When the amount of urea used is further increased to 20 g, the color yield drops significantly, and is even paler than that when 5 g of urea is used. This drop in color yield with respect to an increasing amount of urea in the pretreatment paste may be due to the increased moisture regain of the fibers during steaming. Such a large amount of urea could enhance moisture absorption and also cause hydrolysis of the reactive dye during steaming.

From the Pareto chart analysis, the amount of alginate used in the pretreatment paste is located in the second position compared with all the other factors for cyan. This implies that it is another dominant factor with respect to the color yield of cyan. The interaction plots of cyan show that when the amount of alginate in the pretreatment paste increases, the color yield of the printed fabrics is correspondingly enhanced. In the pretreatment paste, alginate serves as a migration inhibitor to control the sharpness of borders in the final inkjet-printed pattern (Schneider, 2002). When the alginate concentration is too high, the fixation yield correspondingly decreases. One reason is that a thick film of alginate may act as a diffusion barrier for the dye, and so less dye will be fixed onto the fibers (Schulz, 2002).

From the Pareto chart analysis, the amount of sodium bicarbonate is located at the second position compared with all the other factors for magenta.

From the Pareto chart analysis, the duration of steaming time is located at the second position compared with all the other factors for yellow and black colors. The interaction plot shows that both yellow and black exhibit the best color yield when the steaming time is 5 minutes. When the steaming time extends to more than 5 minutes, the color yield with prolonged steaming may be a combined effect of both chemicals and steaming time.

Yuen et al. (2005) found that each of the factors – the amount of alginate, amount of sodium bicarbonate, amount of urea and steaming time – has its own contributing

effect to the final color yield of each color in inkjet printing. Based on the experimental design study, we have further confirmed that each factor has an interaction effect with the others, affecting the maximum color yield.

8.14.1 THICKENERS

A water-based ink was prepared from polyacrylate-based thickener. The physical and chemical properties of the polyacrylate-based thickener used for preparing the inkjet printing ink, as well as its printing effects on carpet, were investigated by Zhou (2017). Before printing, the properties of the ink, including its surface tension, electrolyte resistance, storage stability and percentage removal, were investigated. After printing, the efficiency of coloration of printed carpet and the fastness of printed carpet were studied. The results concerning the surface tension and percentage removal of printing ink show that the polyacrylate-based thickener printing ink is suitable for nylon carpet inkjet printing. Meanwhile, its storage stability and electrolyte resistance make it suitable for printing. The efficiency of coloration of printed carpet and the fastness of printed carpet satisfy the requirements of application at appropriate ink concentration and viscosity.

A typical inkjet pigment-based ink stoichiometry for two types of printer is given in Table 8.2 (Momin, 2008).

For high quality ink, the following steps may be followed:

- The inks may be filtered to nano-size for trouble-free prints.
- Every bath should be tested against specified standards to maintain consistency in color and quality.
- The ink should sustain long time firing up to 40 KHz.
- Every ink should be balanced in color. Each color is selected to ensure the greatest color space, in relation to the highest fastness achievable and related to the specific applications.

TABLE 8.2 Typical Composition of Pigment-based Inkjet Inks for CIJ- and DOD-Type Printers

Ink Component	CIJ (CMYK)	DOD (CMYK)		
Polymer emulsion	8–14%	8-14%		
Water	Balance	Balance		
Surfactant	0.05-1%	0.05–1%		
Humectants	5-10%	5-10%		
Conditioning agent	0.25-0.5%	0.0%		
Thickener	0.0%	0.5–5%		
Crosslinker	0.5–1%	0.5-1%		
Pigment dispersion	2–5%	2.5%		
Particle size	1 micron	1 micron		
Viscosity	3–5cps @ 25°C	10-14cps @ 25°C		
Surface tension	30–35 dyne/cm	30–35 dyne/cm		

Ink Properties	CIJ Binary	CIJ Multi- Deflection	DOD Piezo	Valve-Jet	Office Piezo	Office TIJ
Viscosity (cP)	1.5	1-10	5-30	100	1.5	1–3
Surface tension (dyne/cm)	>35	25-40	>32	>24	>35	>35
Maximum particle size	1	3	1	5	1	0.2
(Microns)						
Conductivity	Yes	Yes	No	No	No	No
(Micro Siemens)	>500	>100				

TABLE 8.3Indicative Inkjet Ink Requirements (Xu et al., 2005)

The tail or ligament that comes up with the ink drops during droplet formation is required to be absorbed by the head during its fall, otherwise several drops may form and land in different places on the substrate, which may impair print quality. There is still a possibility of spatter as the drop jets on to the substrate even if heads and tail merge; so, ink developers are required to keep a balance between controlled dot gains and overspreading. Viscosity, surface tension and drop size are key variables to maintain this balance. Moreover, the pressure and molecular weight of the gas through which the drop falls play a vital role in addition to the viscosity (Xu et al., 2005). Table 8.3 gives the indicative requirement for accurate jetting for various inkjet printing machines.

8.14.2 RHEOLOGY OF INK

Rheology is the study of the flow and deformation of matter (Oyarzun, 2000; Żołek-Tryznowska, 2016). Inkjet inks for textile printing should exhibit Newtonian behavior, determined by examining the shear stress and viscosity of the inks under various shear rates (Samane et al., 2016). The ideal ink should exhibit constant viscosity as shear rate is increased while the relationship between shear stress and shear rate must be linear (Żołek-Tryznowska, 2016). The main parameters that govern the ejection process of inkjet printing are the surface tension, the viscosity and the rheological properties of the ink. The rheology of ink is an extremely important parameter because it aids droplet formation through the nozzle in a controlled manner for any given inkjet technology (Żołek-Tryznowska, 2016; Dharmesh et al., 2005).

8.15 DYE-SPECIFIC PRINTERS

Ink chemistries and respective inkjet printers are listed by Shell (2016) as follows:

Acid Dyes

- Organic acid salt (sodium or ammonium)
- Affinity for natural protein fibers like wool, alpaca, mohair; also effective on silk and nylon
- Does not work on other synthetic fibers

Acid Dye Printers

- DigiFab (StampJet)
- Konica Minolta (Nassenger)
- SHIMA SEIKI (SIP)
- Expand Systems (Diva)
- Mutoh (1628TD, 2628TD).

Reactive Dyes

• Most used method for the coloration of cellulosic fibers (cotton, Rayon, hemp, linen, bamboo)

Reactive Dye Printers

- Mimaki (TX500)
- Expand Systems (Diva)
- Mutoh (1628TD, 2628TD)
- d.gen (Teleios Grande, Hexa)
- DGI (FD1908, FD1904).

Disperse

• Limited to polyester

Disperse Printers

- Low energy: Epson, Mimaki, Mutoh, Roland, etc.
- High energy: ATPColor Srl, d.gen, DigiFab, Durst, EFI, Expand Systems, Hollanders

Pigment

Most suitable for coated fabrics

Pigment Printers

- d.gen, Expand Systems, Kornit
- MS Printing Solutions SRL
- Reggiani Macchine SpA.

Latex

- Water-based ink using latex as the pigment binder
- Comes out of the printer fully dried and "ready-to-use"
- Eco-friendly vs. solvent-based ink
- "Graphic" applications only (backlit, banner, signage)

Latex Printers

- Mimaki (JV400LX)
- HP
- Low-volume: 110, 310, 330, 360, 370
- Mid-volume: 850, 3100, 3500

UV-Protecting Printer

- Uses acrylic monomers with a photo-initiator
- 100% solids
- "Graphic" applications only (backlit, banner, signage)

UV Printers

- EFI
- Durst
- Mimaki
- Roland

Depending on the average production rate, the inkjet printers can be classified into four categories (Shell, 2016), namely:

- Category I: 5-30 Linear m/hr
- Category II: 31-100 Linear m/hr
- Category III: 101-400 Linear m/hr
- Category IV: Single Pass, 20-100 Linear m/min.

8.15.1 DESIGN POSSIBILITIES

The widespread adoption and rapid growth of digital inkjet printing is creating a whole new world of opportunity, opening up totally different possibilities in terms of design options, production methods and, ultimately, profitability at every stage of the process chain. And the design opportunities for inkjet-printed goods are enormous (Owen, 2003).

At present, most of the research are about dyes or inks (Yoon, and Choi, 2008; Kim et al., 2009), fabric pre-treatment, surface modification (Kan, 2007; Phattanarudee et al., 2009) and so on, with the aim to improve the quality of inkjet printing. But little attention has been paid to digital textile pattern design. There is no doubt that printing is an art and that pattern design plays an important role in textile printing. A beautiful pattern can admirably induce infinite artistic charm in a textile.

During the traditional course of design, the patterns are first composed by professionals in their minds, and then manifested onto the paper or other media. The composition relies on the viewer's imagination, therefore, pattern creation and modification processes can be very cumbersome. Also, it is difficult to produce numerous and various designs in a short time. So, pattern design has become a bottleneck in modern textile production.

Based on a kind of nonlinear scientific technology – weak chaos – Xu-Hong and Jian-Hua (2010) developed a parameterized program to generate various Uniform Stochastic Web (USW) images, and proposed the methods of transforming mapping functions to obtain abundant colorful digital images for inkjet printing. The ways to edit the images to be textile patterns were also explored, and the patterns were successfully transferred to the textiles by an inkjet printing machine.

8.16 EFFECT OF FABRIC STRUCTURE

The structure of warp knitted polyester (WKP) fabric had a significant effect on the diffusion behavior of disperse dye ink and printing accuracy, especially its unique loops and underlap structure. The ink volume also had a great influence on the diffusion behavior of ink. When the droplet size was less than 0.2 μ L, the results showed that the diffuse width of disperse dye ink on WKP fabric in the wale direction was larger than that in the course direction, whereas when the droplet size was greater than 0.2 mL, disperse dye ink diffused mainly along the course direction. The choice of pretreatment agents for different compact fabrics was also different. SA was selected as the pretreatment agent for the thin WKP fabric. For thick WKP fabric, the cationic modification (CM) agent had a better performance on the anti-bleeding property. The CM pretreated 230 g/m² fabric produced much better color quality and printing accuracy as compared to the untreated and pretreated fabric using PVA or SA. The pretreatment agents had no effect on fastness properties of WKP fabrics compared with untreated fabric (Zhao et al., 2017).

8.17 ECO-FRIENDLY CLEANER PRODUCTION

With the recent quest for cleaner productions, special attention has been paid to inks that eradicate waste emissions, and reduce energy input in manufacturing. The reduction or eradication of volatile organic compounds (VOCs) from inks has received a major boost (Niaounakis, 2015; Hawkins, 2003). So far, water-based inks have proven to be the solution to reducing VOC emissions because these inks are generally cheaper, reduce atmospheric pollution, have less solvents, lower fire risks, produce less print odor and are easier to wash-up on printing equipment (Ali, 2008). Water-based inks with little or no VOCs have been developed for both thermal and piezoelectric inkjet applications (Yeates et al., 2011; Ujiie, 2006). It has been commonly used in home and small office inkjet printers like the Hewlett-Packard Desk Jet series, Canon BJC series and Epson Color Stylus series. These inks have superior advantages due to less bubble formation, which is common in most thermal inkjet printers for digital textile printing (Provost, 2010; Tyler, 2005). Water-based inks are easy to clean from printheads and ensure less nozzle clogging once the rheology of the ink is Newtonian (Xu et al., 2005; Żołek-Tryznowska, 2016). The composition of water-based digital textiles inkjet inks is stoichiometrically formulated to meet specific requirements of substrates. Table 8.3 shows a typical composition of water-based inkiet ink for printing textiles.

There is no universal stoichiometry for all colorants; the formulation normally varies depending on the specific desire of the chemist. For instance, a study conducted by Wassim Kaimouz in 2010 gave a similar formulation to the one by Le (1998) for bi-functional reactive dye water-based inkjet inks.

Important properties of inkjet inks described by Tawiah, Asinyo and Howard (2016) are described subsequently.

8.17.1 VISCOSITY

Schulz asserts that viscosities must be adjusted in such a way to produce a flow that is high enough to avoid starvation at the nozzle as well as not so high that it flows out

Component	Function	Concentration (%)
Deionized water	Aqueous carrier medium	60–90
Water-soluble solvents	Humectants, viscosity controller	5-30
Dye or pigment	Provides color (Chromophore)	1–10
Surfactant	Wetting agent, penetrating agent	0.1-10
Biocide	Prevents growth of biological organisms	0.05-1
Buffer – 0.5	pH controller	0.1
Other additives	Chelating agent, binder, defoamer etc.	.>1

TABLE 8.3 General Composition of Water-Based Inkjet Inks (Le, 1998)

on the nozzle plate. Viscosity greatly affects the size of the droplet and drop speed. If drop speed is too low, then there is a possibility of drop deflection on its way to drop formation on the substrate by air currents; thus, affect plays a very important role in increasing the reliability and quality by controlling the drop formation and break.

If the molecular weights of viscosity modifiers are very high, then jet break-up becomes difficult due to their elasticity (Syed, 2016). There are several viscosity modifiers available, of which glycerol, polyethylene glycol of molecular weight 200 (PEG200) and carboxymethyl cellulose (CMC) are some examples. Polyethylene glycol (PEG) is a synthetic polyether, which is available in a range of molecular weights. Low molecular weight PEG is a clear, viscous liquid product with molecular weight lower than 10,000, whereas polyether with molecular weight higher than 10,000 is known as weight 200 (PEG200) and carboxymethyl cellulose (CMC) are some examples polyethylene oxide (PEO) (Bin Bao and Song, 2016). Similarly, CMC is used as a viscosity modifier thickener, and to stabilize emulsions in various products including textile printing inkjet inks (Heinze, 2005; Lii et al., 2002). It is also a constituent of many non-food products, such as toothpaste, laxatives, diet pills, water-based paints, detergents, textile sizing and various paper products (Magdassi, 2010). It is used primarily because it has high viscosity, and for its nontoxicity.

Glycerol is also colorless viscous solution belonging to the alcohol family of organic compounds (Rosen, 2004). Natural or native glycerol can be obtained as a byproduct in the conversion of fats and oils to soaps, whereas synthetic glycerol can be produced from propylene. The fastest growing method of producing glycerol is from the conversion of fatty acid methyl esters for biodiesel, where 100 kg of glycerol is formed in 1,000 kg of biodiesel (Spinelli, 1998).

These viscosity modifiers help inkjet textile printing ink maintain stable viscosity, which ensure constant jetting pressure and less nozzle clogging (Niaounakis, 2015). The quantity of viscosity modifiers used in a particular formulation is dependent on the type of colorant being used, the kind of inkjet machine and nozzle (i.e., DOD or CIJ), and the target textiles material to be printed (Ujiie, 2006).

8.17.2 SURFACE TENSION

Surface tension is one of the most important properties of inkjet inks for textile applications. It has been suggested that surface tension of ink is a primary factor

determining droplet formation and spreading on the substrate upon contact (Magdassi, 2010). Ideally, inkjet inks should have a surface tension in the range of 25–60 dynes/ cm (Ujiie, 2006.). Surface tension can be controlled by using surfactants and by selecting proper solvent compositions. For example, adding propanol to water will cause a large decrease in surface tension, from 72.8 dyne/cm to below 30 dyne/cm, depending on the propanol concentration. Surface tension of the inks must be in the range of 25-60 dynes/cm, so that it wets the capillary channels, flows through the nozzle and forms the droplets correctly to ensure proper jetting (Le, 1998; Ali, 2008). Surfactant – also called surface-active agent – is a substance such as a detergent that, when added to a liquid, reduces its surface tension, thereby increasing its spreading and wetting properties. In the dyeing of textiles, surfactants help the dye penetrate the fabric evenly (Mallinson, 1999). They are used to disperse aqueous suspensions of insoluble dyes and perfumes. The surfactant possesses two different chemical groups, one compatible with the liquid to be modified, and the other having a lower surface tension. Typically, 1% or less is sufficient enough to efficiently lower the surface tension of inks, coatings and paints (Mallinson, 1999).

Fluor chemicals, silicones and hydrocarbons are common categories of surfactants, which are capable of lowering surface tension of any material and are the most efficient wetting agents. Silicones are next in efficacy and are lower in cost. Certain types of silicone, however, can become airborne, causing serious environmental problems and as well as contaminating the substrate (Flick, 1993).

8.17.3 HUMECTANTS

Humectants are mainly used to control or limit the evaporation of the inks (Pekarovicova, 2016). Humectants such as glycols and alcohols act as hygroscopic agents to remove moisture from the air during printing or in the idle position of printer, thus preventing clogging of printheads.

8.17.4 FOAMING AND DEFOAMERS

A severe problem in ink performance is the presence of bubbles in the ink. Foaming is often observed in inks, which contain surfactants and polymers. A common solution to this problem is addition of a defoamer, which is a molecule that causes breakdown of foam. The defoamers act by reducing surface tension in a local area to very low values, causing these local areas to be thinned rapidly (example: amyl alcohol); and by promoting drainage of liquid from the lamellae (example: tributyl-phosphate, which reduces surface viscosity) (Kelvin, 1977).

8.17.5 DIELECTRIC PROPERTIES AND CONDUCTIVITY

Ink conductivity is also important for printing systems in which ink recirculation sensors are triggered by conductivity signals obtained by contact of the sensor with the ink (Blank et al., 2004; Pekarovicova, 2016). These properties are essential for continuous inkjet inks, in which the droplets are deflected due to an electrical field. The charging ability is obtained by adding charge control agents like electrolytes and

ionic surfactants, which are soluble in the ink medium. The conductivity should be very precisely controlled such that any slight variation in conductivity during storage should be prevented. Variation in conductivity may occur due to salt precipitation, as well as interactions with other components and the wall of the container (Bin Bao and Song, 2016; Gregory, 1991).

8.18 COLOR MANAGEMENT

In a digital textile printer, the colors are mixed or dithered directly onto the fabric, and almost all systems use the four base colors, CYMK. Some systems, such as the 2020, use up to eight colors. The color information is in a digital file and must be converted to the correct color by mixing or dithering the colors available in the printer.

The most common color data format for printers is $L^*a^*b^*$. L^* is the lightness ranging from 0 (dark) to 100 (light). The a* value defines the colors of a red-green axis and b* defines the yellow-blue axis. Using a spectrophotometer to measure the colors in $L^*a^*b^*$ space, a printer's color gamut can be determined and a lookup table can be created. The lookup table tells the printer what colors to mix or dither to create the required color. This is measured against a color standard such as a CIELAB reference. The user can print a "color book" for a visual representation of the color gamut.

One of the most difficult challenges is to match the process color of the printer to the spot color of the screen system. Digital printers are not economical for printing long run lengths. After sampling and short runs are complete, a large production run may need to be done on a rotary screen printer. If the color gamut of the digital printer is outside the available spot colors or vice versa, a color match may be difficult to achieve. The DuPont ArtistriTM Color Management System has been optimized to deal with these issues.

If one were to take a print design and digitally print that same pattern from a variety of different printers using the same type of ink sets and printing them on the same cloth, the color results would vary widely. The results might even vary from day to day using the exact same printer and inks.

Digital textile printing color management software must answer three key questions:

- First, what is the color gamut (range of printable colors) of the system taking into account the printer, inks and fabric used?
- Are the desired colors within the digital printer's color gamut?
- And last but not least, how can the system produce all of the colors that are within the color gamut?

It is important to understand which colors are attainable within the limits of specific printers and ink sets. If a printer is incapable of producing a desired color, no amount of color management can make it possible. In addition, there are some colors that can be displayed on an RGB monitor, but not printable using a CMYK device, and vice versa (CMYK representing the cyan, magenta, yellow and black inks used in process color printing).

Some of the first digital printing systems introduced to the textile industry using CMYK process printing were originally developed for the graphics and paper printing industries. These systems were not well received because the color gamut obtainable in CMYK is considerably smaller than the gamut of spot color inks used in conventional rotary screen printing of textiles. Digital textile printers are developed, tested and marketed with the use of specific ink sets in co-operation with ink vendors offering inks specially formulated for the textile market.

Color management and RIP software manage color by creating profiles or characterizations specific to the printer, ink, fabric and any post-processing, such as steaming and washing. All of these variables have an impact on color and each variation must be profiled for accurate color match. When a design is printed, a profile is selected based on the printer/ink/media combination to ensure that the colors in the original design or target colors match the digitally printed output.

The process of creating a profile or characterization of a digital printer begins by printing out a linearization file of the inks in the printer, typically from 0-255 saturation. Data on ink density limits can be gathered at this stage as well. These color targets are measured by a spectrophotometer. Next, a number of color targets are printed and measured to map the color space of printable colors. From all these data points an algorithm is used to calculate the color space, and the profile is complete.

Various software packages offer different levels of profiling capabilities, from supporting standard ICC profiles created in third-party profiling software, to vendor supplied profiles, to end user capability to create custom profiles using proprietary color systems.

Textile-specific software is needed to handle textile design images, including flat and continuous tone designs and separation files, in addition to color management. Important software features for digital printing of textiles include:

- Accept textile industry file formats from CAD design and screen separation programs: CST, MST, PUB, GRT, SEP, SCN, XPF, etc.
- Accept common graphic file formats: TIFF, Indexed 8 bit TIFF, PSD, EPS, AI, BMP, TGA, etc.
- Print layout functions such as step and repeat, design coordinates and colorways, color chips, multi-image placement, scaling, rotating, spooling or batching, etc.
- · Manage expanded ink sets beyond CMYK, depending upon printer
- Ink control functions; manage higher ink densities required for color saturation of fabric
- Color catalogs, color palettes, and/or Pantone Textile Color System
- · Profiling: supplied by vendor or custom profiling capability
- · Color gamut visualization and comparison to see if target color is attainable
- Screen print simulation features if digital output needs to match to production
- Capability to link color data to the textile mill's color kitchen.

The color management and RIP software options available to the textile industry reflect a growing market and growing acceptance of digitally printed fabric for proofing, sampling and short-run production. It is no longer enough to be able to print

fabric digitally; the industry is requiring color matching and management throughout the complete design workflow, from scanning to calibrated monitors, to spectrophotometers, to the digital printer. Future hardware and software developments for the textile industry may include combinations of spot and process printing systems, and customization of a wider range of ink colors that can be selected depending upon the color space requirements of the design to be printed. With all of these future developments, the color management and RIP software will be the engine that drives these systems (Gordon, 2006).

8.17.6 PH AND ELECTROLYTES

The pH is important in water-based inks and may significantly affect the solubility of the various components and the stability of the dispersed pigments. The solubility effect is often observed when the ink contains a polymeric binder such as acrylic resin, which is insoluble at low pH (Campbell, 2008). Colloidal stability is affected by the zeta potential of the particles: the higher the value, the higher the stability (Magdassi, 2010; Ali, 2008). He further stated that adsorbed polymers, which are effective while they are charged, achieve stabilization; the charge is usually dependent on the pH of the system. Therefore, some ink formulations contain buffers, which make the ink less vulnerable with regard to slight variations in ink components and water quality (Raymond, 2006).

8.19 COLOR MATCHING

Digital transfer textile printing (DTTP) differs from conventional digital textile printing (DTP) in that images are not printed directly on the fabric but printed on a decal paper first and then transferred onto the fabric by the heat press process. Although it takes a long time to print decal papers, the overall printing process is shorter than that of DTP, because DTP requires complex preparatory and finishing processes.

In general, four kinds of basic ink are used in DTP, namely cyan, magenta, yellow and black. Additional colors, such as orange, topaz, dark cyan, dark magenta and dark yellow, can also be used to enhance the color expression. As the color is one of the most important elements in product design, accurate color communication is necessary. However, a color printed on the fabric usually looks different from how it is seen on the designer's display monitor. This is because the same color may appear differently according to the characteristics of the display device, illumination, observer, fabric surface property and so on.

A color matching algorithm was developed (Hwang et al., 2015) to solve the color mismatch problems encountered during the digital transfer textile printing process. To match the colors between display and fabric, standard red, blue, green (sRGB) and International Commission on Illumination (CIE) color systems were used. For an affordable color matching process, sRGB values of printed fabric were extracted by a general flatbed scanner instead of an expensive spectrophotometer. Extracted sRGB values and originally intended target sRGB values were used as input and output values to form artificial neural networks and multiple regression equations to establish the relationship between those values. To verify the color matching

algorithm, a total of 100 random color samples were printed, scanned and analyzed. Both methods showed good correlations between input and output color values, which implied that the color matching algorithm developed in the study by Hwang et al. (2015) improved the color correspondence between the original design and its printed results.

8.20 JUST-IN-TIME PRINTING

The textile printing industry is a highly competitive industry. Risk consideration, timing and inventory management are critical for winning in the conventional textile printing process. The terminal demand of textile products is changing to "smaller quantities" and "shorter manufacturing cycles" gradually. Digital inkjet textile printing is the new method to meet market change. Wantuck (1989) explained Just-In-Time (JIT) – a production strategy to balance quality and productivity. He summarized JIT into seven principles:

- 1) Produce exactly what customers demand
- 2) Control waste
- 3) Produce one-at-a-time
- 4) Continuous improvement
- 5) Respect people
- 6) Zero contingency
- 7) Provide long-term emphasis

JIT means delivered in a timely fashion and in direct response to market demands for the textile printing industry. Compared to conventional textile printing, digital inkjet textile printing has the flexibility to adjust printing length according to individual customer specification and changing market demand. It minimizes the impact of time and cost changeover caused by new designs or colorways by simplifying the design stage (sampling, strike offs). Multiple printing works can be done through one digital inkjet textile printer. The printer can switch design, colorways and print types quickly. Since digital inkjet textile printing is still a developing technology, it offers the possibility of continuous development by promoting technology and augmenting experiences. Digital inkjet textile printing technology utilizes individual creativity and opens the door for a unique design; it meets the principle of "respect people" in this way. By the decrease of waste and increase of production flexibility, plans for dealing contingency – such as excess inventory – can be avoided.

Finally, the application of digital inkjet textile printing is a long-term strategy, and it provides "prints on demand" methods (King, 2006; Fang, 2011).

In the past, manufacturers first forecasted the trends of textile design and customer demand. Then they designed patterns and printed in different fabrics as choices for retailers. Retailers selected products from limited options to put in the shop and wished their customer would like what they selected. Nowadays, the application of JIT in the supply chain turns a manufacturing driven economy to a demand driven economy. The development of digitization becomes a paramount factor to realize the "prints on demand" principle (Fang, 2011).

8.21 ENVIRONMENTAL IMPACTS OF DIGITAL PRINTING

Digital printing is more ecologically friendly than offset printing or screen printing. No ink or dye is wasted with digital printing since it is all consumed in the print. There are no plates, blankets or screens to be washed off, eventually ending up in our environment, which does damage to our planet. The fact is, switching to digital printing saves wasted resources and time. Plus, compared to analogue, or conventional printing, digital printing is a far more sustainable option since it uses less energy, produces less waste, and has a smaller carbon footprint overall. There are no screens or plates to produce (as for screen printing or rotary printing) and so less setup equipment is needed. Printing direct to fabric means less wasted surplus ink (unlike dyeing) through precise application of the artwork.

Conventional textile printing needs to use a large amount of water to wash the screen during the engraving process. Textiles, after printing, need to be washed and soaked to remove the floating color. The effluent water contains dyes; chemical additives cause a serious water pollution problem. Conventional textile printing uses more energy and water resources. The traditional textile printing industry is a highly pollutive and high resource consuming industry. The unique advantage of digital inkjet textile printing has revolutionized the concept of the traditional textile printing, because the digital inkjet textile printing needs only dye – thickener and other auxiliaries are not used. There is no wastage of dye; whole dyes go onto the fabrics, resulting in less polluted water. Digital methods used in textile printing moved the textile industry from a labor-intensive to a technology-intensive industry. The textile industry can achieve clean production by applying digital DOD inkjet printing technology. The whole process excludes the emission of wasted ink and noise pollution.

There is little published research on the environmental impacts of digital printing. The analyzed literature indicates that digital methods have a higher energy and ink/ toner consumption than mechanical methods, but their chemicals and water consumption and waste output are lower. Paper consumption and air emissions are difficult to assess due to lack of data. More research is needed to obtain a better and more reliable understanding. Environmental indicators used in earlier studies of printing can be used for digital printing as well. These include physical and monetary input and output figures like energy and materials consumption, emissions and waste output. The suitable functional units are the weight and the surface area of products – for example, tons of printed products or million duplex printed A4 sheets.

When the lifetime and usability of printed textile product is assumed to be the same for both printing methods, digitally printed textile products have slightly smaller environmental impacts than screen printed textile products. Screen printing is more dye, energy and water consuming whereas digital printing needs fabric pre-treatment, which in turn requires raw materials and energy and causes environmental impacts. While the lifetime and usability of printed products are assumed to be the same for both printing methods, digitally printed products have slightly smaller impacts than screen printed products in studied environmental impact categories.

When smaller printing batches are studied, digital printing causes less greenhouse gas emissions than screen printing. Digital printing is better for small batches also because of the flexibility of the system and fewer amounts of production waste. The water consumption of textile printing processes (with a gate-to-gate approach) is much higher for screen printing, the main reason being washing. There are new types of technological solutions to reduce water consumption in washing.

Water quality of textile printing effluents is influenced by nitrogen emissions while all the other quality parameters have decreased over the past ten years period at the beginning of the twenty first century.

The Water Availability Footprint (WAF) results show that the digital printing and screen printing do not differ much in water requirements – a study conducted in Finland, where there is good availability of water (a competitive advantage). The significance of water consumption would increase if the textile manufacturing instead occurs in an area of high water stress (Kujanpää and Nors, 2014).

8.22 3D PRINTING

3D printing, also known as additive manufacturing, is the general term for those technologies that, based on a geometrical representation, create physical objects by successive addition of material according the ISO/ASTM 52900:2015. The history of 3D printing begins in 1981 with Dr. Hideo Kodama's patent application for a rapid prototyping device. In this system, a vat of photopolymer material is exposed to a UV light that hardens the part and builds up the model in layers. Other attempts have been made by other engineers but the first patent was taken by Charles Hull for the technology stereolithography (SLA). 3D printing is the opposite of traditional manufacturing technology. Here, the object is created by placing successive layers of material with a given thickness, generated by the slicing software (Spahiu et al., 2020).

3D printing shows advantages in producing complex geometries which can be difficult to create with common industrial production or to produce objects in aeronautics or other situations where no other production machines are available.

The fashion industry has adapted these technologies to revolutionize their brands. Applications in the textile industry are presented in fashion shows by well-known fashion designers. In the academic arena, case studies of 3D printed fabrics are developed and presented by different authors. A lot of work is being done to develop materials similar to textile fabric, due to the unique characteristic of textiles as comfort, flexibility, and so on.

Recycled materials such as nylon, TPU (thermoplastic poly-urethane) or PLA (polylactic acid) for 3D printers have attracted attention of fashion designers to develop 3D printed textiles (Abdullah, 2019), assisting waste reduction by material recycling. 3D printed fashion shows are not new for a number of fashion designers who see this technology as the future. One of the challenges to overcome is the comfort and the flexibility of these 3D printed textile fabrics. Researchers have shown great interest in designing and 3D printing various structures. Starting from traditional textile structures translated to digital code, different structures are tested to produce 3D printed textile fabrics (Melnikova et al., 2014) similar to knitted or woven structures (Young, 2019), where knitted structures are more flexible. Moreover, by changing the geometry and size of the print, bending and deformation properties of 3D printed structures can be manipulated (Gürcüm et al., 2018). As the nozzle of 3D printers behaves like the spinneret of a melt spinning machine, by controlling the movement of a fused deposition modeling (FDM) printer head, soft and flexible

textile structures can be produced (Takahashi and Kim, 2019). Printing with fibers to create textile structures is proposed for further studies. Modeclix, a system of additively manufactured links, allows garment production by simply adding or removing links to adjust the size and shape of a garment (Bloomfield et al, 2018). Using the FDM technology, a new method for 3D printing textile-like surfaces indicates a reduction of the steps for garment production (Uysal and Stubbs, 2019). Nevertheless, there are limitations compared to other types of 3D printing technology, such as SLS (selective laser sintering) or SLA, which uses powder or liquid types of materials. An FDM-type 3D printer can only use solid materials such as acrylonitrile butadiene styrene (ABS), PLA and TPU (Bandyopadhyay et al., 2016).

Apart from fashion applications, within the academic area, 3D printing researchers at the University of Maryland (USA) have developed a fabric structure operating as a personal, powerless air conditioner. Another case of research from MIT (Massachusetts Institute of Technology) has focused primarily on structure by modeling fabric after protein collagen using TPU material. They believe their fabric could have many applications in the medical field as well as in textiles, since 3D printing enables the creation of limitless shapes and sizes. The case of "space fabric" is another example of advances made in 3D printing to fabrics that have four essential functions: reflectivity, passive heat management, foldability and tensile strength (Landsou, 2017). These studies show the increased impact of 3D printing for several applications. Furthermore, in the case of 3D printed fabrics and garments created, consumer behavior related to this new technology replacing traditional processes of garment production plays an important role. Thus, consumer perceptions of 3D printed dresses have been studied by different authors and the results are different. One of the studies done for a small group indicated that participants were more interested in accessories than in clothing due the low flexibility of materials used for 3D printing, which was different from the other study which gathered positive answers regarding 3D printed clothing. Apart from 3D printed textiles, a combination of 3D printed geometries on textile fabric shows interesting potential. One of the most important benefits of 3D printing - not only from the fashion design aspect - is the functionality added to these textiles for various applications. Studies conducted by different authors present the combination of 3D printed geometries on textile fabrics (Spahiu et al., 2017a; Narula et al., 2018) by showing the possibilities and technical limits of these novel composites (Martens and Ehrmann, 2017). The case of self-forming structures printed on fabrics shows attention for its significant functionality and aesthetic value (Jing and Yingchun, 2019). One of the issues encountered is the adhesion between both materials. Investigations of fabric pre-treatment have resulted in significant modifications of the adhesion force (Meyer et al., 2019). In addition, printing parameters such as nozzle temperature, printing bed temperature (Spahiu et al., 2017b) and infill orientation have a significant impact on the adhesion force. Besides, fabric properties such as areal density, yarn fineness, fabric thickness and fabric handle show a positive correlation with adhesion force. Comparison of test methods can help in standardizing the research of 3D printing on textiles. In the work by Spahiu et al. (2020), structures with different geometries are designed using Tinkercad, a free modeling software from Autodesk, Inc. For 3D printing of 3D models, an Orcabot XXL (Prodim International) FDM printer produced in the Netherlands is applied. The 3D printer is equipped with Orcabot Repetier Host V1.0.6 software where the 3D CAD models are imported and sliced.

After evaluation of aesthetic, flexibility, and difficulties encountered regarding viscosity of materials during the 3D printing process, which in various cases resulted in failure of the 3D printed model, the geometrical structures chosen for garment production is an arrowhead structure with negative Poisson's ratio (NPR).

3D printing as an innovative technology implemented in different areas of production has gained an increased interest in the fashion industry. The work presented here shows another application for garment production using the FDM technology, which is less expensive compared to other 3D printing technologies. Due to the flexibility of FilaFlex material, the final dress is easily wearable. Nevertheless, there is still a lot of work to be done regarding materials, as they are still far away from the properties of textile materials. 3D printed garments are seen as a complimentary to fashion products. In the survey conducted to evaluate consumer behavior for 3D printed garments, the majority of respondents believe that 3D printing will be beneficial for garment production. This can be related with the wastage of garments and the possibility to produce personalized garments even at home.

8.23 3D PRINTING ON TEXTILES

The technology of 3D printing is taking over manufacturing sectors around the globe. Since its inception in 1986 through now, 3D printing has taken over many things around us – and most of us are not aware of this. Very a few of us know that most cars are first prototyped using 3D printing before they get launched.

3D printing is the process of creating three-dimensional objects through joining or solidifying material under computerized control. In this process, a computer-aided design is converted into a 3D object by printing the material layer by layer and joining them in the form of a cohesive object. This technology is being extensively used both in prototyping and additive manufacturing.

Three-dimensional (3D) printing is a booming industry that has made rapid prototyping and small-scale manufacturing easier, more accessible and affordable, and is used in aerospace, architecture, automotive, medical and dental fabrication, defense, and commercial and consumer product manufacturing industries (Ryan and Hubbard, 2016). Advantages of using 3D printers include less time from design to manufacture, material waste and energy consumption.

Three-dimensional printing, also called additive manufacturing, is a "process of making three dimensional solid objects from a digital file". This is a method of creating a three-dimensional object layer-by-layer using a computer created design. As a result, 3D printing creates less material wastage. 3D printing is used to produce architectural scale models, enabling a faster turnaround of the scale model and increasing the overall speed and complexity of the objects produced.

In an additive process an object is created by laying down successive layers of material until the object is created. Each of these layers can be seen as a thinly sliced cross-section of the object. 3D printing is the opposite of subtractive manufacturing, which is cutting out/hollowing out a piece of metal or plastic with, for instance, a

milling machine. 3D printing enables to produce complex shapes using less material than traditional manufacturing methods.

3D printing begins with digital design of an object. A user typically creates the design of an object with the help of computer-aided design (CAD) software or a 3D scanner. The object is designed in layers or slices, based on the notion that every 3D object can be viewed as a stack of two-dimensional (2D) slices. These digital slices are then sent to a 3D printer, which recreates the object one slice at a time. The 3D printer uses a raw material such as powdered plastic nylon, powdered ceramic, plastic filament or even titanium to reconstruct the object. Since 2006, open-source 3D printing projects have enabled the technologically inclined, such as hackers, programmers and engineers, to build their own 3D printers. Today, there are numerous companies which sell fully assembled 3D printers that are geared to a wider audience of consumers who are interested in taking advantage of the benefits of a 3D printer, but may not have the technical knowledge or desire to build a 3D printer or design an object from scratch using software (Santoso and Wicker, 2016).

Adoption of 3D printing has reached critical mass as those who have yet to integrate additive manufacturing somewhere in their supply chain are now part of an evershrinking minority. Where 3D printing was only suitable for prototyping and one-off manufacturing in the early stages, it is now rapidly transforming into a production technology. As it evolves, 3D printing technology is destined to transform almost every major industry and change the way we live, work and play in the future. Most of the current demand for 3D printing is industrial in nature. Acumen Research and Consulting forecasts the global 3D printing market to reach USD 41 billion by 2026.

3D printing encompasses many forms of technologies and materials as 3D printing is being used in almost all industries one could think of. It's important to see it as a cluster of diverse industries with myriad different applications.

A few examples include:

- Consumer products (eyewear, footwear, design, furniture)
- Industrial products (manufacturing tools, prototypes, functional end-use parts)
- Dental products
- Prosthetics
- Architectural scale models and marquettes
- Reconstructing fossils
- Replicating ancient artefacts
- Reconstructing evidence in forensic pathology
- Movie props (naramore, 2019)

8.23.1 3D Printing in the Fashion Industry

Not only 3D printing, but 3D technology itself, is changing the entire value chain in the apparel industry from design and prototyping to the finished product and its delivery (Zapel, 2021). Up to now, the designer has designed a product with twodimensional materials and then created one or more cost-intensive prototypes and sample collections before the product could go into mass production. These cost drivers can now be replaced by a virtual 3D simulation. The software is now mature enough to test cuts on virtual size avatars as well as colors and patterns. The folds and movement of the avatars are also realistically simulated.

The 3D simulation makes the creation of the collection faster, more accurate and more cost-effective. If the prototype production is shortened, idle times and waiting times are eliminated and variants are possible at any time. This gives the company more flexibility and enables it to react much faster to new trends.

The technology is primarily driven by online trading, which hopes that the avatar in the web shop will solve the massive returns problem. The data material for the avatars of the simulation is currently obtained from complex and cost-intensive Bodyscan series measurements in the population. This makes human body data digitally available, which also makes 3D simulation useful for the development of new collections. According to some experts, mobile body scanners in shopping centers could be used in the near future to create individual avatars that could be used for virtual fitting.

8.23.2 INNOVATIVE APPLICATIONS FOR TECHNICAL TEXTILES

In the production of technical textiles, the main focus is on functional properties. For textile companies, 3D printing processes open up possibilities that cannot be realized with conventional processes. Elements such as plug-in connections can be applied directly to textile surfaces using 3D printing. In this way, textiles are created that integrate functionalities right from the start.

However, the use of 3D printers in the production of textiles is extremely complex, as plastic filaments are not used as usual. Researchers at Fraunhofer UMSICHT have now set themselves to the goal of optimizing the 3D printing process for the textile industry with the three-year joint project "AddiTex". Together with partners from research and industry, researchers are working on the development of functional textiles for technical applications that can be produced using 3D printing.

Possible applications include tailor-made components made of narrow textiles and plastics for technical applications, the application of 3D structural elements for textile sun and noise protection, sportswear and the application of adapted mold reinforcements for protective and functional clothing.

By using 3D printing in production, the textile industry can not only functionally optimize its products right from the start, but production steps such as cutting, sewing or gluing functional components to a textile can even be saved in this way.

8.23.3 New Dimensions with 4D Printing

Fascinating new possibilities are offered by smart materials that are printed in the conventional 3D process and then transformed into a new state on their own. In 4D printing, 3D objects take on a new shape as soon as they are connected to a specific medium.

At the Self-Assembly Lab of Massachusetts Institute of Technology (MIT) (https:// selfassemblylab.mit.edu/), Skylar Tibbits was one of the first scientists to develop a 4D printing process with the option of programming physical and biological materials. If Tibbits supply smart materials with energy in the form of heat or a magnetic field, they can assemble themselves into a product. "It's like robotics, but without cables and drives", says Tibbits.

Another interesting 4D printing process for the textile industry has been developed by scientists at the WYSS Institute at Harvard University (USA). For 4D biometric printing, the researchers use a special hydrogel that contains cellulose fibers and transforms into an appropriate form upon contact with liquid. Areas in which the hydrogel could be used range from biomedicine and robotics to textile production and electronics.

At the University of Aachen, the flexibility and elasticity of textile materials is combined with the structures of rigid polymers to create systems that can convert two-dimensional structures into three-dimensional structures. The research focus is on innovative material combinations and novel geometric structures for 4D textiles.

The digitalization of the textile industry and further development of 3D/4D technology is leading to a strong change in the industry. In the near future, tailor-made products will become realistic for consumers, production will be replaced by flexible production facilities at the point of sale, and innovative applications for functional and smart textiles will be developed. The environment also benefits from the elimination of transport routes and textile waste generated during production.

The advancing technical possibilities in 3D printing and 3D scanning make developments possible that will revolutionize production and trade in the fashion and textile industry. Clothing and shoes will soon be coming out of 3Ds printer in a customized way, new possibilities will open up for functional textiles, and 4D printing will take the 3D process to a new level with fascinating applications.

Inkjet-based 3D printing is a widely applied additive manufacturing method that made an industrial-scale transformation from two-dimensional graphical to threedimensional structural print (Sridhar et al., 2011). It is typically divided into two broad categories determined by the mechanism used to form droplets: continuous inkjet (CIJ) and drop-on-demand (DOD) 3D printing. Both techniques produce uniform droplets from the printhead. Fueled by a global shift towards lean manufacturing, DOD 3D printing is found to be advantageous over CIJ, with less waste and no need for complicated ink recycling systems. DOD 3D printers can form and eject droplets on demand by mechanisms including thermal, piezo, pressure and electro-hydrodynamic (EHD) methods. Regardless of the droplet formation methods, it was deemed important that the droplets were produced from a fluid channel within the 10–150 µm diameter range as in the DOD 3D printing literature and industry (Derby, 2010).

The ability to precisely manipulate and control extruded materials is essential in the additive manufacturing industry. In addition to the gravity force acting on the extruded medium, Plog et al. (2020) demonstrated that the employment of a Coulomb force, which results from a strategically applied electric field, holds a great promise to enhance 3D printing systems and derive new products. In particular, it was shown experimentally and theoretically that a strategically applied electric field can be used to pre-charge low-volume droplets (non-contact and direct methods), enhancing control during printing. Selectively applying the electric field (E.F.) allows a modified printer more flexibility during a multi-layered print on nearly any chosen substrate. For testing, droplets created on-demand from orifices within inkjet printing parameters were subjected to a transverse electric field. The electric field was generated by retrofitting electrodes to a direct writing (DW)-based 3D printer. The application of electrodes to the printhead not only reduced the need for mechanical motion during printing but also revealed novel solutions to problematic printing applications, namely 3D printing within confinements. These results divulge a plethora of new design opportunities for ink droplet control in 3D printing processes (Plog et al., 2020).

8.23.3.1 3D Printing Methods

In an additive process, successive layers of material are laid down until the object is completed. Although several methods can be used to print, the ways layers are built to create the final product differ. Some methods melt or soften material to extrude layers; other methods cure a photo-reactive resin with an ultraviolet laser layer by layer.

3D printing imposes virtually no limits to the complexity of the geometry of an object. It also allows rapid prototyping and the fabrication of low volumes of custom parts. The methods and materials are diverse: 3D printers can extrude liquid, gel or paste through a nozzle; cure photosensitive liquid polymers with lasers or projected light; selectively sinter or melt an object from a bed of powdered material with a high-powered laser; bind layers of powder through an inkjet-like process; or laminate layers of paper, foil or film (Table 8.4).

The most widespread processes in the consumer sector are fused deposition modeling (FDM) printers and stereolithography (SLA) printers, which use polymers such as acrylonitrile butadiene styrene (ABS) and polylactic acid (PLA) or photosensitive resin as printing materials. There are also other printing processes such as selective laser sintering (SLS) or polyjet modeling (PJM), which can be used to print metals and ceramics or photosensitive polymers. However, these processes are not common in the consumer sector because of the high cost and more dangerous processes that involve high-energy lasers. All these processes have in common that the printed parts are created by means of computer-aided design (CAD) software and then usually exported to the slicer software via the historically determined so-called stereolithography file format (STL), regardless of whether the SLA process is to be used for printing or not. Based on the STL file, this software generates automatically an executable G-code, a numerically controlled programming polymer language, with which the object can then be printed. However, this code can be manually modified by the user. Utilizing the FDM process for 3D printing on textile substrates was investigated (Kozior et al., 2019; Kozior et al., 2020). 3D printing on textiles using the SLA process is advantageous compared with the FDM process, because it is possible to print much finer structures down to about 0.01 mm. These finer structures also allow more complex parts to be printed without support. Furthermore, unlike FDM printers, most SLA printers are "plug and play", so no understanding of the printer setup is required. This has the disadvantage that the SLA printers can hardly be modified, especially for home use, which is by contrast easily possible with most FDM printers. In addition, only photosensitive resin can be used, which in comparison to the widespread FDM process greatly limits the choice of materials. There are

TABLE 8.4Comparison of 3D Printing Processes and Materials

Extrusion methods Light Polymerization Powder Bed Powder Bed (Heat/Laser Lamination (FDM, FFF, TPE) (SLA, DLP, CLIP (Binder Jet) Melting/Sintering) Method details Material is extruded through Liquid resin is cured with Liquid is selectively Powdered material is Layers of paper or film are adhered a nozzle that follows a path laser light or with a deposited across a layer of selectively sintered or together and cut to shape with a in x and y dimensions projected image powdered melted with a laser or knife or laser; may incorporate standard inkjet printing methods substrate electron beam Layer height 0.050 - 0.4000.010-0.200 ~0.100a ~0.100a ~0.100 Materials Various thermoplastics Various acrylic Powdered plaster, sugar Almost any metal alloy, Paper, metal foil, plastic film (ABS, PLA, PVA, HIPS, PC, photopolymers; properties titanium, thermoplastic or nylon, etc.); molten glass or can be rigid, flexible, ceramic powder sugar, clay, wax, edible castable, or transparent materials (chocolate, etc.) Support Dependent on materials and Dependent on None None None geometry; dissolvable printer type and structures required supports can be used model geometry Wide variety of inexpensive Very fine detail achievable, High resolution with full Strong, durable parts; does Full color printing; does not require Merits and low noise operation materials: two or more color print; does not require not require support structures support structures extruders, multiple colored support structures prints, support structures dissolvable Limited materials, and Drawbacks Complex geometries and Material cost higher: Expensive printer and Limitations in 3D geometry: better overhangs require support difficult post-processing; materials; highly specialized typically less durable for solid structures material: limited for consumables: difficult relatively brittle method single-extruder printers post-processing

Methods

already different types of resin available, such as flexible resin, but these are much more expensive than the classic ABS, PLA or flexible filament, which are used with FDM. Nevertheless, the combination of SLA with textiles is as interesting as the combination with FDM, as it allows finer structures to be printed on textiles to reinforce them as the FDM process. The combination of FDM and textiles enables, for example, electroluminescence applications or the printing of "complete clothing". In addition, the combination of SLA and textiles could be used for applications in the field of micro-electromechanical systems (MEMS) in combination with the complete integration into the textile. However, to the best of our knowledge only publications on printing with the FDM process can be found in the literature, but not about the SLA process. The proof-of-concept show by Grothe et al. (2020) presents the possibility to print resin on different textiles and other surfaces with a 3D printer using the SLA process. The focus is on a wide range of textiles with different manufacturing processes such as warp knitting, knitting, weaving and nonwoven. In addition, it shows which combinations of textiles and SLA processes work (Grothe et al., 2020).

The most affordable method, and the one dominating the consumer-level market, is fused deposition modeling (FDM), also known as fused filament fabrication or thermoplastic extrusion. FDM printers feed plastic filament through a heated nozzle, which moves in both horizontal and vertical directions along a computer-guided path to deposit layers of molten material. The most commonly used FDM filaments are made of acrylonitrile butadiene styrene (ABS) or polylactic acid (PLA), but a multitude of alternatives with varying strength, temperature and material properties are available. ABS in particular is inexpensive, lightweight, durable and resistant to impact (Coakley and Hurt, 2016).

Grothe et al. (2020) conducted a study on 3D printing of resin on various textile substrates using stereolithography, described as follows:

- Low-profile cylinders as test prints were printed with a Photon S 3D printer (Anycubic, China).
- As resin, the "clear 3D printing 405 nm UV resin" from Anycubic, China was used.
- Test prints were cured under a 50 W ultraviolet (UV) LED lamp from Eleganted, China.
- Autodesk Fusion 360 version 2.0.7046 from Autodesk was used for CAD.
- Chitubox Free version 1.6.2 from Chitubox was used to create the G-code for printing.
- Investigation of the contact angle and thickness of the nanofiber mat were performed with the contact angle system OCA from Dataphysics, Germany and Fischerscope MMS PC2 from Helmut Fischer, Germany.
- The thickness of the other samples was measured with the gauge J-40-T from Wolf, Germany.

It was found that it was possible to print on more than two-thirds of the investigated textiles and other structured surfaces. Only the substrates that were too thick and had little to no structure on their surface were problematic to print on, because the resin did not adhere to the surface.

In this regard it is suspected that the surface of the substrate is too smooth, which will be investigated in future studies. Also, the application of the substrates on the printing bed was problematic. The double-sided adhesive tape does not adhere as strongly to the substrates as to the printing bed. In addition, the resin slowly dissolves the adhesive in the tape, which results in a continuous decrease of the adhesive during the printing process. Here, future investigations will also look at more effective ways in which to attach the substrates to the printing bed (Grothe et al., 2020).

8.23.3.2 Merits/Drawbacks of 3D Printing

3D printing technology is quite new and still in the developmental stage. In the present stage, it has several merits and drawbacks, a few of which are listed next (Stitchdiary, 2018).

8.23.3.2.1 Advantages of 3D Printing

- In traditional manufacturing, irrespective of the effectiveness and efficiency of the operations, wastage of raw material is inevitable.
- With 3D printing, we are using as much raw material as required to print, which means we are eliminating the need for additional raw material, as we can print the exact size of the panel for each garment.
- Beyond zero wastage, 3D printing eliminates many labor-intensive processes from the complete apparel manufacturing cycle, reducing the labor costs.
- Apart from cost savings, another big advantage that 3D printing offers is improved quality, as the occasional human error is eliminated from the manufacturing process.

8.23.3.2.2 Disadvantages of 3D Printing

- We still have a long way to go when it comes to 3D printed textiles. Currently, 3D printed textiles and garments fail to offer comfort and flexibility that a garment is expected to provide. They do not absorb moisture as the layers of the raw material fuse with each other, leaving no air gaps.
- Apart from the material problems in 3D printing, more research is needed to understand how design elements can impart drapeability and breathability into the 3D printed garments, making them wearable.
- Also, 3D printed textiles cannot be sewn into garments like traditional manufacturing. Alternatives, like melting of edges and fusing them to other panels, are being explored, but we are still in the starting phases.
- Lastly, the cost of material for 3D printing of textiles and garments is high. Producing samples and limited pieces might be possible, but for mass production, we still need to identify materials that can make the process commercially viable.

8.23.4 HAZARDS OF 3D PRINTING

Each 3D printer uses specific types of materials such as thermoplastics (e.g., acrylonitrile butadiene styrene or polylactic acid), photopolymers, phenyl phosphates, powder metals (e.g., titanium and aluminum), ceramics and paper. Ultrafine particles (UFPs) or nanoparticles are emitted during the 3D printing process and have been associated with adverse health effects. Heating of certain thermoplastic filaments can generate toxic vapors and vapors with high volatile organic compounds. Excessive exposure to VOCs can lead to eye, nose and throat irritation, headache, loss of coordination and nausea. Biological materials (i.e., cells for engineered-tissue generation) can be printed causing potential exposure to aerosols generated in the process. Other hazards are overall safety related to 3D printing equipment, high power voltage, multiple moving parts, hot surfaces, indoor air quality and static electricity.

3D printing shows advantages for producing complex geometries, which can be difficult to create with common industrial production, or to produce objects in aeronautics or other situations where other production machines are not available.

Due to the capability of 3D printers to generate potentially harmful exposures, workplaces should establish policies and a written standard operating procedure to address health and safety concerns. Occupational health nurses should collaborate with members of the occupational health team to provide input for review and approval of 3D printer purchases. Key information to consider are the type of 3D printer, type of print media to be used, proposed location of the printer, and number of printers that will be in each area. Ventilation requirements and exhaust capabilities must be assessed prior to 3D printer operation. The ventilation rate for 3D printers in lab locations will be dictated by the exhaust ventilation for the fume hood and/ or other local exhaust systems but must be at least 8 air changes per hour. If possible, 3D printers should be placed in a room separated from workstations or a significant distance from workstations, in a fume hood if available. As the popularity of 3D printers increases, more research is needed to evaluate the benefits and risks of this technology. Occupational health professionals should stay abreast of new recommendations to protect workers from exposures to 3D printer emissions (Randolph, 2018).

The energy stored in a 3D printed pre-strained textile can be used to make responsive materials, including 4D textiles, that will find applications in a broad range of industrial sectors. The need exists to make these structures rugged and durable. To that end, it is necessary to understand the interface between textile and printed polymer.

There has been a rapid growth in research regarding three-dimensional printing in recent years driven by the low cost and material efficiency associated with the technology. Combining 3D printing and textile materials is still a relatively new research area (Brinks et al., 2013; Pie et al., 2015). This represents a growth area that offers the promise of "4D textiles" – hybrid textile/3D printed structures that can change structural form with time.

8.24 FUTURE TRENDS

Any major improvements in digital printing of textiles are likely to come from machinery developments rather than from the design, encoding or operating software. From the electronic operating point of view, modern computers have very fast processors and large memory (random access and fixed disc) capabilities, and can be fitted with high capacity color processing cards and fast external communication systems. On the other hand, those jet printers offering improved production capabilities $(1 \pm 3 \text{ m/min})$ that have been introduced, such as the Canon TPU (multihead bubblejet system), the Reggiani DReAM (Scitex/Aprion piezo technology) and Zimmer Chromotex 2003 (with Jemtex continuous ink jet print-heads) appear to be less economically attractive than lower productivity machines, such as the Mimaki and Ichinose, originally developed for the reprographics market. In general, inkjet printing still continues to exploit only niche markets (sampling, strike-off, haute couture and customization) rather than the short run/rapid response printing business for which the technology could be ideally suited. From a purely design point of view, digital printing methods will continue to give a new freedom to designers who are no longer shackled with the conventions and mechanical constraints of screen printing. Thus, quite apart from the lack of color and pattern repeat constraints and the ability to produce photorealistic effects, designers can now introduce novel shadow, moiré, textured, blurred and layered effects and in general greater individualism.

Digital inkjet textile printing is an emerging technology integrated with computer science, precision machinery and optic-mechanical-electric technology. In the 1950s, the invention of screen textile printing was a milestone in the textile printing industry. Later, digital inkjet textile printing was promoted by the application of Computer Aided Design (CAD) and Computer Aided Manufacturing (CAM) technology. It was predicted that digital inkjet textile printing will bring a significant revolution to the textile printing industry. However, this new technology will probably never be able to replace traditional technology overnight. Digital inkjet textile printing is still in the process of developing. People are excited about the potential of printing unlimited images on fabrics. It is true that digital inkjet textile printing can print thousands of colors with photo-like resolution.

The reasons for steady growth in digital textile printing are numerous. Digital printing is not only a higher creative form of textile printing; it also provides greater design flexibility compared to screen printing. Designers prefer digital printing for small prints, as it is more cost efficient. One of the biggest plus points of digital printing is its eco-friendly process, with less levels of physical inventory leaving smaller carbon footprints (Dawson, 2006).

Digital printing involves direct printing on fabrics with printers, which saves almost 95% of water, reducing energy usage by 75%, and leading to minimal textile waste. Designers like Mary Katrantzou, Alexander McQueen and Basso & Brooke have often used digital textile printing in their designs. Moreover, manufacturers that rely on digital textile printing easily adapt to swift changes in global trends in comparison to people involved in other forms of printing.

These factors support the rising growth of digital printing in the global textile sector. Nevertheless, the future growth of digital textile printing widely depends on deeper penetration of digital printing into commercial print production. The machine manufacturers also need to develop technologically advanced production printers in order to survive competition from conventional forms of textile printing machinery (Fibre2Fashion, 2015).

However, there are problems that have come up during bulk production of digital printed textile in practice. For example, the edge of fabrics easily gets curly, the printhead is difficult to maintain, extra ink droplets destroy the printed image, and so on. The high requirements for the operation environment and the operator's expertise also limit the wide application of this emerging technology currently. Gradually people are coming to know more and more about the benefits of this new advanced technology. All the obstacles in the application of digital inkjet textile printing will be removed when related technology is further developed. The ergonomics and features of digital textile machines need to be developed further to facilitate this new technology in the textile industry (Wang, 2017).

Shell (2016) predicted the following future developments in digital printing

- Single stage digital printing
- Deliver operating speeds that are faster than rotary screen
- 35 to 75 linear meters per minute
- Targeting rotary screen printers producing 3M to 10M meters per annum
- · Digital printing with pigment colors
- · Continued adoption, growth, falling ink/fabric prices

Two-dimensional traditional and inkjet printing processes are well established in the textile industry, catering to the global demands of printed textile materials. But in recent years, three-dimensional printing methods are rapidly penetrating the textile printing market.

3D printing as an innovative technology implemented in different areas of production has gained an increased interest in fashion industry (Spahiu et al., 2020). A study by Spahiu et al. (2020) shows the application of 3D printing for garment production using the FDM technology, which is less expensive compared to the other 3D printing technologies. Due to the flexibility of FilaFlex material, the final dress is easily wearable. Nevertheless, there is still a lot of work to be done regarding materials, as they are still far away from the properties of textile materials. 3D printed garments are seen as complementary to fashion products. In the survey conducted to evaluate consumer behavior for 3D printed garments, the majority of respondents believe that 3D printing will be beneficial for garment production. This can be related to the wastage of garments and the possibility of producing personalized garments even at home.

Regarding the future of 3D textile printing, we are still at the conceptual stage with using this technology in fashion, but we can be optimistic that this technology can change the game for future retailers. Both in high-end and mass market fashion retail, 3D printing can eliminate the need for the extensive manufacturing process.

We still need to overcome the obstacle of finding the right material. Although flexible polymers are being explored for this purpose, the industry needs a bigger range of raw materials that can be converted into comfortable and wearable garments through 3D printing. Another big challenge is the development of specialized 3D printers that are suitable for garments, and can print wearable fabrics.

Even though 3D printing is used to realize designs without boundaries, it cannot replace the traditional way of garment manufacturing, but the latter can be used as an innovative technology in apparel products.

Three-dimensional printing provides individuals with the opportunity to more actively engage in the process of production and creation by enabling consumers to take their ideas, design new products and bring them to market independently, or in collaboration with other individuals or companies (Santoso and Wicker, 2016).

Circular economy (CE) is a broad term that has diverse meanings in different contexts, but generally refers to an economy that operates with closed material loops. In its broadest elaboration, a CE is envisioned as a sweeping transformation away from the linear "take-make-waste" production models that dominate current manufacturing approaches. 3D printing is not necessarily more environmentally sustainable than current manufacturing approaches and, if not guided by CE principles, could actually exacerbate resource and environmental problems.

The technologies needed to establish a closed-loop, additive-manufacturing production system are available today in nascent form. Guided by the Biosphere Rules framework, this disruptive technology could serve as one foundation of a sustainablemanufacturing revolution. It is probable that an era of ferment will lead to the founding of entirely new business models that dominate for decades to come (Unruh, 2018).

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