CHAPTER 1

TEXTILE PROCESSING INDUSTRY
1.1 GENERAL OVER VIEW

Textile Processing is an important sub-sector in the textile industry. It converts a virtually unbrandable raw product to a differentiable consumer product. In so doing, it provides a link between the design and fashion requirements of the market and the processes involved in converting grey fabrics into finished fabrics.

Textile wet Processing uses a large number of workers as well as huge quantities of water, steam (fuel) chemicals and dyes and is a big drain on resource as compared with the other sub-sectors of the textile industry.

1.1.1 CAPACITY

There are 601 Textile Processing units, of which 30 are integrated with Spinning Weaving & Finishing Mills and remaining are independent commission finishing units. Most of these are of small size in capacity. The main concentration is in Karachi, Faisalabad, Gujranwala and Lahore. Total cloth production (cotton & synthetics) is estimated at 4400 M. Sq. Meters. Approx 80% of cloth produced is processed. About 50% of the capacity is 15 years old and requires to be replaced. The capacity utilization is very low.

1.1.2 LOCATION

The distribution of the Textile Processing units is in line with the location of the cloth production industry. Major concentration is in and around Karachi, Faisalabad, Lahore and Gujranwala.

1.1.3 EMPLOYMENT

Textile Processing units generally employ only one or two dyeing and finishing technicians and perhaps one or two laboratory technicians. The bulk of the employment is unskilled or semi skilled labor used as machine operators, material handlers and supervisor. There is no reported data on employment. However, it is estimated that approx. 35000 persons are employed directly or indirectly. Since the qualified persons are in short supply therefore, the skill level is low and the wage level is also low.

1.1.4 QUALITY OF DYED/PRINTED FABRICS

Textile Processing Industry is characterized by a large printing capacity and very small scales continuous dyeing capacity. This structure alone reflects that the fabric supply is good enough for printing purposes where the defects are covered by prints and despite the facts that quality level is not very good the printed fabric out put is accepted in markets since its application for bed wear and household items. In piece dyeing fabrics, there are disparities of dyeing between fabric’s lots and unevenness in dyeing so that the output is not appropriate for exports. In the local market the supply of dyed fabric is in short length where defect part is cut and quality requirements are not very high.
Only some units carry out quality inspections of processed items (color fastness against washing and light) and in most cases lengths are only carried out at the time of dispatch. There is hardly any attempt to collect data concerning processing defects, weaving defects, yarn defects etc. to serve as a feedback base. There is awareness to set up laboratories and apply quality control measures but the overall approach is production oriented.

1.1.5 PROBLEMS

- The cost of machinery has gone very high.
- The rate of duty on the spare parts and other ancillary requirements is high.
- The cost of inputs (gas, water and power) has increased a lot.
- High import duty on dyes and chemicals has increased the cost of these important inputs rendering the industry to a cost disadvantage situation against our competitors India, China, Indonesia.
- Lab. equipment, which is very expensive and only 5% of the industry at present, has the facility of in house laboratories, which also need to be modernized.
- Textile Processing Industry has been subject to sales tax on capacity basis.
- Processing Industry requires qualified and skilled technicians.
FIBERS
2.1 Fibers and Classifications of Fibres

2.1.1 Fibers

Fibers - units of matter characterized by flexibility, fineness and high ratio of length to thickness. Other necessary attribute for textiles are adequate strength and resistance to conditions encountered during wears, as well as absence of undesirable colour, and finally the property of dye ability.

In generally, the steps in the manufacture of fabrics from raw material to finished goods are as follows:

- Fibre, which is either spun (or twisted) into yarn or else directly compressed into fabric.
- Yarn, which is woven, knitted, or otherwise made into fabric.
- Fabric, which by various dyeing and finishing processed becomes consumers’ goods.

2.1.2 The principle classifications of textile fibres

The principle types of textile fibre in general use may be classified as in Table 2.1.

<table>
<thead>
<tr>
<th>Animal</th>
<th>NATURAL FIBRES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wool and hair fibres</td>
<td>Sheep’s wool (many varieties)</td>
</tr>
<tr>
<td></td>
<td>Cashmere: hair of the cashmere goat</td>
</tr>
<tr>
<td></td>
<td>Mohair: hair of the agora goat</td>
</tr>
<tr>
<td></td>
<td>(South Africa, turkey, and USA)</td>
</tr>
<tr>
<td>Cocoon fibres</td>
<td>Camel</td>
</tr>
<tr>
<td></td>
<td>Rabbit fur</td>
</tr>
<tr>
<td></td>
<td>Cultivated silk (Asia, Europe)</td>
</tr>
<tr>
<td>Vegetable</td>
<td>Cotton</td>
</tr>
<tr>
<td>Seed fibres</td>
<td>Flax</td>
</tr>
<tr>
<td>Bast fibres</td>
<td>Jute</td>
</tr>
<tr>
<td></td>
<td>Hemp</td>
</tr>
<tr>
<td></td>
<td>Ramie etc.</td>
</tr>
</tbody>
</table>
Man-made Fibres

<table>
<thead>
<tr>
<th>Natural starting material</th>
<th>Synthetic material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rayon</td>
<td>Organic origin</td>
</tr>
<tr>
<td>Lyocell/Tencel</td>
<td></td>
</tr>
<tr>
<td>Cellulose acetates</td>
<td></td>
</tr>
<tr>
<td>Viscose, including polysonic</td>
<td>Polycrylonitriles</td>
</tr>
<tr>
<td>Normal or secondary acetate, and triacetate</td>
<td>Polyamides (nylon)</td>
</tr>
<tr>
<td></td>
<td>Polyesters (PET)</td>
</tr>
<tr>
<td></td>
<td>Polyurethane (spandex/lycra)</td>
</tr>
</tbody>
</table>

2.1.3 Classification of fibres according to dyeing properties

For convenience in studying their dyeing properties, fibers be broadly divided into three classes as showed in Table 2.2.

<table>
<thead>
<tr>
<th>Cellulosic</th>
<th>Cotton</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cotton</td>
<td>Linen</td>
</tr>
<tr>
<td>Linen</td>
<td>Jute</td>
</tr>
<tr>
<td>Jute</td>
<td>Ramie</td>
</tr>
<tr>
<td>Ramie</td>
<td>Viscose rayon</td>
</tr>
<tr>
<td>Viscose rayon</td>
<td>Polysonic fiber</td>
</tr>
<tr>
<td>Polysonic fiber</td>
<td>Lyocell/Tencel</td>
</tr>
<tr>
<td>Lyocell/Tencel</td>
<td>Acetate</td>
</tr>
<tr>
<td>Acetate</td>
<td>Triacetate</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Protein</th>
<th>Wool</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wool</td>
<td>Goat fibre</td>
</tr>
<tr>
<td>Goat fibre</td>
<td>Silk</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Synthetic-polymer fibres</th>
<th>Cellulose acetates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose acetates</td>
<td>Polyesters</td>
</tr>
<tr>
<td>Polyesters</td>
<td>Polyamides (nylons)</td>
</tr>
<tr>
<td>Polyamides (nylons)</td>
<td>Polyacrylonitriles (acrylics)</td>
</tr>
<tr>
<td>Polyacrylonitriles (acrylics)</td>
<td>Polyurethane elastic fibre (spandex/lycra)</td>
</tr>
</tbody>
</table>
2.2 Fiber Properties

2.2.1 The structure of fibres

Textile fibres are composed of molecules that are very long and flexible, as are the fibres themselves. These molecules are polymeric, i.e. they are composed of a large number of small repeating units, which may be either all the same or of several types, occurring at intervals along the length of the molecule. Such molecules are usually referred to as molecular chains. The chemical structure of some important fibres will be showed later in discussing their properties.

Fibres have properties that make it appear that these molecular chains are in places held together lengthwise by various faces, fanning tightly packed bundles known as crystalline regions, whereas in other places, known as the amorphous region, they are less firmly held and can be readily separated, for example. Water is strongly attracted by portions of the molecular chains of most fibres, and so quickly enters the amorphous regions, forcing them apart so that the whole fibre structure becomes interpenetrated by minute pores and channels, into which any substance dissolved in the water outside can freely enter. The fibre in this water-swollen state is something in the nature of a sponge.

It is important to understand the infinitesimally minute scale on which this molecular architecture of fibres is constructed. Perhaps the most vivid illustration of this is conveyed by the severed; the pores through which water enters may be only about one-millionth of an inch in diameter.

2.2.2 Cellulose and its properties

Cellulose pertains to the class of carbohydrates. It contains 44.4% of carbon, 6.2% of hydrogen, and 19.4% of oxygen. The elementary unit of a cellulose macromolecule is anhydrous-d-glucose, which is repeated a great number of times in the cellulose molecule; i.e. cellulose is a high-molecular compound.

In the cellulose molecule, the d-glucose anhydrides of β-form are interconnected the glucosidic linkage 1-4, characterized by the following atomic structure:

The chemical structure of cellulose is showed as follows, each elementary unit the macromolecule (except the end ones) contains three (one primary and two secondary) alcohol hydroxyls. In many reactions (mainly esterification) the primary hydroxyl groups have a greater reactivity; it is possible that in other reactions, primary hydroxyls may have a lower reactivity than secondary hydroxyls.

An important characteristic of cellulose is its molecular weight. For cotton cellulose it equals from 100,000 to 1-2 million; for flax, up to 6 million; for viscose rayon, from 20,000 to 230,000.

The degree of orientation of cellulose macromolecules in vegetable fibres varies greatly, being the highest in flax and ramie fibres (as the degree of polymerization). In cotton fibres it is lower and differs from one layer to another depending on the maturity and on the kind of cotton; corresponding changes are observed in the viscosity and specific density of cellulose, characterizing the length of macromolecules and the closeness of their packing.
Cellulose fibres are complex structures consisting of cellulose macromolecules, which are arranged in certain, order and do not completely fill their geometrical volume. Fibrillation is inherent not only in nature cellulose fibres, but has also been observed in high-tenacity viscose fibres, and the fibrils are considered to be identical in both cases.

From the investigation of the morphological structure of cellulose it may be concluded that super molecular elements (cell layers, fibrils, etc.) do not form dense sum dense in the fibre. They have a great number of pores and cracks through which great reagent diffuses inside the structure in most heterogeneous reactions. However, in some cases when almost no swelling of cellulose occurs, the reaction may be localized on the surface of the fibres.

- **The action of pH and chemical agents on cellulose**

  a. **Effect of temperature**

  The thermal stability of cellulose is very limited and depends in the large measure on its time during which it is subjected to the effect of temperature. Prolonged heating even at a temperature of 100°C impairs the swelling properties of the fibre and consequently its dye ability. Cellulose withstands short-term heating at a temperature of 180-200°C. A temperature above 275°C, intensive decomposition of cellulose takes place with the formation of liquid and gaseous products of different composition. At 400 – 450 degree centigrade all gaseous decomposition products disappear and a hard residue (carbon) remains.

  Notwithstanding the great number of hydroxyl groups, which are hydrophilic in nature, cellulose is not soluble in water, which is probably due to presence of hydrogen and vanderwaals’ intermolecular bonds and is capable only of limited swelling.

  On immersion in water the cross section of cellulose cotton fibre increase at most by 15-50% and its length by 1-2%. But water penetrates only into the parts with less orientation. The moisture content and swelling at constant humidity somewhat decrease with an increase in temperature.

  The fiber strength is reduced by prolonged action of steam with the formation oxy cellulose. Cellulose is not soluble in any of the usual organic solvents, such as alcohol, etc. The treatment of fibres with certain organic solvents, however, considerably increases the reactivity cellulose.

  b. **Action of acids**

  The glucosidic linkages of cellulose molecules are highly unresisting to the action of mineral acids and are readily hydrolyzed, i.e. the break up, combining with water which results in the disintegration of macromolecules.

  The hydrolysis equation may be written as follows:

  \[(C6H10O5) n + nH2O \rightarrow nC6H12O6\]

  The intermediate product of hydrolysis is called hydrocellulose. The hydrolytic action of acids depends on the nature of acid and temperature.
c. **Action of salt solutions**

Solutions of acid salts have the same effect on cellulose as acids. The ammonical solution of copper oxide, the cupriaminohydrate [Cu(NH3)(OH)2, is the specific solvent for cellulose.

d. **Action of alkalies**

It is characteristic of the glucosidic linkage of the cellulose molecule that it is highly resistant to alkalies. At normal temperature weak solutions of caustic soda have no effect on cellulose. But on boiling in a 1 % solution of caustic soda, a small part of cellulose passes into solution. As the alkali concentration increases, the cellulose solubility becomes considerably higher. The action of alkali solutions on cellulose is particularly pronounced in air. In this case, caustic soda promotes cellulose oxidation by atmospheric oxygen and cellulose is transformed into oxycellulose.

In concentrated solutions of caustic soda (over 10 per cent) at normal temperatures, the fibre swells, becomes elastic, and contracts in length. If shrinkage is impeded, the fibre acquires luster which is retained after the alkali has washed out. From the chemical standpoint, the essence of this is process is in the absorption of alkali with the formation of alkali cellulose. Caustic soda combines with cellulose forming a molecular compound according to following equation:

\[
\text{C6H7O2(OH)3 + NaOH} \rightarrow \text{C6H7O2(OH)3NaOH}
\]

Alkali cellulose is an unstable compound; it is easily decomposed by water to form cellulose hydrate which is more hygroscopic than native cellulose, has a high swelling capacity, is more liable to undergo hydrolysis and is characterized by a more intensive dye acceptance. Gray cotton fibres contain on the average up to 7% of moisture, while the moisture content of cellulose hydrate amount to 9.5 -10.5%.

Using above mentioned property, cellulose fibres is treated with strong alkali solution in dyeing-finishing process which is called mercerization.

e. **Action of reducing and oxidizing agents**

Reducing agents have no effect on cellulose, while oxidizing agents readily convert it to oxycellulose. For chemical treatment of fibrous materials, large use is made of various oxidizing agents: sodium hypochlorite, hydrogen peroxide, sodium chlorite etc, and such acids that are capable of oxidizing, as for instance, nitric acid.

These reagents may cause more or less intensive oxidation of cellulose functional groups and breakage of chains as a result of glucosidic- linkage rupture. The oxidizing agent first act on the functional groups located on the cellulose fibre surface and then progressively penetrate into the depth of the fibre.

Bleaching treatment can he applied to cellulose fibres according to above properties.

f. **Effect of light and atmospheric conditions**

Under the action of light, cellulose is oxidized by atmospheric oxygen and due to photo oxidation, oxycellulose is formed as a result of which the strength of the cellulose is considerable reduced, the copper and iodine numbers are correspondingly increased, and the viscosity of cuprammonium solution is reduced.
g. Effect of microorganism on cellulose

If the moisture content in fibres is over 9% and the relative humidity is over 75-85%. Some bacteria and mildew fungi may cause cellulose decay.

2.3 Cotton

Raw cotton contains, in addition to cellulose, the usual constituents of vegetable cell. These are oil and wax, pectoses and pectins, proteins and simple related nitrogen compounds. Organic acids, mineral matter, arid natural colouring-matter, or piece goods may contain in addition, adventitious dirt, size, and machine oil; the approximate composition of raw dry cotton is as showed in table 2.3:

<table>
<thead>
<tr>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
</tr>
<tr>
<td>Oil and wax</td>
</tr>
<tr>
<td>Proteins, pectose, and colouring-matter</td>
</tr>
<tr>
<td>Mineral matter</td>
</tr>
</tbody>
</table>

If cotton is properly purified before bleaching it must lose 6.5 % in weight. When all the impurities have been removed the main constituent of the fibre, cellulose remains. Cotton fabric is stable even in strong alkali solution, but it will be hydrolysis in acidic solution as well as in the solution with strong oxidizing agent. It must be very careful controlling the bleaching process to avoid the cotton over oxidizing and hydrozing.

The wet strength of cotton fabric is higher that that of dry. The cotton fabrics are very absorbent due to the presence of countless polar-Oil groups. Because of this hygroscopic nature, it prevents from developing static electricity.

Cotton posses many desirable properties, especially hydrophilic and attractive handle. So that cotton is suitable for comfort wear, such as underwear. However, its main undesirable property is dimensional unstable, because it is not thermoplastic, so it can not be permanent heat set, therefore it is easily to get wrinkles. The cotton fabric is relatively inelastic because of its crystalline polymer system. The finishing process for cotton mainly focuses on anti crease, i.e. crease resisting finishing.
The main types of commercial cotton are showed in table 2.4.

<table>
<thead>
<tr>
<th>Name</th>
<th>Characters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sealan cotton</td>
<td>Gulf of florida</td>
</tr>
<tr>
<td></td>
<td>Spinning count is 1/200</td>
</tr>
<tr>
<td>Egyptian cotton</td>
<td>Two types, brown and white</td>
</tr>
<tr>
<td></td>
<td>Spinning count: 1/200 for brown</td>
</tr>
<tr>
<td></td>
<td>1/70 for white</td>
</tr>
<tr>
<td>South American cotton</td>
<td>Good for blends</td>
</tr>
<tr>
<td>American cotton</td>
<td>Most abundant type</td>
</tr>
<tr>
<td></td>
<td>Good natural colours</td>
</tr>
<tr>
<td></td>
<td>Cannot be use for fine counts</td>
</tr>
<tr>
<td>India cotton</td>
<td>Short fibres</td>
</tr>
<tr>
<td></td>
<td>Cannot be used of fine count</td>
</tr>
<tr>
<td>China cotton</td>
<td>Short fibres</td>
</tr>
<tr>
<td></td>
<td>Cannot be used for counts</td>
</tr>
</tbody>
</table>
CHAPTER 3

WATER FOR TEXTILE INDUSTRY
Water is the most abundant and also the most important compound that exists on the planet Earth. No life whether vegetable or animal can exist without water. The human body for example contains water up to 60% of its weight and cucumber is 97% water. Nature has provided our planet with abundant water and about 70% of the surface of earth is covered with it. However, in spite of this apparent abundance potable water is becoming increasingly scarce. This scarcity is due to the fact that 97.2% of the total water is in the oceans and this has a high concentration of dissolved salts that makes it unfit for bio-consumption. Out of the remaining 2.8%, about 2% is perpetually frozen and 90% of it is in Antarctica. Even out of the balance 0.8%, all cannot be used because sonic is brackish and some is lost to oceans and atmosphere.

It has been estimated that with rising population consumption of water is increasing by 2-3% annually. It is thus easy to anticipate that water for industry will keep on becoming more expensive because the first charge on the fresh water is for human consumption and for growing crops. Agriculture uses about 70% of the total available water and its utilization may be judged from the figures that one-kilo of rice, potatoes and beef require 1,900, 500 and 100,000 liters of water respectively. An individual person consumes, on the average, about 100 m3 (100,000 liters) of water annually. Fortunately some of the consumed water can be reclaimed but it is not enough to check the increase in cost of water.

3.1 Sources of Water

The only source of fresh water on earth is evaporation from the seas and lakes and it has been estimated to be about 230 cubic miles every day. (One cubic mile is about 5,000 billion liters) Unfortunately, out of this total evaporation, 210 cubic miles rain back on the seas and only 20 cubic miles are blown over to land to support life on earth. The main sources of water for drinking, irrigation and industry such as rivers, lakes, sub-soil water, canals etc are all fed by the rainwater.

3.2 Special Properties of Water

Water (H₂O) is a very simple compound but has very unique physical and chemical properties. Its density for example, increases with lowering of temperature but unlike other substances, it starts decreasing after reaching a temperature of 4°C. This unusual property is perhaps responsible for existence of any li lb on our planet today. The fall in density below 4°C creates an insulating layer of ice on the surface of oceans and lakes. In the absence of this layer, all the water sources would have frozen from bottom to top during the ice ages and the entire marine life would have perished.

Water has a highly surface tension and a high dielectric constant. The latter property is responsible for the great capacity of water to dissolve ionic and polar compounds thus making water an excellent solvent. Water has a low relative molecular mass (18) but still it has a very high boiling point of 100°C. This phenomenon indicates presence of an inter-molecular bonding force that is termed as “hydrogen bonding. This bonding is also responsible for a high specific heat or heat capacity of water and steam, the latent heat of vaporization of steam is 537 calories per gram of steam at 100°C and this property makes it a very economical and efficient medium for heat transfer in
industry. Interestingly, water is corrosive to metals and minerals and yet it is essential for the living organisms.

3.3 Impurities Associated with Water

Dew and rain, as condensed from water vapors, are in a very pure state but on coining in contact with air, water dissolves gases like carbon dioxide and oxides of nitrogen and sulphur that are usually present in the atmosphere of the urban areas. Dust and soot prudes is well is bacteria are also washed down with rain and add to the impurities. The following water while passing over land normally consists of calcium and magnesium carbonate rock strata, converts these minerals into soluble bicarbonates by reaction with carbon dioxide that is already dissolved in it.

As the rivers flow towards sea, concentration of both the dissolved and suspended impurities keeps on increasing. In addition to leaching of salts of the soil on which river flows, the municipal sewerage and industrial effluents from downstream cities are also added. The river water, therefore, contains both the suspended and dissolved mineral and organic matter in addition to dissolved gases and bacteria. The main dissolved mineral matter consists of cations of calcium, magnesium and sodium and anions of bicarbonate, carbonate, chloride and sulphate. The calcium and magnesium ions create a special difficulty in use of water for household and industrial purposes that is known as hardness. Hardness wastes soaps because the calcium and magnesium ions replace the sodium ions soaps and convert these into insoluble soaps destroying thereby their detergent quality. Reaction of soap with the metal salts may be represented as under.

\[ 2 \text{C}_{17}\text{H}_{35}\text{COONa} + \text{CaCl}_2 = (\text{C}_{17}\text{H}_{35}\text{COO})_2\text{Ca} + 2 \text{NaCl} \]

3.3.1 Hardness of Water

Hardness is due to presence of any metal ions in water that will react with soap and make it insoluble but these ions are normally of calcium and magnesium metals. In most of the science textbooks hardness is classified as temporary and permanent; the former is produced by anions of bicarbonate and the latter by chloride and sulphate of calcium and magnesium. Temporary hardness is so termed because it is supposed to be removed on boiling t hard water when the bicarbonates are converted into insoluble carbonates that are precipitated.

The white particles and scale formed on the water-boiling vessels are mainly calcium and magnesium carbonates. However, it is worth noting that the temporary hardness is never completely removed even on prolonged boiling. In modern literature the terminology of temporary and permanent hardness has been replaced with alkaline and non-alkaline hardness respectively.

Determination of hardness: Hardness was estimated in the past with a standard soap solution the end point being formation of foam that is stable for a definite time. The foam is formed after the hardness causing salts have been precipitated by soap. This method is time consuming arid is also not very accurate. Presently alkaline hardness is measured with a standard hydrochloric acid solution using methyl orange and phenolphthalein as indicators.
The non-alkaline hardness is determined by titration with a metal chelating compound, such as disodium salt of ethylene diamine tetra acetic acid, commonly termed as E.D.T.A. or Versene. EDTA forms complexes with calcium, magnesium or other metal cations and removes these from the solution. The indicator is an acid dye (Eriochrome Black T) that changes colour from bluish red to brilliant blue. To find calcium and magnesium hardness separately, caustic potash is added to the hard water which suppresses ionization of magnesium ions and only calcium ions react with EDTA. The magnesium hardness is determined as the difference in total and the calcium hardness.

Hardness is usually indicated as parts of calcium carbonate per million parts of water (PPM) irrespective of the nature of the ions present.

### 3.3.2 Total Dissolved Solids

Quantity of total dissolved solids (TDS) is an important parameter in assessment of quality of water. Evaporating water and weighing (lie dried residue can directly measure it. However, a more convenient and rapid method is to determine the electrical conductivity of water and calculate the TDS from calibrated tables. Currently pre-calibrated digital meters are available that directly read the TDS in PPM.

### 3.4 Effect of Water-Impurities on wet processing

Impurities in water can seriously affect quality of wet processing and even damage the fibres depending on their nature and concentration. The major impurities and their effects are briefly discussed below:

- **3.4.1 Organic Matter, Turbidity and Colour**

  Turbidity and colour are usually due to presence of organic matter in water and these detract 1 brightness of the bleached and purity of shade of the dyed goods. The organic matter whether dissolved or suspended also breeds micro organisms that may develop mildew, fungi etc. which in turn produce colored spots, foul smell and even holes in the fibrous material. The microorganism also grows inside the water pipes and chokes these and sometimes even dissolves the pipe-metal.
3.4.2 Hardness

The immediate difficulty associated with hardness that comes to one’s mind is wastage of soap used in scouring of wool and silk fibres and soaping of Reactive, Vat and Azoic dyed and printed goods. However, this wasteful problem has been more or less overcome by replacement of soap with synthetic detergents or “syndets”. The syndets are made water by introducing sulphonic acid groups in the long-chain organic molecules whose sodium salts are highly hydrophilic. The synthetic detergents can withstand hardness because their calcium and magnesium derivatives are fairly soluble in water. However, it may be kept in mind that efficiency of the syndets, which is not better than soaps to start with, falls if hardness is too high.

Hardness creates many other undesirable effects in wet processing. The textile dyes for each fibre are designed to have low solubility in water and these become difficult to dissolve in very hard water. Due to insufficient solubility the dye-shade becomes weaker and may also produce spots on the dyed fabric. Further on heating or on coming in contact with alkalis during dyeing and soaping, calcium and magnesium ions are precipitated on fabrics as whitish carbonates and hydroxide particles.

Although concentration of these salts is small yet their overall reflection lowers depth of the dyed shade and mars purity and brightness of the hue. If hardness of water is very high, it may even cause non-uniform dyeing. In package yarn dyeing, the precipitated particles hinder free flow of liquor through the packages and tend to cause uneven dyeing. The precipitated salts also impart harshness to the fibers.

In textile mills including the spinning and the weaving sections, certain equipment are installed that are required to circulate water through pipes. These include humidification plant, boiler, multi-tubular heaters or coolers of the dyeing machines. Under the normal working conditions, the hardness producing salts in the water precipitate and form scale inside the pipes. The scale is a bad conductor of heat and thus lowers the rate of heat transfer and is responsible for wastage of fuel in boilers and lowering of efficiency of the other equipment. The scale deposits also gradually start choking the pipes. Removal of the scale from inside the tubes is a time consuming and an expensive proposition and adds to the cost of processing.

3.4.3 Total Dissolved Solids

In addition to hardness causing calcium and magnesium salts, water contains other dissolved salts that are mainly sodium cations and chloride, sulphate and bicarbonate anions. These sodium salts increase TDS of water and also create many difficulties in processing of textiles. Dyes of low solubility are likely to be precipitated even in softened water of high TDS on dissolving and the same can happen in preparing printing pastes. Presence of excessive amount of sodium ions also gives a damp and limp handle to the finished fabric due to their tendency to hold water. High TDS in the boiler feed water causes foaming and carry over problems that lower efficiency of the boilers and also create difficulties in processing. Excessive concentration of sodium ions in
boiler water also accelerates corrosion of the iron plates due to their high electrical conductivity. Such waters also require more frequent blow-downs and result in loss.

### 3.4.4 Dissolved Gases

Water normally has small quantities of oxygen and carbon dioxide dissolved in it. The latter reacts with steel pipes carrying water and steam, to form soluble ferrous bicarbonates. The dissolved ferrous ions, besides producing unsightly stains, catalyze reactions of hypochlorite and hydrogen peroxide during bleaching and damage cotton goods by lowering their strength and even making holes. The dissolved oxygen can cause serious damage to the boilerplates by converting the ferrous bicarbonate, formed initially, into ferric oxide and releasing carbon dioxide to react again with more iron. The reaction continues till the entire dissolved oxygen is exhausted by reacting with the boiler-plates. Oxygen in water also wastes the reducing agents like dithionite that is used in application of vat dyes.

### 3.5 Water Management in Wet Processing industry

Good quality (potable) water had been abundantly available at a negligible price till recently and so had been taken for granted and no importance was given to it while preparing feasibility studies for a new project. This situation has now changed radically and water is being given status of a “raw material” and due consideration is given to its availability and quality as well as to its disposal arrangement after use. Quantity of water required in a dye house to process one kilogram of the fabric varies between 70 to 150 liters depending upon nature of fibres, class of dyes, method of dye-application and the processing machines used. On the average, one may take water consumption as 100 I of the material plus 200 liters per day for each employee of the mills.

The ideal quality of water would be zero TDS but most of the river-waters that are the major source of water in many countries are quite satisfactory for processing, drinking and factory lawns. Depending upon the extent of upstream contamination and time of the year, the river waters us have a hardness of about 100-150 ppm and TDS of 300 to 600 ppm. However, the first charge on water of this quality is always for growing crops, drinking and household consumption and so the industry always suffers from chronic shortage of good quality water. To meet their needs, the mills resort to extraction of the sub-soil water but its quality and even quantity is not dependable and further deteriorates on prolonged extraction; the water shortage problem is more severe in arid and semi-arid lands where the sub-soil water is always brackish.

The rivers flowing over such lands leach salts of the land and so the TDS of the subsoil waters depends upon the distance from rivers; those close to the rivers and canal banks has comparatively low TDS. There is no simple solution for the industry to overcome the problem of water shortage and it requires a multi-dimensional approach to ensure production of the quality products at an acceptable cost. A few suggestions are made below to meet this challenge.
3.5.1 Conservation of Water

This is the single most effective method to meet water shortage in textile industry and may be practiced in a number of ways as explained under the following sub-heads:

3.5.2 Processing Machines

It has been established that the continuous bleaching and dyeing machines are more efficient in water consumption than the batch processing ones. Even within these two groups, consumption of water may vary considerably for the same class of dyes as is shown in the following table:

<table>
<thead>
<tr>
<th>DYEING MACHINE</th>
<th>WATER CONSUMPTION (liters/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jigger</td>
<td>40</td>
</tr>
<tr>
<td>Winch</td>
<td>110</td>
</tr>
<tr>
<td>Soft Flow Jet</td>
<td>70</td>
</tr>
<tr>
<td>Continuous dyeing with</td>
<td></td>
</tr>
<tr>
<td>Counter-current washing</td>
<td>12</td>
</tr>
</tbody>
</table>

The above table clearly shows that the modern continuous processing machines are very economical in use of water. However their installation is not always possible because of considerations of high capital cost, small running lengths in one shade and also for unsuitability for fabrics that need tensionless handling like knitwear and crepe fabrics.

3.5.3 Choice of dyestuff

Consumption of water depends upon the class of dyes used but most of the water is required for post-dyeing washing and soaping treatments. The pigments, for example, require no washing also consume very little water (about 1:1). On the other hand, vat, azoic and reactive dyes need extensive washing and soaping and so need large quantities of water. Consumption of water by different classes of dyes in the ascending order is Pigment, Disperse, Direct, Acid, Sulphur, Reactive, Vat and Azoic. It is normally not possible to choose a class of dye on the basis of water consumption but the above comparison may be kept in view when an alternative is possible.

3.5.4 Use of brackish Sub-Soil water

In places where sub-soil water has TDS not above 2,000 ppm, it is possible to use it selectively for rinsing off the unfixed Reactive and Direct dyes. This rinsing should be followed by a treatment with dilute acetic or formic acid to remove calcium and magnesium salts and washing with low TDS water before soaping or any other treatment. To use brackish water, it is necessary to have separate storage tank and pipelines.
3.5.5 Utilization of Cooling Water

Large quantity of good quality water is used for lowering temperature of dyeing machines and power generators that is often allowed to go to waste. This water can be best used for boiler feed water to take advantage of its heat content. The cooling water should preferably be softened prior to use so that alkaline hardness salts are not precipitated in time cooling tubes during heat transfer.

3.5.6 Good Housekeeping Practices

A careful inspection of machines and processes will indicate where improvements could be made for saving water; the leaking joints and faulty valves on the waterlines not only waste water but also make the dye house untidy. Jiggers and winches are rarely calibrated to relate volume of liquors to its height in the machine. This is responsible for lack of control over liquor-ratios when dyeing fabric of varying weights and densities. Such conditions result in poor matching and considerable redyeings that not only waste water but also cause loss of expensive dyes and auxiliaries.

Saving of water by good housekeeping measures may not be substantial but such practices have important indirect advantages. These, for example, help inculcate mental discipline and develop scientific attitude in operators that ultimately benefits the organization.

3.5.7 Reuse of the Dye House Effluent

In cotton and polyester-cotton dyeing mills, large quantities of electrolytes are used to exhaust the dyes on cotton fibres and so the effluent is normally not fit for reuse because of its high TDS. Moreover cotton scouring and mercerizing processes introduce large quantities of alkalis in the effluent. However, effluent of the synthetic fibre processing mills is fit for reuse after some simple treatments of neutralization, sedimentation, colour removal and aeration.

It is possible to use washings of the cotton bleaching and dyeing processes a her separating the first rinsing water from the subsequent washings because the initial rinse-water contains most of the colour, salt and other impurities. The latter washings can be purified by the above-mentioned treatments. The Process however, requires careful monitoring of the different washings and challenging these into separate drains.

Demineralization of Brackish and Sea Water

As discussed above, the quality water is going to be in short supply for the textile industry permanently and this shortage will be progressive. It is, therefore, necessary to consider alternative processes to supplement the existing water sources and the most obvious choice is demineralization or desalination of the brackish sub-soil water and even seawater. There are three major methods that are being successfully used for desalination of water. These are based on the following principles:

- Vaporization ion and Condensation
- Reverse Osmosis
- Ion Exchange
3.6.1 Vaporization and Condensation

In this system, saline water is heated preferably under reduced pressure to boiling point in flash evaporators and the water vapors (steam) are cooled to condense into pure water. This process is comparatively expensive and so is mainly used in oil producing countries like Saudi Arabia, Kuwait and UAE where cost of the fuel is low.

3.6.2 Reverse Osmosis Process or hyper filtration

According to the well-known principle of osmosis when a salt solution is separated from water with a semi—permeable membrane water molecules tend to move across the membrane towards the salt solution under the concentration gradient. If the salt solution is contained in an enclosed vessel, a pressure known as the ‘Osmotic Pressure’ is developed that is directly proportional to the difference in concentrations of salt on both sides of the membrane. If pressure equal to the osmotic pressure is applied on the salt- solution side of the membrane, inward flow of water is stopped. If pressure exceeds the osmotic

Pressure, water will start flowing in the opposite direction i.e. from the salt—solution to the waterside of the membrane. This principle is used in the reverse osmosis process for reducing salt concentration in brackish waters.

The process was known for quite sometime but could become commercially feasible only after robust and long lasting synthetic semi-permeable membranes were developed and became available at competitive prices. With reduction in cost of the membrane, the reverse osmosis method of demineralization of water has now acquired a great commercial significance and its use is rapidly increasing in the semi-arid countries for bottled drinks, textile wet processing, and boiler feed-water and for many other industries.

The semi-permeable membranes are mainly of two types the spiral and the hollow fibre. Former is a composite of polyamide polymer on polysulphone support membrane and is rolled over a thicker porous-material layer that collects and transports the demineralized water. The hollow-fibre module consists of polyamide or cellulose triacetate fibers of 25-250-micron diameter that are sealed on one end. A large number of the hollow fibres are bundled together and placed in a saline water-pressure vessel. Pressure required for making water flow across the membrane depends on salinity of water; type of membrane and the desired purity and it varies from 100 to 400 psi for brackish waters.

One square meter of the membrane whose pore size is of the order of 10-20 A. is capable of demineralizing about 500 liters or 110 (British) gallons of water per day. Power consumption for treating seawater is about 5-9 KWh and for brackish water 2-3.5 KWh per m3 or 220 gallons of demineralized water. Life of the membrane depends upon quality of the water and conditions of working. Acidic pH, presence of soil and microbes in water deteriorate the membrane rapidly. The saline water should, therefore, be filtered and chlorinated to kill microorganism followed by removal of its excess. Addition of certain chemicals to prevent scaling by calcium sulphate and foam-formation is helpful in prolonging life of the membrane.
The reverse osmosis process is being successfully used all over the world and the plant is quite compact and simple to operate. The brackish water is forced through a number of rolls of membrane by pressure pumps and the desalinated water flows out through in a perforated pipe fitted inside the membrane rolls. The treated water is left with only 3-5% of the total salts originally present in the raw water. The total cost for lowering TDS of water from 3,000 to about 150 ppm, is fairly high (although cheaper than the other two methods) and may in some cases be double of the municipal water but the extra cost is justified by surety of continuous supply of this raw material.

**3.6.3 Ion-Exchange Demineralization Process**

This system works on the principle of the water softening plant but differs from it in having two columns of resins. In the one cations and in the other anions of the dissolved salts are replaced with hydrogen and hydroxyl ions respectively and water of a very high purity or zero conductivity is obtained. After exhaustion, the resins are regenerated; the cationic with a mineral acid and the anionic with caustic soda.

The capital cost of the equipment is lower than the oilier two systems but the high cost of chemicals required to regenerate the resins is high and so makes the process uneconomical for the textile industry. Pharmaceutical and certain chemical industries are the main users of this process where water of ultra-high purity is needed.
PRE-TREATMENTS
The term “pre-treatment” includes all operations of preparing the textile materials, such as fibres, Yarn. Woven and knit fabric for the subsequent processes of dyeing, printing and finishing. For all practical purposes pretreatments are carried out in continuation of dyeing or printing and their equipment is part of the wet processing plant. The main object of pretreatment is to impart a uniform and high degree of absorptivity for aqueous liquors with the minimum possible damage to the Fibrous material. The cotton fabric, for example, after the pretreatment should become free of all natural impurities like pectin, wax, protein and husks and the sizing chemicals comprising of adhesives and softeners. Besides high and uniform absorptivity the textile materials should have adequate degree of whiteness so as not to mar colour and brilliance of the applied colours. Normally achievement of whiteness of about 80% remission (As. c 100% reflectance from barium sulphate) and a D.P. of 1,600 to 2,000 are aimed at for the cotton goods.

The grey cotton fabric normally undergoes the following pretreatment procedures:

- Inspection and marking
- Shearing or cropping
- Singeing
- Desizing
- Scouring
- Mercerizing
- Bleaching

Shearing and singeing are always carried out in open width but desizing, scouring and bleaching of woven fabric may be done either in rope or in open-width Forms by batch, semi-continuous or hilly continuous systems. The rope processing equipment is comparatively less expensive but is not quite suitable for the heavier-weight and the wider-width fabrics. Such fabrics tend to develop “rope marks” that cause uneven dyeing later. In the rope form, woven and knit fabrics are scoured and bleached in kiers (autoclaves), winches and jets for batch and in J box or a similar storage system for continuous working. In open width processing, jiggers, pad-batch and pad- roll machines are used for batch system and J-box, U-box, normal steamer, pressure steamer, roller bed conveyor steamer or perforated belt steamer are employed for the continuous working. Choice of the equipment depends mainly on the volume of cloth to be processed but the present clay trend is to install the open-width continuous pretreatment machines.
Loose cotton fibres, slubbing and yarn in both hank and packages of cone, cheese or warp beams are scoured and bleached in package processing equipment. If the yarn is to be mercerized later, pretreatment is carried out on hanks because yarn is commonly mercerized in hank form. Hanks are made into a chain by linking together in the form shown in fig. 4.1 and are then packed in kiers for scouring.

A brief description of the above pretreatment processes and the equipment used in these is given below. Mercerization of cotton fabric and yarn is a special pretreatment that can technically he consider a finishing process.

### 4.1 Inspection and Marking

In composite or vertical mills, the grey cloth is thoroughly checked to identify its defects and to determine its quality. Inspection is carried out on slanting ground glass plate tables that are illuminated from below by neon tube-lights. The machines are often fitted with ultra-violet ray illumination system that spots oil stains and variation in different qualities of the cottons that are blended prior to spinning. The cloth is pulled over the glass plate either manually or by a variable-speed motor and different cloth defects are marked and recorded for the quality control purposes. The fabric pieces are next marked, for identification purposes and flat stitched end to end to make a continuous length. Marking done with special ink that would withstand subsequent contact with scouring and bleaching chemicals. This indelible ink is usually made with mineral pigments dispersed in a solution of chlorinated rubber binder,

### 4.2 Shearing

Purpose of shearing is to remove loose threads and fibre tufts on the surface of the fabric. These are shaved off by carefully running cloth in close contact with razor-sharp helical blades mounted on steel cylinders that are rotating at a high speed in a direction opposite to the movement of the cloth. Shearing is not always necessary for fabrics meant for bleaching or dyeing but is useful for printing that requires a fabric with a very smooth face. For the same reason, the cloth meant for printing is sometimes sheared after bleaching.

### 4.3 Singeing

Fabrics made from staple fibres show protruding fibre ends at the surface of cloth and this nap disturbs appearance of the dyed and the printed fabrics. To improve the
surface appearance of fabric, the fibre ends are removed by singeing with a flame or a hot plate. Cotton yarn especially that used for sewing thread is also singed to give a smooth appearance. Prior to singeing, the fabric is brushed to loosen and raise the fibre ends and then rapidly moved at a speed of around 100 meters per minute, over a row of gas burners to burn projecting fibres without scorching the cloth.

Singeing can also be done by contact with hot plates but the flame singeing is preferred because flames penetrate into pores of the material, in some machines indirect heat is provided by a red-hot clay plate that is heated by the gas flame as shown in Fig. 7.2. The best result is achieved by singeing after desizing but it is not practiced because it involves an extra drying of the fabric. The burner flame should be free from soot to avoid discoloration of the material and so only the more volatile and non-aromatic fuels are used for this purpose. An exhaust fan continuously removes fumes of the burnt fibres.

Modern singeing machines have proper safety arrangements against fire hazards and fuel supply is cut off immediately on an unforeseen stoppage of the machine. The machine room has also fireproof doors that automatically close in case of an accidental fire to eliminate any chance of spreading fire in the entire department. To quench any lingering flame, the singed fabric is directly fed into a trough full of water that usually contains a desizing agent also.

### 4.4 Scouring

Cotton goods as yarn and woven and knit fabrics contain about 8 to 10% of natural impurities and the woven fabric carries additional 5 to 7% of the sizing material. While most of the sizing material is removed from the cloth during desizing, the natural impurities require treatment with strong alkalis like caustic soda at elevated temperature for their breakdown and dispersion in water.

For this purpose, a variety of equipment is available to process the materials in different forms and by batch, semi-continuous and continuous processes. The ultimate aim of scouring is to make the material tin formally and highly absorbent in a cost effective manner so that there are no difficulties in the later processes of dyeing, printing and finishing. Some of the more common batch and continuous scouring machines are described below.

#### 4.4.1 High Pressure Kier

A kier is cylindrical steel autoclave that is capable of withstanding high steam and has a capacity varying between 1 to 3 tons. To eliminate formation of rust marks, kier is coated with a mixture of lime and sodium in silicate that is periodically renewed. Kier has a false bottom at the base on which the cloth pieces, already sewn end to end to loon a rope, are piled up to its entire height. A manhole with a pressure lid is provided at the top for entry of the fabric rope that may be fed manually or mechanically by an overhead.

After closing the manhole the scouring liquor is circulated by a centrifugal pump after collecting it from the bottom and sprayed at top of the fabric pile through a circular perforated pipe. On its way up, the liquor is heated with steam indirectly in a multi-tubular heater, an air escape valve at top is left open till the liquor starts boiling and steam starts issuing from it for a few minutes. This is done to remove all the air from the kier otherwise oxygen in the air will react with cellulose to for oxy cellulose that causes severe
tendering of the material. Composition of the scouring liquor, its temperature and duration of the treatment depend upon density of the fibre to be processed and ultimate degree of absorption required.

A typical recipe, based on the dry weight of the fabric and a liquor ratio of 4:1, is as under:

- Sodium Hydroxide 3.0%
- Sodium Silicate 0.5%
- Wetting Agent 0.1%

At elevated temperatures sodium hydroxide completely breaks down proteins and pectates that are mainly present in the cuticle layer and converts these into water-soluble products. The oils and fats are converted into soap and this in turn emulsifies waxes that are removed by washing later. Residues of leaves and husks are degraded but are not completely removed by hot caustic soda solution. However, the degraded substances are destroyed in the subsequent hypochlorite or peroxide bleach. Sodium silicate by virtue of its colloidal nature serves to keep the reacted impurities suspended and reduces their tendency to settle on the scoured fabric.

The wetting agent that may be a mixture of anionic and non-ionic surfactants for having synergistic effect reduces surface tension of the scouring liquor and so helps in its quick penetration into the fibres. The wetting agents should be able to withstand high temperature and strong alkaline solutions. The liquor is rapidly raised to a temperature of 130°C and is kept circulating for 6 to 8 hours. When scouring is complete the brown colored liquor is discharged, preferably in stages with addition of hot water in to the kier so that the impurities do not settle and stick to the fibres and are removed more completely. After washing fabric in the kier, the remaining impurities are removed in a rope washing machine (Fig.) preferably with a counter-current flow of water.

### 4.5 Desizing

To improve efficiency of weaving, warp yarns are ‘sized’ i.e. coated with an adhesive containing an oily product to prevent their fraying and breaking during weaving. The sizing materials hinder absorption of water or dye-liquor and so their removal is essential prior to attempting any wet process. The cotton warps are usually sized with a preparation based on starch. Starch swells hut does not dissolve in water and dispersible products by either certain enzymes so it is removed by breaking it down into water or
oxidizing chemicals. The latter products are comparatively expensive but are faster acting and so are suitable for the continuous processing.

4.5.1 Enzyme Desizing

The enzyme preparations are of 3 types. Diastatic, Pancreatic and Bacteria!. These stereospecific enzymes split a-glucoside bonds of starch but not the 3-glucoside bonds of cellulose. The enzymes break down starch (amylose) chains into water-soluble or water-dispersible products. Activity of the enzymes depends on pH temperature and presence of activators (Na\(^+\), K\(^+\) and Ca\(^{++}\) ions) and also the wetting agents.

Of all the enzymes the bacterial amylase are the most popular because these are faster in action and more tolerant to pH and temperature variations. The quenching box of singeing machine contains about 1 % solution of the enzyme with 5g sodium chloride. The optimum pH and temperature of the solution is 6-7 and 60-70 at 18°C respectively. The fabric saturated in the solution is batched on a roller rotating at about 4 rpm. To improve penetration, the material is padded twice with an intermediate passage on the timing-guide rollers before batching.

The roll of cloth is wrapped in plastic sheet to avoid drying of fabric and slowly rotated for a couple of hours. The degraded starch products are then removed by washing the fabric in boiling water in a washing range. Addition of 5 to 10 g/l of sodium hydroxide in the first two washing cisterns promotes the washing efficiency. In the earlier practice, the amylase soaked fabric rope was piled in wooden tanks or cement pits and after about 24 hours the degraded starch was washed off with boiling water in a rope washing machine.

4.5.2 Oxidative Desizing

Under controlled conditions, certain oxidizing agents decompose starch into water dispersible particles without damaging cellulose of the fabric. The starch degrading action is sufficiently rapid to make the process compatible with the continuous fabric scouring and bleaching system. Another advantage of the process is that motes and other non-cellulosic impurities present in fibers are also attacked resulting in partial break down and this helps in their removal in the subsequent scouring and bleaching processes. The more popular oxidizing agents are Sodium Bromite (NaBrO\(_3\)), Hydrogen Peroxide (H\(_2\)O\(_2\)) and Ammonium or potassium Persulphate (NH\(_4\)SO\(_4\)) Sodium Bromite has proved very effective.

For rapid oxidation of starch and is applied in a concentration oil 1 g/l of active bromite at a pH of 10 to 10.5(brought with Disodium Hydrogen phosphate-Na\(_2\)HPO\(_4\)) at 70-90 temperature at 180°C. After a short dwell time of about 20 minutes, the decomposed starch products are thoroughly washed off with boiling water’ in a washing range. Alternatively the oxidative desizing agent is added into the scouring liquor to reduce the production time.

The water soluble sizes like carboxymethyl cellulose (CMC), Polyvinyl alcohol (PVA) and acrylates need no chemical desizing and only thorough washing with hot water is enough for their removal, Addition of 1-5 g of a wetting agent and provision of a little dwell time is helpful in removal of the size especially those containing PVA that takes comparatively longer time to swell and dissolve in water.
4.6 Bleaching

Scouring removes almost all the impurities of cotton fibres except husk and natural coloring matter that are ultimately removed by oxidizing agents. The oxidation treatment or bleaching is necessary for producing white goods as finished products or for dyeing paste shades. Even for dark shades, bleaching improves the brilliance and evenness of the shade. Bleaching is normally carried out with hypochlorites, hydrogen peroxide or sodium chlorite.

4.6.1 Bleaching with Hypochlorite

The active constituent of the hypochlorites is chlorine or hypochlorous acid that is stabilized as calcium or sodium salts. In earlier times, the calcium compound known as bleaching powder was used exclusively. It is a mixture of calcium hypochlorite Ca(OCl)₂ and basic calcium chloride, CaCl₂Ca(OH)₂H₂O. Bleaching powder being solid is easy to transport and has a long shelf life but its use involves excessive and careful handling in dissolving and removal of the non-oxidizing solid constituents.

Sodium hypochlorite has now replaced bleaching powder because it is more economical and easier to handle. It is often prepared in the mills by dissolving chlorine gas slowly in a cold solution of caustic soda or sodium carbonate as per the following reactions:

\[
\begin{align*}
2 \text{NaOH} + \text{Cl}_2 & \rightarrow \text{NaOCl} + \text{NaCl} + \text{H}_2\text{O} \\
\text{Na}_2\text{CO}_3 + \text{Cl}_2 & \rightarrow \text{NaOCl} + \text{NaCl} + \text{CO}_2
\end{align*}
\]

Chlorine is abundantly available as a by-product in the electrolytic manufacture of sodium hydroxide. A percentage of 15-18% of available chlorine are generally maintained in the concentrated hypochlorite solution but it may be noted that the concentration falls gradually during storage and needs to be checked before use.

Hypochlorites are strong oxidizing agents and it is, therefore, necessary to carry out bleaching under the prescribed conditions of pH, temperature and time so as to avoid damage to the cellulose. Careful control of the pH is very necessary because the oxidizing entity changes with variation in pH. At pH above 10, the oxidizing component exists as hypochlorite ion (-OCl⁻) but at lower pH between 5 and 8.5, it is converted into hypochlorous acid. At pH below 5, liberation of chlorine gas starts and at pH 3, the whole of the hypochlorous acid is converted into chlorine. It is well known that the rate of bleaching or oxidation of cellulose becomes maximum between pH 5 and 9 and that pH range corresponds to maximum generation of the hypochlorous ion.

For the minimum damage to the cotton goods bleaching should, therefore, be done at pH 10-11. Sodium hypochlorite solution has a pH of 11.5 but during the bleaching reaction, hydrochloric acid is generated and pH of the solution starts falling. To counter this, the hypochlorite solution is buffered with 5-10 g/l of sodium carbonate. Rate of bleaching also depends on temperature and rises with increase in the reaction temperature. Normally bleaching is carried out with 5 to 9 g/l of active chlorine at room temperature for about 2-4 hours but it is quite safe to process at 40°C to reduce the production time. Contact with copper and iron metals should be avoided as these catalyze
the oxidation reaction and may tender the goods. Equipment for bleaching may be same as that used for scouring.

4.6.2 Discolorination or anti-color treatment

It is necessary to remove traces of the residual chlorine alter bleaching otherwise it may damage cotton goods during storage. This is done either by treatment with 5 g of sulphuric or 20 g/l of hydrochloric acids or with 5 to 10 g/l of sodium bisulphite (NaHSO₃) solution at 60°C for 30 minutes. The acid converts hypochlorite into volatile chlorine while the bisulphite reduces it into a harmless sodium or calcium chloride.

In an alternative method alkaline hydrogen peroxide (3cc/l H₂O₂ + 0.3 g/ NaOH at 90°C) is used that besides dechlorination improves quality and stability of the whiteness. This principle is also a basis for a continuous bleaching process for cotton goods the reaction may be expressed as under:

\[ \text{HOCl} + \text{H}_2\text{O}_2 \rightarrow \text{HCl} + \text{H}_2\text{O} + \text{O}_2 \]

4.6.3 Bleaching with hydrogen Peroxide

The oxidizing agent most commonly used today in bleaching of textiles is hydrogen peroxide. It is used in batch; semi-continuous and continuous processes as well as for bleaching colored goods and for combined scouring and bleaching of the lightweight cotton goods. Other advantages of peroxide over the hypochlorites are lower loss in weight of goods, reduced oxidative damage and economy in water usage and so lesser cost of effluent treatment t. The bleaching equipment is the same as that used for scouring for both the batch and continuous processes.

In the latter, two storage chambers can either be installed in tandem for scouring and bleaching or these processes may be done in one chamber alternately. Hydrogen peroxide has a low dissociation constant and is a weak acid. In an alkaline solution the peroxide anion is produced that is the active bleaching agent (Reaction 1 and 2). In a secondary reaction (3) molecular oxygen is formed that has no bleaching action.

\[ \text{H}_2\text{O}_2 + \text{OH}^- = \text{H}_2\text{O} + \text{HO}_2^- \] \[ \text{HO}_2^- = \text{OH}^- + \text{O} \]
\[ 2\text{H}_2\text{O}_2 + 2\text{H}_2\text{O} + \text{O}_2 \]

A high concentration of the hydroxyl ions has an accelerating effect on the rate of bleaching and so to control the tale of reaction it is necessary to add a stabilizer. The most common stabilizer is sodium silicate and it also gives protection against metal contaminants. Silicate is more effective in the presence of salts of magnesium and this provides a rare case where hard water is preferred over the soft type. Magnesium salts are sometimes added into the peroxide bath in calculated concentrations.

A disadvantage of the silicate is that it deposits hard insoluble incrustations on tile sides on the side of machine, which scuff the fabric and the scuffmarks show in
dyeing. For this reason silicate is sometimes replaced partly or completely with tetrasodium pyrophosphate (Na$_2$P$_2$O$_7$) or organic proprietary stabilizers.

**A typical recipe for a wet on wet bleaching in a roller bed continuous system is as under:**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Peroxide 35% (135 volume)</td>
<td>50-60 ml/l</td>
</tr>
<tr>
<td>Sodium Silicate 30°Be</td>
<td>10 ml/l</td>
</tr>
<tr>
<td>Organic Stabilizer</td>
<td>10 g/l</td>
</tr>
<tr>
<td>Sodium Hydroxide</td>
<td>3 g</td>
</tr>
<tr>
<td>Wetting Agent</td>
<td>1-2 g/l</td>
</tr>
<tr>
<td>Liquor Pick-up</td>
<td>100%</td>
</tr>
<tr>
<td>Impregnating Temperature</td>
<td>20-30°C</td>
</tr>
<tr>
<td>Reaction Time</td>
<td>1-2 hours at about 95°C</td>
</tr>
</tbody>
</table>

Concentration of the reactants and the time of treatment may however, vary according to the degree of impurities and quality of whiteness required. Concentration of the chemicals in the feeding bath is about 3 times of the above mentioned concentrations in the padding bath but that of hydrogen peroxide needs to be controlled by checking with periodic titration, usually with the standard permanganate solution. In the semi-continuous pad-roll process time of treatment is usually 4 to 5 hours.

Addition of certain peroxide ‘activators’ like tetra acetyl ethylene diamine in the bleaching bath is claimed to achieve good bleaching at comparatively lower temperatures and pH. It also causes minimum damage to the fibres and is specially recommended for bleaching viscose and spandex blends to protect the fibres from fibrillation.

**4.6.4 Cold Pad-Batch Process**

This process is very simple and consists of padding fabric with 40- 50 ml/l hydrogen peroxide (35%), 15-20 ml/l sodium silicate 38° Be, 10-15 g/l caustic soda and 3-5 g/l of a wetting agent to a pick-up of 100%. The batch roll is covered with a plastic sheet and slowly rotated (4 rpm) for 15 to 24 hours and then washed in an open width washing range with boiling water. The process has the advantages that it requires inexpensive equipment and is free of danger of catalytic damage to the fibres. However, the degree of whiteness is inferior to that obtained by the steaming process.

If deep shades are to be dyed, bleaching of the grey fabric is occasionally done in one step by the cold-hatch or the pad-roll process. However, the process is not always satisfactory because impurities like traces of the heavy metals in cotton have decomposing effect on the peroxide and may also cause tendering on the fabric.

Bleaching with Sodium Chlorite: Sodium chlorite (NaClO$_2$) was originally introduced for bleaching the synthetic fibres but is now finding increasing use for cotton goods because of all the bleaching agents it is the least damaging to cellulose. It is sometimes used for bleaching grey cotton goods without prior boil-out but absorbency obtained is just tolerable. In the grey bleaching the impurities of cotton are not removed.
but are oxidized to colorless products and so there is very little loss in weight of the goods after the treatment.

Sodium chlorite is commonly marketed in the form of a crystalline powder in 80% strength but it is available in liquid state also. The aqueous solution of the chlorite is slightly alkaline and has a pH of about 8.5. However, it must be acidified to a pH value within a range of 3.5 to 4.5 to liberate the oxidizing agent. Doubts exist about the real oxidizing entity and different workers have suggested this to be chlorine dioxide (ClO$_2$) chlorous acid (HClO$_2$) or even atomic oxygen.

Chlorine dioxide gas is poisonous and explosive and is also very corrosive to metals in the aqueous medium. Chlorite bleaching is therefore often carried out in an exclusive room in the dye house that is very well ventilated. The machines are fabricated from special stainless steels that have a high proportion of molybdenum or titanium. Alternatively bleaching is done in equipment made of stone, PTFE coated steel or wood. For protection of the stainless steel metal of the machines, it is not uncommon to add sodium nitrate in a quantity equal to the chlorite that moderates decomposition of the chlorite and inhibits corrosion of metals.

The pH of around 4 ± 0.2 required for bleaching is maintained with buffers or as termed in industry activators, like sodium acetate or sodium dihydrogen phosphate (NaH$_2$PO$_4$) Latter is usually preferred because it improves whiteness of goods. Neutral or slightly acid chemicals that liberate acid on heating are also used occasionally. Organic esters like ethyl lactate or titrate and their ammonium salts are also suitable for this purpose. Common recipes for the batch and the continuous bleaching are given below:

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Batch Process</th>
<th>Continuous Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium chlorite (80%)</td>
<td>5-7</td>
<td>20-25 g/l</td>
</tr>
<tr>
<td>Sodium nitrate</td>
<td>2-3</td>
<td>2-3 g/l</td>
</tr>
<tr>
<td>Sodium dihydrogenphosphate</td>
<td>2-4</td>
<td>0.5-1.0 g/l</td>
</tr>
<tr>
<td>Wetting agent</td>
<td>1-2</td>
<td>1-2 g/l</td>
</tr>
<tr>
<td>Formic acid to adjust pH to</td>
<td>3.8-4.2</td>
<td>6-6.5</td>
</tr>
<tr>
<td>Temperature</td>
<td>85-90°</td>
<td>85-90° C</td>
</tr>
<tr>
<td>Reaction time</td>
<td>1-3</td>
<td>2-4 Hours</td>
</tr>
</tbody>
</table>

After the treatment, washing with boiling water and dechlorination with 0.5-1 % cold sodium bisulphate solution is carried out.

### 4.6.5 Bleaching of Knit Fabrics

Cotton tubular knit goods are commonly scoured and bleached by a one step process in winch or jet machines using 4-5 ml/l caustic soda solution (38° Be), 5-8-ml/l hydrogen peroxide (35%) with a peroxide stabilizer and a wetting agent. Semi-continuous cold pad-batch method has also been developed in which the fabric is first padded with reactants under a minimum of tension, wrapped on a perforated stainless steel tube and
covered with a plastic sheet. After the due reaction time, water is forced through the tube into the batch of the fabric and the oxidation-degraded products are washed off. M/s Dornier has modified their “floating cigar” mercerizing machine. For continuous scouring and bleaching of the knit fabric. The fabric may be mercerized first leaving about 2% alkali in the material during washing off. The wet fabric is next padded with hydrogen peroxide its stabilizer and other auxiliaries and stored in a roller-bed steaming unit for 1-2 hours. The bleached fabric is finally washed again on the floating cigars thus making the bleaching process a semi-continuous one.

It may not be quite out of place to mention that certain direct dyes are applied to the unbleached (grey) knit fabrics in the presence of hydrogen peroxide and caustic soda, which is a very economical process as scouring, bleaching and dyeing are combined. Recently it has been suggested that combined scouring and bleaching at a temperature of 130°C in a high-pressure jet machine can save time, steam, water and electric power without sacrificing whiteness and absorbency of the finished material. The main difference of the process from a conventional one is that rinsing of the fabric is started at about 120°C by simultaneous feeding of fresh water and draining of reactant liquor while the system is still under pressure.

This technique reduces a considerable quantity of water that is normally required for washing off. Moreover treatment with hydrogen peroxide and washing off at temperatures above the boiling point of water reduces the processing time from 170 minutes required for the conventional process to only 70 minutes. The method essentially consists in raising temperature of the liquor to 130°C in 40 minutes, treating for 5 minutes at that temperature and then adding a hydrogen peroxide killer. To save time rinsing is started during the liquor cooling stage and continuous addition of cold water and discharge of hot liquors is carried out simultaneously. The rinsing stage is completed in 25 minutes. It has been calculated that the high temperature process saves about 25% water, 60% electric power, 6% steam and 59% time as compared with the conventional system.

4.7 BLUEING

After bleaching, the cellulosic materials retain a slight yellowish tone to which the human eye is very sensitive to detect. The principle of blueing is to neutralize this tone with a blue or violet light and this is achieved by the following two procedures.

4.7.1 Blueing by Subtractive Effect

In this cotton is shaded with a blue or violet disperse pigment dispersion that are not substantive to cellulose. This application suppresses the yellow tone but slightly reduces brightness of the white. Disperse dyes; vat pigments and Ultramarine Blue are commonly used for this effect.

4.7.2 Blueing by Additive Effect or Optical Brightening

Certain organic compounds have the property of fluorescence i.e. they can absorb light of short wavelengths and re-emit it at the longer ones. Many of such compounds absorb ultra rays and re-emit as visible light in the range of 4,000 to 7,000 A°. Textile fibres containing a fluorescent compound reflect more light than an untreated one and thus increase its brightness and whiteness. During the last half century a large number of
fluorescent chemicals, also termed as optical brighteners or FBA have been developed for both natural and man-made fibres that have affinity to the fibres and most of these can also be applied during the bleaching process.

Chemically these can be classified as derivatives of stilbene and behave like the direct dyes for the cellulosic fibres. These can be applied by both exhaustion and padding techniques in concentrations that would fix about 0.2-0.4% of it on the fibres. For cotton fibres, these are generally applied along with the peroxide during bleaching but only a selected few can withstand the hypochlorite. It may be kept in view that the degree of brightness obtained with the FBA depends on proportion of the ultraviolet light in the incident light and is less apparent in the artificial light than the sunlight.

4.8 Continuous Washing Range

After scouring and bleaching the fabric is required to be freed off the residual watersoluble impurities and the reacting chemicals. As mentioned earlier in the batch rope processing the washing machine of the type shown in Fig. 7.4 is used. With introduction of the J-box, rope washing machines were modified to work in tandem with scouring and bleaching units. Basically these washing machines are steel boxes, divided in compartments with partitions and have freely rotating top and bottom guide rollers. The fabric rope is squeezed and then moves forward either in tight or slack form while hot or cold water is fed in a counter-current manner.

4.8.1 Open-Width Washing Range

High-speed open-width scouring and bleaching machines created a demand for washing machines that would efficiently remove soil from fabrics without their creasing. The standard open-width washing machine (Fig. 7.9) consists of a stainless cistern fitted with a series of freely rotating top and bottom parallel guide rollers and a pair of pneumatically pressed squeeze rollers at the end. In modern machines, some or all of the top rollers are positively driven to reduce tension on the moving fabric. Sonic manufacturers have installed small diameter squeeze rollers over the top rollers.

To improve the washing efficiency, the cisterns used to be fitted with stirrers to enhance water-fibre contact but the latest thinking considers these unnecessary as movement of fabric at high speeds causes plenty of turbulence of its own. The cisterns are totally covered but have glass panes fitted on the sides for viewing the fabric. More compact machine lies have also been designed in which double threading is employed on additional freely moving rollers (Fig. 4.1). This system increases the capacity per unit but the arrangement is costly. It is also more complicated and so reduces accessibility and makes threading difficult.

In order to conserve water and heat energy, the cisterns are interconnected to have a counter current flow of water. The cisterns are placed on a slopping floor with the last one at the highest level. Heating is primarily done at the last hot washing unit and heating coils are provided in other units to maintain the required temperature. To further conserve the heat energy, the incoming cold water is heated in a heat exchanger with the outgoing hot wastewater.
For conserving water and saving floor space, horizontal machines have also been developed which rollers are fitted in two vertical banks. The fabric moves horizontally from bottom to top of the cistern and water flows downwards through the fabric. This machine has been further modified to wash fabric at about 110°C. However, advantages of such machines have not been fully established and these are not very popular as yet.

### 4.9 WATER EXTRACTION

Textile materials require drying after washing that is carried out in two stages. First water removed mechanically and then by application of heat. Evaporation of water by heat is expensive and so maximum quantity of water is extracted by mechanical means, which are:

- Centrifuging
- Mangling and
- Suction methods.

Comparative water retention values of different types of fabrics extracted by different methods are given in Table 4.1.

<table>
<thead>
<tr>
<th>Fabric</th>
<th>Centrifuging</th>
<th>Mangling (%)</th>
<th>Suction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cotton</td>
<td>45-50</td>
<td>45-70</td>
<td>40-55</td>
</tr>
<tr>
<td>Viscose</td>
<td>80-100</td>
<td>60-100</td>
<td>70-80</td>
</tr>
<tr>
<td>Sec. Cell. Acetate</td>
<td>30</td>
<td>40-50</td>
<td>27</td>
</tr>
<tr>
<td>Nylon6.6</td>
<td>15-25</td>
<td>20-40</td>
<td>14-20</td>
</tr>
<tr>
<td>Polyester</td>
<td>12</td>
<td>20-30</td>
<td>15</td>
</tr>
<tr>
<td>Wool</td>
<td>42</td>
<td>58</td>
<td>84</td>
</tr>
</tbody>
</table>

Mangling is the most economical of all the three methods of extraction and its cost is about one hall of centrifuging and one third of suction methods, for comparison sake it is
worth noting that cost of evaporation of water is about 15 times on cylinders and 20 times on stenters for removal of the same quantity by mangling.

4.9.1 Centrifugal

Water extraction by centrifuge is mainly used for yarn in banks, staple fibres held in fine mesh nets, knit goods and woven fabrics that do not crease severely. The centrifuge consists of basket/cage of Ito 1.5 meter diameter that rotates at 450 to 350 rev/min respectively inside an outer cover. As a safety precaution, an interlocking lid is provided that does not allow motor to start until the lid is locked and does not open until the basket becomes stationary. Centrifuging of fabric is a batch wise process as opposed to mangling and suction. For loading, fabric is fed by a pulley at top while the basket is rotated slowly by hand to achieve a balanced distribution of weight.

4.9.2 Mangles

Mangles for water extraction have the same principle as pad mangles except that the main requirement is efficiency of squeezing in contrast to even application of dyes or finishes. The rollers of water mangles are hard and are made of even stainless steel and ebonite. To improve the squeezing efficiency of mangles increase of diameter of the rolls, very high pressures or high speed of passage of cloth have very little advantage.
A considerable improvement in water extraction is achieved by using resilient type of rollers, named after the inventor as Roberto bowls. The filling of the resilient rollers is composed of rubber-coated nylon fibres pressed under high press tire. The rollers tend to suck off water held in fibre interstices of yarns and are very effective on knitted or open-weave structures of fabrics.

4.9.3 Suction De-watering

Many fabrics made from textured filaments or that have delicate structures and also the tufted carpets are damaged on hydroextracting by spinning in a centrifuge or squeezing between the mangle rollers. A suction machine safely removes water from such materials. Essentially the machine has a 1 to 3 mm wide slot cut on top of a horizontal cylinder of about 20 cm diameter and the slot is connected to a vacuum pump through a fibre-filter and a water separator. Air is drawn through the slot that is kept open according to the width of fabric by adjustable rubber or plastic sleeves. For high porosity fabrics like knits, a small roller is placed over the slot to improve efficiency.

4.10 Drying Of Fabrics

4.10.1 Cylinder Dryer

This is the oldest, simplest and so the least expensive equipment for drying wet fabric. The fabric is passed round a series of 56 cm diameter stainless steel steam-heated cylinders that are assembled in two or more vertical banks. The cylinders are driven with chains from a common drive. The hollow shaft of each cylinder is fitted, through a doll-head mechanism, with flexible steam and condensate removal pipes; the latter extends to within 5 mm of the bottom of the cylinder. Most of the machines operate at about 210 kPascals (30 Pounds per square inch or psi) steam pressure.

Each cylinder is fitted with a safety valve to automatically release steam if the pressure becomes excessive. An anti-vacuuming air-inlet valve is also provided to let air into the cylinder on its cooling after the dyeing operation is over.

During drying the cotton fabrics gets stretched due to lengthwise tension and so the dried fabric shrinks in width and gets a stiff handle. To reduce this tension, certain manufacturers provide slip-clutch for each cylinder on the chain drive system that allows it to reduce its rotation speed according to the tension on the fibre.
The cylinder dryers or cans are very efficient in fuel consumption due to conduction mode of heat transfer. These give a smooth look and crisp handle to the finished fabric but suffer from lack of control on its width. Cylinder drying is also not the best choice for drying the dye-padded fabrics because of the face/back colour variation defect. Dyed fabrics are frequently dried on hot flue machines.

4.10.2 Drying of Knit Fabrics

Unlike the woven cotton fabrics, the knit goods are easily stretchable and so their loops are distorted under the stretching tension of the drying cylinders. Special drying machines have, therefore, been developed to dry knitwear with minimum tension. In one simple system, the knitted tubes are slipped over perforated steel pipes and then hot air is blown through the perforations while the fabric is gradually pulled up at a rate consistent with adequate drying.

This equipment has a low capital cost and is economical in fuel consumption but is labor intensive and the finished fabric gets slightly stretched. More desirable results are obtained by carrying fabric on a polyester mesh-conveyor belt into a chamber in which hot air is blown on both sides of the fabric alternately. The fabric is slightly buffeted during the drying operation and a tension-free fabric with a lofty handle is obtained.
HISTORY OF TEXTILE COLORATION AND ITS CLASSIFICATION
Human nature is always restless and eager to improve and develop its own self and its surroundings and environment. This applies to dress also that has always been a symbol of social stature, dignity and prestige of a person. It is, therefore, only natural that a lot of human energy and ingenuity is spent in improvement of apparel and also the home textiles for their qualities of comfort and attractiveness. At the same time, constant efforts are also made for reduction in the cost of their manufacturing. A brief definition of coloring of textiles that is dyeing and printing will not be out of place before discussing its history. The term dyeing denotes imparting the fibrous textile materials a colour in a uniform manner that penetrates the fibres and is held there with certain force.

Dyes are app from the aqueous solutions and are stable to laundering, sunlight, perspiration and common chemical reagents in varying degrees depending upon the chemical nature of the dye. Textile printing is a special form of dyeing in which the colour is restricted to certain defined portions of fabric with the help of thickeners and then made to penetrate the fibres usually by a heat treatment. The equipment used for dyeing is entirely different from that required for printing but the fibre-dye interactions are same in both the processes for the same class of dyestuffs.

History of transfer of human clothing from skins and barks to the woven fabric is obscure but made for embellishment of dresses with dyeing and printing processes are. There is a general consensus among the researchers that dyeing is as old as textile industry itself. According to the Greek mythology “Ariadne” the goddess for spinning and weaving is daughter of “Idon” the dyer of wool. This interesting description indicates intimacy, even in the hoary past, of the crafts of fabric formation and its beautification by coloration. The earliest evidences of existence of this very ancient craft have been found in clay tablets excavated from Mohenjadoro site in Pakistan and in the well preserved brightly colored paintings in tombs of the Egyptian Pharaohs.

One of the Mohenjadoro tablets depicts a King priest in which his dress carries a printed motif (Fig. 1.1). This establishes that art of dyeing and printing was in a high state of development in this part of the world even about 5-6 thousand years ago. The colored fabrics found in the Egyptian tombs had been dyed with indigo whose plant is not indigenous to Egypt. And was then grown only in the Indo-Pak sub-continent. This fact indicates existence of not only the trade routes between far-flung countries but also importance of the coloring matters as to be considered a worthwhile product in the risky and hazardous trade ventures of those days. Ancient historians especially Pliny, (AD 23-79) have also mentioned the purple-dyed fabrics that

![Figure 5.1](image-url)
were worn by the nobles of the Persian and the Roman empires even before the advent of the Christian era.

These were dyed with an extract of molluscs in the Mediterranean town of Tyre and so the colour was known as the Tyrian purple. Pliny also describes how Egyptians produced variegated colours with one dye by using different stones (mordant). Bible mentions red colored curtains that were most probably dyed with kermes insects. In the pre-biblical period Phoenicians living on the coast of Mediterranean excelled in the craft of coloration and had a thriving trade. Plutarch (AD 46-120) in his writings about the Imperial Rome has mentioned about the govt. patronage of the craft of coloration and also existence of a school on this art.

Before the beginning of the modern scientific investigation age, most of the coloring matters were of natural origin obtained from vegetable, animal or mineral sources. The more important of these were of vegetable origin such as Indigo, Woad, Madder (Turkey red), Logwood, Persian berries, Walnut husks etc. The animal kingdom provided the Tyrian purple from molluscs and red dyes from Kermes and Cochineal insects. Techniques were developed later to use minerals to get deep and fast shades. The lead salts gave yellows and oranges and iron and chromium salts yielded browns and khaki shades. The craftsmen of yore learnt by the trial and error methods that the coloring matters obtained from the vegetable and animal sources can directly dye the animal fibres like wool and silk.

However, the cotton goods could be dyed and printed only with a prior application of oxides of the metal salts of aluminium, tin or iron. These metal salts are termed as mordants in the trade and literally mean the biting agents. The mordants act as intermediates in binding the coloring matters with cotton. However, there are two important exceptions of indigo and Tyrian purple (bromoindigo) that dye cotton directly without the help of mordants. It is really surprising that by the 16th century, a large variety of shades of different colours could be obtained of reasonably good fastness to washing and light for dyeing and printing of cotton, wool, silk and linen fabrics from the naturally occurring coloring matters. Developments in the art of dyeing were accompanied by simultaneous progress in desizing and bleaching of fibres by simple chemicals that became available with passage of time. The centre of the coloring craft at that time appears to be the Indo-Pak sub continent and evidence exists that large quantities of dyed and printed goods were exported to Central Asia and Europe before invention of the synthetic dyes.

The science and technology era that had begun in Europe after the renaissance started making its impact on the coloration craft also by the 18th century when mineral pigments and mordants were improved. At that time, the French govt. started a scientific approach to the craft and disclosed dyeing method of the famous Turkey-red that was till then guarded by the Turkish govt. with the penalty of death. The French govt. also set up, for the first time in Europe, a teaching institute for the dyeing technology. These development efforts were further strengthened during the blockade of Napoleonic France by England when substitution of the imported coloring materials with the locally available products became a necessity. At that time, investigation of chemical nature of dyes and pigments, along with the other natural products, became a rage in many parts of Europe.

Effect of water quality on Reactive dyeing of cellulose Textiles
In pursuit of such studies, the British govt. established a school of chemistry in 1845 and brought a distinguished German chemist, “Professor Hoffmann” to head the institute. One of the Hoffmann’s students, Perkin got the distinction of being the first to synthesize a dye, Mauveine in 1856 which he pr accidentally while trying to synthesize quinine from an aromatic amine by oxidation. This discovery was followed by production of other dyes of the same chemical group such as Magenta, Aniline Blue, and Imperial Violet etc. Another of the Hoffmann’s student, Griess, discovered the Diazotization reaction in 1859 that opened the door rather the hood-gate to the manufacture of Azo dyes, which form by far the largest group of the synthetic dyes.

\[
\text{NH}_2
+ \text{HCl} + \text{NaNO}_2 \rightarrow \text{N}^+ \equiv \text{NCl}^- + \text{NaCl} + \text{H}_2\text{O}
\]

\textit{Diazotization Reaction}

In 1865, Kekule, an intuitive German chemist, made a fundamental contribution to the advancement of synthetic organic chemistry by postulating the ring structure of the benzene molecule. Soon after this development, Alizarin, the coloring matter of madder and the Indigo dye were synthesized in England and Germany and their manufacturing on industrial scale followed soon after. Such syntheses resulted in elimination of the agricultural production of these two important dyes and other natural coloring matters.

Until 1884 only lengthy and complicated processes involving mordanting could dye cotton. A very welcome development took place when Bottiger patented the first direct dye “Congo Red” that could dye cotton directly in a saline solution without the need for mordants.

\[
\text{N}^+\text{H}_3
\text{N}=\text{N} - \text{SO}_3^- - \text{N}=\text{N} - \text{SO}_3^-
\]

\textit{Congo Red (C.I. Direct Red 28)}

Diazotization and coupling reaction gave an unlimited opportunity for making azo dyes and more than 3 million potential dyes have been made so far in this class of dyes. The metal complex azo dyes wet-c introduced that have comparatively better light-fastness properties. As more and more dyes were marketed and their structures were elucidated, the beginning of a connection between colour and its chemical constitution started to become apparent. Witt, ill 1876 postulated that all coloring matters contained unsaturated groups that he termed as “Chromophores”. The colour is also modified by the presence of certain groups in the dye molecule that he named “Auxochromes”.

Effect of water quality on Reactive dyeing of cellulose Textiles
Coming back to the chronological order of developments, Croissant and Bretonniere in France marketed in 1873 the next important class of dyes, the Sulphur dyes. They produced this dye by rising organic refuse with sulphur and this route soon led to the manufacture of many other dyes that are based on reaction of sulphur with the dye-intermediates of known structures.

The next most important group of the synthetic dyes, the Vat dyes is derived from various quinones. The Vat dyes are the fastest class of dyes for cotton and are water-insoluble pigments that are much more difficult to than the direct dyes. The vat dyes, like the sulphur dyes are first reduced to make these water-soluble and after sorption are oxidized to reform the pigments inside the fibres. Interestingly, the earliest known natural dyes Indigo and Tyrian purple also belong to this class and one wonders how the ancients mastered the complicated technique of their application involving reduction and oxidation of the reduced dye.

In 1954, Rattee and Stevens developed the Reactive dyes, (Procions) in the I.C.I. laboratories in Manchester (U.K.) that for the first time in the history of dye industry, attached dyes to cellulose with covalent bonds. After this pioneering line of thought, almost all the major dye manufacturers developed their own reactive groups and in a very short time, many new ranges of the reactive dyes were marketed. Going back to the chronological order, a new dyeing system may be discussed at this stage.

In 1921, a predominantly hydrophobic fibre, Cellulose acetate was launched but its use in the apparel trade was delayed till suitable dyes were developed for their coloration while trying to dye it with all the existing dyes, it was discovered that this hydrophobic fibre gets dyed with water-insoluble chromophors. The promising dyes were then modified to convert into water-dispersible pigments and marketed as the Disperse dyes. This class of dyes is also used for dyeing other hydrophobic fibres such as Nylon, Polyester, acrylics and many other synthetic fibres as well as for the “dope” dyeing of the filaments.

A historical development of the dyes will not be complete without mentioning coloration of the protein fibres like wool and silk. The earliest synthetic dyes, the basic dyes were used for dyeing these fibres but their fastness properties left much to be desired. After the discovery of the azo dyes many of these were found suitable for dyeing the keratin fibres with varying fastness properties; the fastness being inversely proportional to their level dyeing capability. These were named as the Acid dyes. Later; it was learnt that certain acid dyes with specific molecular structures could have much improved wash fastness properties if the dyed fabric is treated with chromium salts. These dyes were christened as the Acid Chrome or acid mordant dyes.

Application of these dyes is a lengthy process and matching is difficult because the shade alters after treating with the colored chromium salts. To overcome these two shortcomings, Neolan dyes were introduced in which the chromium or sonic other metal ion was chemically combined with the chromophoric group. The Neolans were later replaced with a new range of 2:1 metal-complex dyes that are easier to apply and have a wider range of shades. However, the metal complex dyes are dull in shade as compared with the acid dyes.

Effect of water quality on Reactive dyeing of cellulose Textiles

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A special chromogen, based on Copper Phthalocyanine pigment may also be mentioned which after attaching a solubilizing/reactive group to the molecule, yields brilliant blue and green shades in Direct, Acid, Reactive and other ranges of the dyes. With the advent of the industrial revolution in Europe, the craft of dyeing was changed into a very profitable industry and dyed and printed fabrics once reserved for the nobility, continued to become less and less expensive and affordable by the commoners. This situation greatly altered methods of production and marketing of the colored fabrics.

Along with the exciting developments of newer and better dyes for natural and man-made fibres, continuous struggle was also on to have wet-processing machines that would have higher productivity and improved quality of the processed fabric. After the World War 2, when there was a great shortage of manpower, a large variety of continuous wet-processing machines were developed and the industry entered into a new era of large scale production. Later when the electronic controls (microprocessor) became available, the processing machines were rapidly automated and exact monitoring of time, temperature and other parameters became possible.

The automation besides saving the manpower provided an unanticipated bonus of improved quality control that accompanied with minimization of the human factor in production systems. Requirement of dyeing polyester fibres at temperatures above the boiling point of water as well as high speed processing opened new vistas for the machinery designers in the second half of the twentieth century. At about the same time, a revolutionary development took place in the knitted goods becoming fashionable as outerwear garments. This necessitated evolution of new wet-processing techniques and introduction of the high capacity and high-speed jet dyeing machines.

The present day space-age technology has further transformed the wet processing industry and one cannot imagine of running it efficiently without the aid of computers. Use of the computers is especially successful in the inventory control, making print recipe pitching for dyeing and printing and quality assurance in the mills. Computers have contributed tremendously to improve quality and productivity of the finished products in recent years.

Presently a large number of synthetic coloring materials and a variety of their application methods exist and both need to be classified in a systematic manner. The dyes and pigments can be classified according to their application and usage systems and the Society of Dyers and Colourists (SDC) of the UK and American Association of Textile Chemists and Colorists (AATCC) have adopted this method of classification in preparation of the Colour Index that is published jointly by the two organizations. The Colour Index is the most comprehensive reference work on the coloring matters and gives detailed information regarding their structures, methods of synthesis, application methods and fastness properties.
DYES AND ITS CLASSIFICATION

Colour is entirely subjective. The phenomenon of colour may be defined as the sensation created in the brain by the message stimulated by the impact of radiation of a particular wavelength on the nerves in the eye.

Any colour can be matched by mixing together with different proportions of blue-violet, green-red. It is called additive primaries. All materials are colored because they reflect certain of the wavelength of the white light, which falls upon them, and absorb others. This is referred as productions of colour by subtractive process, and yellow, blue and red is called subtractive primaries (but perfect combination has proved to be magenta, yellow and cyan).

When a beam of sunlight passes through a prism it is separated in to a spectrum of seven easily discernible colours, which are shown in table

Table 5.1

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Colour seen (Light transmitted)</th>
<th>Light absorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>390-430</td>
<td>Violet</td>
<td>Yellow-green</td>
</tr>
<tr>
<td>430-460</td>
<td>Blue</td>
<td>Yellow</td>
</tr>
<tr>
<td>460-500</td>
<td>Blue-green</td>
<td>Red</td>
</tr>
<tr>
<td>500-570</td>
<td>Green</td>
<td>Blue-red</td>
</tr>
<tr>
<td>570-590</td>
<td>Yellow</td>
<td>Blue</td>
</tr>
<tr>
<td>590-610</td>
<td>Orange</td>
<td>Green-blue</td>
</tr>
<tr>
<td>610-700</td>
<td>Red</td>
<td>Blue-green</td>
</tr>
</tbody>
</table>

Dyes are very highly colored organic substances, mainly synthesized from chemicals derived from coal tar. Except in a few special treatments, e.g. vapor-phase dyeing. Dyeing is carried out from aqueous solution, but not all dyes are soluble in water. However, dyeing can occur only from solution, so that chemical processes must be used to give the normally insoluble dyes water-solubility during the actual dyeing process. Coloring matters that are applied to any material in the form of insoluble particles are known as pigments.

The four principal properties that dyes must possess are:

- Intense color
- In almost all cases, solubility in an aqueous solution (either permanently or only during the dyeing operation)
- Ability to be absorbed and maintained by the fiber (substantivity) or to be chemically combined with it (reactivity)
- Fastness, i.e. ability to withstand the treatment the fiber undergoes in manufacturing processes and in normal use.
Dyes are divided into classes by the dyer according to their ability to dye various fibers. But the chemist uses a different method of classification, based on their chemical formulae. The main classed, as they are arranged by the dyer, may be illustrated as in Table 5.2.

**Table 5.2 Classification of Dyes According to Use**

<table>
<thead>
<tr>
<th>Dye Class</th>
<th>Applied to</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water soluble (as applied)</td>
<td>Wool, nylon</td>
</tr>
<tr>
<td>Acid and metal-complex acid (anionic)</td>
<td>Wool, nylon</td>
</tr>
<tr>
<td>Chrome (anionic)</td>
<td>Wool, nylon</td>
</tr>
<tr>
<td>Direct (anionic)</td>
<td>Cellulose</td>
</tr>
<tr>
<td>Basic (anionic)</td>
<td>Acrylics</td>
</tr>
<tr>
<td>Disperse (very slightly soluble)</td>
<td>Cellulose acetates and synthetic-polymer fibers</td>
</tr>
<tr>
<td>Water-insoluble (on the fibre)</td>
<td></td>
</tr>
<tr>
<td>Azoic</td>
<td></td>
</tr>
<tr>
<td>Ingrain</td>
<td></td>
</tr>
<tr>
<td>Oxidation</td>
<td>Cellulose</td>
</tr>
<tr>
<td>Sulphur</td>
<td></td>
</tr>
<tr>
<td>Vat</td>
<td></td>
</tr>
<tr>
<td>Reactive Pigments</td>
<td>Cellulose and other fibres</td>
</tr>
</tbody>
</table>

The more detailed classification is given below in table 5.3.
Table 5.3  Classification of dyes According to Use

<table>
<thead>
<tr>
<th>Dye class</th>
<th>Cellulose (Cotton, viscose rayon)</th>
<th>Polyester</th>
<th>Protein (Wool)</th>
<th>Nylons</th>
<th>Lycra</th>
<th>Acrylics</th>
<th>Secondary Cellulose Acetate</th>
<th>Cellulose Triacetate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct</td>
<td>**</td>
<td>-</td>
<td>*</td>
<td>*</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Reactive</td>
<td>**</td>
<td>-</td>
<td>**</td>
<td>*</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sulphur</td>
<td>**</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Vat</td>
<td>**</td>
<td>-</td>
<td>*</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Disperse</td>
<td>-</td>
<td>**</td>
<td>-</td>
<td>**</td>
<td>**</td>
<td>**</td>
<td>**</td>
<td>**</td>
</tr>
<tr>
<td>Acid</td>
<td>-</td>
<td>-</td>
<td>**</td>
<td>**</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Basic (Cationic)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>**</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

** This class of dye is of major importance for dyeing and printing

* Although not of major importance for dyeing and printing, this class of dye is of some interest.

5.1 Choice of Dyes

One reason for the existence of the great number of commercial dyes that any textile material may have to withstand one or more of a wide variety of processes of manufacture and later be subjected to a variety of different types of wear and tear in use.

The correct choice of dye for any given circumstance, in fact, requires considerable knowledge and experience, and nothing more than a bare outline of the underlying principles can be given here. A few typical examples, selected at random, of some of the matters to be considered in making the choice are given below under four main headings:

5.1.1 Nature of wear and Tear in Use

Many textiles must withstand severe exposure to sunlight or to repeated washing. Thus curtains and fabrics for outer garments must have good fastness to light. And fabrics for awnings and deck chair must withstand sunlight and also rain: knitted wool material should be fast to washing; shirting and handkerchiefs must withstand boiling in soap solution; and so on.

5.1.2 Nature of Manufacturing Processes

Cotton fabric having colored threads on a white ground may have to be subjected to boiling, with alkali under pressure (kier boiling) and bleaching after weaving. The first kind of dye chose for bland fabrics should be withstood the dyeing conditions of the second kind of dye.
5.1.3 Nature of Dyeing Process

Apart from the above treatments to which the already dyed materials are subjected, the nature of the dyeing process is important in determining the choice of dye. Thus in the dyeing of fabric only the most level-dyeing dyes can be used, because the slightest inequality in colour in different areas of the cloth would spoil the appearance. If loose fiber is being dyed, however, levelness is of less importance, because any portions of uneven appearance in the mass will be evenly distributed when the fiber is subsequently manufactured into yarn. Again, in using package dyeing machine, which the dye-liquor is pumped through a container packed tight with loose fiber, or through a cake or thick reel of yarn, it is important for the dye to be either in true solution or present as extremely fine particles.

5.1.4 Dyeing Costs

The prices of different dyes are quite different. It is better to choose the economic dyes in practice if all above mentioned requirements are conformed.

5.2 A General Survey of the Dyeing Process

Essentially dyeing consists of placing a textile material in a solution of coloring matter, which is preferentially absorbed by the material. If this solution of colour matter is merely absorbed by the textile in a sponge-like manner with no change in the concentration of the external solution, and if the colours can be washed out of the material, then the process is merely imbibition, and not dyeing. True dyeing occurs when the dye is absorbed with a decrease in the concentration of the color matter in the solution and when the resulting colours material possessed some resistance to be removal of colour matter by washing.

Dyeing has been practiced for thousands of years and dyed articles having been unearthed in China, India and Egypt. The well-known ancient Silk Road is the foundation of commerce of dyed silk from China to the Mediterranean countries - a link between East and West. Modern dyeing theory, i.e. the mechanism of the reactions between dyes and fibers, was established in the early years of this century.

5.2.1 The state of fibres in solution

When cellulosic, protein and the ionisable synthetic fibres are immersed in water or aqueous solution (i.e. polar medium), they acquire a surface electric charge. These are caused by ionization, ion adsorption and ion dissolution. This surface charge influences the distribution of nearby ions in the polar medium. Ions of opposite charge (counter-ions) are attracted towards interface and ions of like charge (co-ions) are repelled. This, together with the thermal motion, leads to the formation of an electrical double layer.

When unionisable synthetic fibers are immersed in water or aqueous solution, no surface electric charge appear. Cotton and cellulosic fibers bear a negative charge when immersed in neutral solution and protein fibers are positively charge when the pH values of aqueous phase are below isocleetric point (IEP), and negatively charge when pH is over IEP.
5.2.2 The state of dye in solution

The ionic dyes such as reactive, direct and acid dyes in solution are in ionized state or exist in the form of ionic micelles (dye aggregation) bearing negative charges. An increase in temperature tends to break down micelles into less aggregated units.

Some insoluble dyes such as vat dye, sulphur dye during dyeing are first converted to alkali-soluble forms and present in ionic forms bearing negative charges in solution. Some insoluble dyes such as disperse dyes diffuse in solution in molecular state by dispersing agent.

5.2.3 Chemical forces responsible for dyeing

The internal surface of fibers and its importance

The nature fibres, i.e. the cellulosic and protein fibres have exceedingly large internal surfaces, which are the walls of the channels between the bundles of long-chain molecules composing the fibres. The number of such channels is immense, of the order of ten million in the cross-section of, e.g. cotton or a wool fiber, and the total surface of their walls is of the order of 100 m$^2$ or five acres per lb. This is about one thousand times as the outer surface of the fiber.

When the fiber is wetted, water rapidly penetrates and swells a large proportion of these channels, and Dyes in solution are then able to diffuse into the channels or pores. They can however enter only a relatively small proportion of the total internal space, because the remainder is in pores too small to admit a dye molecule. Many of the synthetic polymer fibres have much less internal surface than the natural fibres, but the dye used with such fibres are able to penetrate between the fiber molecules even though water cannot always do so.

Dyes are surface-active substances, that is, when dissolved in water their molecules tend to concentrate more closely together at a surface than in the body of the solution. The surface (or interface) can be that between the solution and either air or a fibre. The first action in any dyeing operation is the concentration of dye molecules at as much of the internal surface of the fibre as they can reach. The concentration so produced is not usually sufficient to give a useful deep coloration to the fibre, and for such coloration other factors must be brought into play. These are the chemical forces, which can operate between a dye molecule, and fibre molecule, which are classified below, and also those between the dye molecules themselves. Which can cause their association into larger units?

The main physical and chemical effects between fibres and dyes

Broadly, four main chemical effects subsequently responsible for the substantivity of the dye for the fibre are list below:

- Hydrogen bonds
- Non-polar or van der Walls’ forces
• Electrostatic or ionic forces -
• Covalent bonds.

These seldom act in isolation; usually at least two operate in any dyeing process.

• **The hydrogen bond**

  This is the ‘secondary valency’ by which a hydrogen atom in e.g. a hydrogen group can form a weak association with another atom. Most fibres and dyes contain groups that can take part in this form of combination. There is evidence for the importance of hydrogen bonds in dyeing some man-made fibres, e.g. cellulose acetates and possible cellulosic protein fibres.

• **Non-polar forces**

  This is a manifestation of the universal tendency of atoms and molecules to attract one another. They seem to be particularly effective in attracting a dye to a fibre when the two have certain special characteristics, e.g. either when they both have long and fairly flat molecules, as with cellulose and direct or vat dyes and also with cellulose acetate and disperse dyes, or when they both contain a considerable proportion of purely hydrocarbon groups (aliphatic or aromatic) as with some dyes applied to wool and most dyes applied to polyester. In the latter cases the presence of the water of the dye bath assists the dye-fibre attraction because hydrocarbon groups tend to escape from water and associate together. This effect is known as ‘hydrophobic bonding’.

• **Ionic forces**

  The third form of attraction between dye and fibre is due to difference of electric charge between them. In water, fibres become negatively charged and, since most water-soluble dyes are anionic, their coloured ion carrying a negative charged, adsorption does not occur readily. It is then necessary to reduce or even reverse the charge on the fibre before the dye ion can approach closely enough, for the non-polar forces to become effective. (This does not apply with the use of cationic, i.e. positively charged dyeing of acrylic fibres.)

  Adding salt to the bath can have the required effect with cellulose fibre, a suitable with protein fibres and nylon. In the latter case, the reaction for wool dyeing in presence of acid can be illustrated by a series of simple chemical equations.

• **Covalent bonds**

  Only reactive dyes are attached to the fibre by a covalent bond, which is much stronger than the previously mentioned forces and difficult to break down. Some degree of breakdown, shown by bleeding of the dye from the fibre, can with some types of reactive dye be produced to small extent by drastic treatment with acid or alkali, and almost completely by a treatment for 3 h in boiling 49% aqueous hydrazine solution.
5.3 Stages of a dyeing process

Generally, a dyeing process can be sub-divided into the following stages:

5.3.1 Diffusion of dye through the dye solution to the surface of the fibre

If the dye solution is kept on proper flowing or stirring, the dye can move to the interface of the fibre continually. Because the rate of flow of the dye solution becomes slower near the surface of the fibre, the dye solution on the fibre surface is nearly motionless, in this surface layer of dye solution, dye molecules moving to the surface of the fibre depend only on the gradient of the dye concentration, hardly on the flow of dye solution.

This layer, where the ability of dye molecules moving to the fibre surface depends mainly on diffusion, is called the diffusion boundary layer. The faster the rate of flow of the dye solution, the thinner the layer would be. The rate of diffusion of the dye molecules in the diffusion boundary layer is very slow. Reducing the thickness of this layer is one of the methods to increase the dyeing rate.

Moving and stirring is helpful for reducing the diffusion boundary layer. In Fong’s overflow dyeing machines, the circulation of fabric in chamber and the dye solution jetted out from nozzle can reduce the diffusion boundary layer greatly. Therefore, the diffusion rate could be increased.

5.3.2 Adsorption of dye molecules on the outer surface of the fibre

When moving to a certain distance near the diffusion boundary layer of the fibre, the dye molecules can be absorbed by surface immediately. The dye molecules combine with the molecules in fibre surface by hydrogen bond and van-der-Waals attraction. At the same time, there is Coulomb repulsion or attraction existed between the dye anions and the negative charges or positive charges carried by fibre surface. In the former case, if their attraction between the dye molecules and the fibre surface is larger than that of the repulsion, dye molecules could migrate to the fibre surface. The hydrogen bond and van-der-Waals attraction become larger when the distance between the two objects is reduced. Coulomb force is a kind electrostatic force, and can act strongly in a comparative long distance.

Only the dye molecules, which carry high kinetic energy, can migrate closely to the fibre. And if the attraction is larger than the repulsion, these dye molecules could be absorbed by the fibre instantly. The rate of diffusion of the dye molecules in the diffusion boundary layer is one of the major factors, which could affect the rate of adsorption. The faster the rate of diffusion, a larger amount of dye molecules would arrive at the fibre surface and the dye adsorption. Generally the influence of adsorption on dyeing rate is small.

In the cases for reactive and direct dyes, the salt is used to reduce the Coulomb force, i.e. the electrostatic repulsion, to enlarge dyeing rate and dye exhaustion. In the
case of acid dyeing the salt is used to play the retarding role, i.e. increasing the electrostatic repulsion, to obtain a level effect.

5.3.3 Diffusion of dye from the surface to the interior of the fibre

When dye molecules are absorbed on the fibre surface, a gradient of dye concentration is formed. Dye molecules could diffuse from the surface to the interior of fibre, because Diffusion at this stage is in the solid phase, the rate of diffusion is much slower than that in the liquid phase. The rate of dye diffusion at this stage will dominate the dyeing rate. Diffusion will continue until equilibrium of dye concentration in Fibre and in dye solution is achieved, Dye molecules can only diffuse into the amorphous region of the Fibre.

Sonic single dye molecule is absorbed on to the molecular chain of the fibre; some distribute to the solution in the inner channel of the fibre, which keeps equilibrium with the dye molecule on the fibre molecular chain, and a few molecules absorb on the molecular chain of the fibre to form multiple molecule layers. Rising dyeing temperature can enlarge the diffusion of dye molecules in the interior of fibre, therefore increase the dyeing rate.

5.3.4 Chemical bond formation with the functional groups of the fiber

This process is also called fixation and is only applicable to reactive dyes. This type of dyes could react with the functional groups of fibre under certain conditions to form covalent bond. The rate of fixation depends on the reactive group of the dye, the fabric and the dyeing condition. Such as pH (soda ash) of dye solution, dyeing temp electrolyte concentration, etc.

All the above mentioned stages take place either alternately or simultaneously. When dye molecules are absorbed on the surface of the fibre, they may react with the fibre immediately to form covalent bond, or the reaction may take place during diffusion. Dye molecules will lose the ability to diffuse upon the formation of covalent bond. Except for the fixation stage, the first three stages are reversible. During the diffusion stage, dye molecules can be easily detached from the surface. At the absorption stage, both adsorption and desorption of dye molecules could take place.

Before arriving at equilibrium, the rate of adsorption is greater than that of desorption. With an increase in concentration of dye in the fibre, the rate of desorption becomes large gradually. An equilibrium is reached when the rate of adsorption equals to that of desorption. In order to obtain good dyeing quality, the rising of dyeing temperature and addition of salt must be carefully controlled. In Fong’s dyeing machines. The PC control system and Dosing function can well ensure the dyeing quality.

5.4 Some Technical Terms Used in Dyeing

a. Exhaustion
The process of transfer of dye from the bath to the fibre, and it is often expressed quantitatively as a percentage of the dye originally present in the liquor.

\[ E = \frac{\text{Amount of dye on fibre at end of dyeing}}{\text{Amount of dye applied at start of dyeing}} \]

**b. Fixation**

The process of absorbed reactive dye is finally fixed on fibre, and it is often expressed quantitatively as a percentage of the dye fixed on fibre verse the dye originally present in dye bath.

\[ F = \frac{\text{Amount of dye fixed on fibre at end of dyeing}}{\text{Amount of dye applied at start of dyeing}} \]

**c. Levelness of dyeing**

The quality known as levelness of dyeing is essential in a dyed yarn or fabric. A dyeing is level:

- When it is of the same depth all over the yarn or fabric
- When it shows complete penetration of the material, i.e. when the fibres or yarns is pulled apart, show no lighter portions inside.

Both these types of levelness are ensured by careful attention to technique, e.g. by good agitation, by control of the rate of dyeing so that it is not too high, and by allowing sufficient time in the bath.

**The standard affinity of dyeing process**

\[ -\Delta \mu^0 = - (\mu_f^0 - \mu_s^0) = RT \ln \alpha_f / \alpha_s \]

It is the measure of the tendency of a dye to move from solution to fibre during standard state in each phase.

**a. Substantivity**

Under a certain condition, the ability of fibre that dyes or other chemicals is absorbed by it. The substantivity is quantitatively expressed as the percentage of dye absorbed on fibre and the dye residual in dye bath in dyeing equilibrium.

### 5.5 Factors Affecting the Dyeing Process

The choice of dyes depends on the nature and the property of the fibre to be dyed. The conditions applied in a dyeing process can also significantly influence the overall results. The state of dye in solution is closely related to the dyeing process. The structure of dye molecules affects their solubility and aggregation in water. Only a single dye molecule or ion can diffuse into fibre. The higher the dye solubility, the faster the dyeing rate, the better the leveling property, but the lower the substantivity or the equilibrium of adsorption. Other components in the solution, such as electrolyte, leveling agent,
retarding agent and die dyeing condition such as pH and temperature, can also change the distributing state of a dye in solution and have a substantial influence in the dyeing process.

The rate of diffusion of a dye in the diffusion boundary layer is closely related to its properties, state in solution, rate of flow and rate of diffusion in solution. Presence of electrolytes and auxiliary agents in the diffusion boundary layer can affect the rate of diffusion of the dye as well as the thickness of the layer.

The rate of adsorption of a dye in fibre surface is very fast. The factors affecting the rate and the capacity of the adsorption are mainly the structure of the dye molecule, fibre property and its surface shape. If both the dye and the fibre carry’ negative charges, their mutual repulsion will reduce the rate and the capacity of adsorption. A higher electrolyte concentration in the diffusion boundary layer (mainly cations, e.g. sodium ions) would result in a more remarkable effect in reducing the repulsion, with a higher rate of adsorption and a larger capacity of adsorption.

The diffusion of dye into the inner part of the fibre is slowest in dyeing process. The rate of diffusion of a dye in this stage depends mainly on the structure of the dye molecule, as well as the microstructure and property of the fibre. Auxiliary agents and dyeing conditions (e.g. temperature, pH, etc.) can change the swelling state of a fibre and the substantivity of a dye for the fibre, and in turn will affect the rate of diffusion of the dye in the fibre equilibrium of absorption.

Most dyeing is carried out in the aqueous phase. Water itself, a cheap and convenient medium for mass transfer and energy distribution within the dyeing machine, is also a direct participant in the essential dye-fibre interaction mechanisms at the heart of the dyeing process. The quality of water therefore will directly influence the properties of the dye and the dyeing quality.

Based on the discussion above, the main factors that will influence the adsorption of the dye can be summarized as follows:

- The nature and property of fibre
- The nature and property of dye
- Water quality
- Dyeing temperature
- pH of dyeing solution
- Electrolyte (especially the metallic ions of salt) and its role in dyeing
- Dyeing assistants/auxiliaries
- Dye concentration and the liquor ratio
- Dyeing method used - batches or continuousness

5.5.1 Rate of dyeing
With most fibres very rapid dyeing or very slow dyeing are both undesirable in practice. The former because it makes levelness difficult to achieve and the latter because it increase fuel and labor costs and may also lead to damage to the fibre, as a result of the prolonged period of contact with hot dye-liquors. The dyer must therefore use means of controlling the rate of dyeing of any fibre, either one way or the other, as required. This lie does either by a variation of the temperature of dyeing or by the addition of various chemical auxiliaries to the bath.

In Fong’s machine, nozzle, Dosing function and temperature control system are effective elements for controlling the rate of dyeing.

5.5.2 Effect of change in temperature

The change of temperature affects dyeing in at least three distinct ways. A rise in temperature

- Increases the speed of dyeing (the strike);
- Decreases (usually) the amount of dye which the fibre can absorb and hence decreases the exhaustion of the bath, and
- Increases the speed with which the dye redistributes from heavily to lightly dyes parts of the material (migration).

5.5.3 Effects of dye bath assistants

Uniform penetration and level dyeing depend upon both mechanical and chemical factors. It is, of course, vitally that there should be adequate movement of goods and liquor in relation to each other. It must never be forgotten that the perfect machine will not give level dyeing unless the proper precautions are taken with regard to addition of chemicals and control of temperature.

The principal types of chemical assistant used in dyeing are listed below:

- Acid, used in dyeing protein fibres and nylon with acid dyes
- Alkalies, used in dyeing cellulose fibres, with azoic, vat or sulphur dyes
- Salts used in dyeing with acid dyes and in all forms of dyeing of cellulose
- Surface-active leveling agents, used with vat dyes, disperse dyes and certain acid dyes
- Carriers, used in dyeing some of the newer synthetic-polymer fibres, e.g. PET / Lycra
- Oxidizing agent, used for bleaching
- Reducing agents

The function of these agents may be summarized thus

a. Acids
Adjusting the pH of dyebath. In dyeing silk, wool etc. with acid dyes, acids can also act by reducing the negative or increasing the positive charge on the fibre. So that the dye anion is able to enter it; the lower the substantivity of the dye, the more acid must be used to enable the dye anion to be attracted. This explains why dyes with good leveling properties, which (a) migrate or transfer readily from one dyed part of the fibre to another and (b) are loose to washing treatments, both effects being indicative of low substantivity, need strong acid (usually sulphuric) for good exhaustion:

b. Alkalis

Adjusting the pH of dyebath. There are also used in dyeing cellulosic fibres with vat, azoic, sulphur and reactive dyes. Vat dyes and sulphur dyes have to be applied from strongly alkaline baths containing reducing agents, and the first component (the coupling component) of the azoic dyes - the napthol - is also dissolved in sodium hydroxide in the dyebath. In dyeing with the reactive dyes, the alkali, often a weak one, e.g. sodium carbonate, serves a different purpose; its function is to promote the reaction between the dye and the cellulose fibre molecules described above.

c. Salts

The sodium sulphate (glauber’s salt) used in dyeing wool with equalizing acid dyes acts as a restraining agent, because its anions, being in large excess, compete with dye anions for adsorption by the fibre. The sulphuric acid present at the same time, however, increases the attraction between dye and fibre. Thus acid and salt have opposing effects, and the same final result could be obtained either (a) by omitting the sodium sulphate and using less acid or (b) by using a weaker organic acid. In the first procedure, however, it would be more ethical, and the second procedure would be less acceptable, because organic acids are more expensive than sulphur acid.

The salt used in cotton dyeing functions partly by its sodium ions reducing the negative charge on the fibre; this enables the dye anion to approach closely enough to become attracted van-der-Waals’ forces. In the dyeing of cotton with the ‘warm-dyeing’ vat dyes, the sodium ions required for this purpose are provided by the sodium dithionite and sodium hydroxide used in the preparation of the vat. The “cold-dyeing” vat dyes have lower substantivity for the fibre, and to obtain good exhaustion when using then it is necessary not only to increase the sodium ion concentration of the bath still further by adding sodium chloride, but also to reduce the temperature of dyeing.

When use Pong’s dyeing machines, sodium sulphate ($\text{Na}_2\text{SO}_4$) (glauber’s salt) is recommended other than sodium chloride ($\text{NaCl}$), because sodium chloride can easily cause the corrosion of the stainless steel of dyeing machine especially in high temperature.

d. Surface-active leveling agents

In some cases it is necessary, to ensure level dyeing to reduce the capacity of the fibre to absorb dye. This must be done by adding some chemical reagent to the bath, which may act in one of two ways: It may compete with the dye for adsorption by the fibre, because the reagent has substantivity for the fibre. An example is the use of certain surface-active agents when nylon-wool mixtures are dyed with acid dyes. Alternatively, the reagent may increase the retention of the dye by reacting with it to form a complex,
which only slowly release dye molecules to combine with the fibre. Some of the leveling agents used in wool dyeing act in this way.

e. Carrier

The most common use of these materials is in dyeing polyester fibres, which can be dyed more deeply in a normal dyeing period with disperse dyes in presence of a carrier, e.g. 2-hydropxydiphenyl, than in absence of one. Carriers appear to act by loosening the fibre structure, and thus allowing the dye to have less restricted entry. In dyeing PET/spandex fabric, to avoid damaging the elasticity of spandex fibre, the carrier is used to reduce the dyeing temperature.

f. Reducing agents

Converting sulphur dyes and vat dyes to the alkali-soluble leuco form. The most convenient reducing agent for sulphur dyes is sodium sulphide (NaS$_2$); for vat dyes is sodium dithionite (vet powder, sodium hydrosulfite, Na$_2$S$_2$O$_6$).
CHAPTER 6

REACTIVE DYSES
Reactive dyes are colored compounds that contain functional groups capable of forming covalent bonds with active sites in fibers such as hydroxyl groups in cellulose, amino, thiol, and hydroxyl groups in wool or amino groups in polyamides. This bond formation between the functional group and the substrate results in high wet fastness properties. These dyes differ fundamentally from other types of dyes that owe their wet fastness to physical adsorption or mechanical retention. The principal commercial applications of reactive dyes are in the dyeing of cellulose, wool, and nylon, either individually or as components of fiber blends. They have also found use in dyeing silk, hair, and leather.

6.1 Development of Reactive Dyes

Cross-and Bevan achieved the first recorded chemical combination of a dye with cellulose in 1895. They used a complicated process involving the benzoylation of soda cellulose, followed by nitration, reduction, diazotization, and finally coupling with phenolic compounds to form the covalently fixed azo-dye. Several other attempts were subsequently made to attach dyes to cellulose by means of a covalent bond. The dominating feature of almost all of this early work was the use of severe conditions such as concentrated caustic soda to prepare soda-cellulose or the use of inert solvents. The use of mild conditions necessary to render the colouration process technically feasible and reasonably efficient was given little or no consideration.

During the 1930s fast dyeing on wool were produced using dyes containing chloroethylsulfamoyl groups (-NHOCH₂Cl) and β-chloroethylsulfamoyl groups (-SO₂NHCH₂CH₂Cl). It was not realized at that time that the high wet fastness of these dyes was due to reaction between the labile chlorine atom and the amino groups in the wool.

Dyes prepared from diazo components containing β-sulfatoethyl sulfone groups (-SO₂CH₂CH₂OSO₃H), were also patented for application to cellulose acetate and nylon, since they contained no nuclear sulfonic acid groups. Hoechst commenced research work on dyes containing vinyl sulfone and β-sulfatoethyl sulfone substituents, which led to the introduction of the Remalan group of reactive dyes. Although it was known that the high fastness of the Remalan dyes was associated with chemical bond formation between the dye and the fiber) the suitability of vinyl sulfone dyes as reactive dyes for cellulose was not realized until after the appearance of the Procion (ICI) reactive dyes.

Previous work on the reaction of soda cellulose with cyanuric Chloride led to a useful industrial method for the production of dyeing in which a covalent bond was formed between the dye and the fiber. This development resulted in the introduction of
the first range of reactive dyes for cellulose marketed by ICI in 1956 as the Procion M Dyes. The initial members of this range were all highly reactive dichlorotriazinyl derivatives capable of reaction with cellulose under cold-dyeing conditions. They were quickly followed by the less reactive monochiorotriazinyl dyes requiring hot-dyeing conditions, which were marketed as the Procion H range.

Direct dyes containing triazine residues patented previously by Ciba were used in the manufacture of a complete range of monoch reactive dyes under the name Cibacron. The success of the Procion dyes was followed by extensive research programs by all the major dyestuff manufacturers. Consequently, reactive dyes containing 2, 4, 5-trichloropyrimidinyl groups were introduced under the trade names of Reactone and Drimarene. In the early 1960s Bayer developed the Lexafix P and E groups based upon 4,5-dichloro-6-methyl- 2-methylsulfonylpyrimidine (1) and 2,3-dichloroquinoxaline (2) reactive groups, respectively; and BASF produced the Primazin P range with 4,5-dichloro-6-pyridazinone 3) as the reactive species.

Hoechst marketed their vinyl sulfone derivatives as the Remazol group. In addition, Brayer introduced similar dyes containing β-sulfatoethylsulfamoyl groups (-SO) which combine with cellulose through nucleophilic addition reactions to form cellulose ether derivatives.

During the mid 1950s the major emphasis was on reactive dyes for cellulosic fibers, but 1959 heralded the introduction of the Procynyl (ICI) group of reactive disperse dyes designed specifically for application to nylon. Although reactive dyes, specifically for application by exhaustion procedures, was marketed by ICI under the trade name Procilan (ICI). These dyes are generally 2:1 premetallized dyes containing reactive acrylamide groups, which are not subject to hydrolysis in the dyebath.

Reactive dyes for wool, however, gained importance with the introduction of the Lanasol (Ciba-Geigy) dyes containing the bromoacrylamide group (- N1-ICOC (Br) =Cl- 1 which are noted for their bright shades, high reactivity and good wet-fastness properties. Similar properties are exhibited by the Drimalan F (Sandoz), Reactolan (Ciba-Geigy), and Verofix (Bayer) dyestuff groups containing a difluorochioropyrimidinyl group. The Hostalan dyes (Hoechst) that were developed to overcome the problems of unlevel dyeing are the reaction products of Remazol (vinyl sulfone type) dyestuffs and N-methyltaurine (4).

\[
\text{CH}_3\text{NHCH}_2\text{CH}_2\text{SO}_3\text{H}
\]

\[
(4) \quad [107-68-6]
\]

Dichlorotriazinyl and monochlorotriazinyl dyes, although primarily designed for cellulose, have also been applied to wool. The Cibacrolan (Ciba-Geigy) group of monoch dyes was introduced specifically for wool.
Tables illustrate the various commercial types of reactive dyes developed for cellulosic fibers. The tables show the major reactive groups, the corresponding chemical structures, and the common trade names.
Table 6.1  Reactive Dyes for Cellulosic Fiber

<table>
<thead>
<tr>
<th>Structure</th>
<th>Name</th>
<th>Trade Name</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>dye—NH—Cl—Cl—Cl</td>
<td>trichloropyrimidine</td>
<td>Reactone</td>
<td>Ciba-Geigy</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Drimaren X</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Drimaren Z</td>
<td>Sandoz</td>
</tr>
<tr>
<td>dye—NH—Cl—Cl—F</td>
<td>monochlorodifluoropyrimidine</td>
<td>Drimaren R</td>
<td>Sandoz</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Drimaren K</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Levafox EA</td>
<td>Bayer</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Levafox PA</td>
<td></td>
</tr>
<tr>
<td>dye—N—Cl—Cl</td>
<td>dichloropyrimidine</td>
<td>Reactofil</td>
<td>Ciba-Geigy</td>
</tr>
<tr>
<td>dye—N—Cl—Cl</td>
<td>dichloropyridazine</td>
<td>Solidazol</td>
<td>Cassella</td>
</tr>
<tr>
<td>dye—N—Cl—Cl</td>
<td>dichloropyridazinone</td>
<td>Primazin P</td>
<td>BASF</td>
</tr>
<tr>
<td>dye—N—Cl—Cl</td>
<td>dichloroquinoxaline</td>
<td>Levafox E</td>
<td>Bayer</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cavalite</td>
<td>DuPont</td>
</tr>
<tr>
<td>dye—N—Cl—Cl</td>
<td>dichlorophthalazine</td>
<td>Solidazol</td>
<td>Cassella</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Reatex</td>
<td>Franccolour</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Elissiane</td>
<td></td>
</tr>
<tr>
<td>dye—N—Cl—Cl</td>
<td>chlorobenzothiazole</td>
<td>Reatex</td>
<td>Franccolour</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Elissiane</td>
<td></td>
</tr>
<tr>
<td>dye—O—Cl</td>
<td>acrylamide</td>
<td>Primazin</td>
<td>BASF</td>
</tr>
</tbody>
</table>
A reactive dye molecule may, for convenience, be regarded as a combination to the following units

### 6.1.1 Dye-B-Y-X

Where dye is the chromophore (usually an azo, anthraquinone, or phthalocyanine residue); B is a bridging atom or group although this, in many cases, is part of the chromophoric system; V is the unit carrying the reactive group (the activity of the reactive group depends to a large extent upon the nature of Y); and X is the group that reacts with the fiber. An additional water solubilizing group, which is not part of the chromophoric unit, may be found as part of the reactive group such as the sulfuric acid ester group of β-hydroxyethyl sulfone reactive dyes.

### 6.1.2 Chromophoric System

In principle, practically any desired chromophoric system can be combined with reactive groups to produce reactive dyes. The properties of the resulting dye, however, are affected by both of these groups. Proper combination is, therefore, needed to obtain dyes with good qualities such as high tinctorial strength, good solubility, good fastness properties, and economy.

Commonly used chromogens include azo, metallized-azo, anthraquinone, phthalocyanine, and metal-complex formazan derivatives. Azo compounds comprise the widest range of shade from greenish-yellow to black. For Yellow dyes, coupling products of pyrazolones and aminopyrazoles are commonly used. Pyridone derivatives have gained much importance in the recent years as coupling components for yellow dyes. Brilliant red colours are usually based on aminohydroxynaphth alenedisulfonic acids. Chromium, copper and cobalt metal-complex azo dyes comprise the majority of metallized azo dyes. These dyes generally possess excellent light fastness.
Brilliant blue and green reactive dyes with high fastness to light are the main contribution of anthraquinone derivatives. Copper and nickel phthalocyanine reactive dyes give bright turquoise shades with good wash fastness and satisfactory crocking fastness. Bright blue to green metal-complex dyes from formazan derivatives have been patented and claimed to possess good fastness properties. Other groups mentioned in patent literature are also used as chromophoric systems for reactive dyes, but they have achieved little commercial importance up to the present.

6.1.3 The bridging Group

The nature of the bridging group between the chromophore and the reactive group not only affects the shade, strength, and affinity of the dye, but also can significantly affect its reactivity and the stability of the dye-fiber bond. Thus the use of oxygen or sulfur bridging groups is unsatisfactory, since they are readily hydrolyzed, and aliphatic or aromatic chains tend to lower the water solubility of the dye. In addition the length and flexibility of the bridging group has an effect on the degree of dye-fiber fixation. Therefore, amino and alkylamino groups are generally used as bridging groups in heterocyclic reactive dyes in view of the ease of synthesis, stability to hydrolysis, and minimum interference with solubility.

In the case of dichloroquinoxaline (2) and dichlorophthalazine (5) reactive dyes that contain only one reactive chlorine group, the chromophore is attached to the reactive system through an amide-bridging group. This bridging group is susceptible to acid hydrolysis, which can result in the rupture of the bond between the chromophore and the reactive system. Sulfonamide and amide bridging groups have been suggested as replacements for the sulfone group in the Remazol dyes. Although the stability of the dye-fiber bond is increased using these groups, a reduction in the reactivity of the dye is observed.

6.1.4 The Reactive System

The combined unit Y-X in the above formula can be regarded as the reactive system. Generally, the reactive systems used in commercially available reactive dyes can be classified into two groups:
Reactive systems based on nucleophilic substitution reactions, in which the mobile reactive group \( X \) is replaced by an attacking base, and

Reactive systems based on nucleophilic addition reactions, in which a 1, 2 trans addition of a nucleophile occurs across a polarized double bond. Examples of reactive systems (1) and (2) are halogeno-heterocyclic and vinyl sulfone systems, respectively. In some cases, both addition and substitution reactions are operable as in the ex-bromoacrylamide types.

The reactivity of a reactive dye, therefore, is governed primarily by the chemical structure and arrangement of the reactive system \( (Y-X) \) and the variation of the chromophore to which the reactive system is attached.

**Synthesis**

Reactive dyes have a great advantage over direct dyes in that they do not depend on molecular complexity for adsorption. This allows a brighter spectrum of shades and more rapid diffusion characteristics compared with direct dyes.

The methods of synthesis of reactive dyes depend largely on the nature of the reactive component. Very thorough reviews have been presented of the methods of production of various types of reactive dyes. In general, the following methods are used to prepare an azo dye containing a nucleophilic group, eg - \( \text{NH} \)-\( \text{OH} \), and then condense the azo dye with a heterocyclic aromatic reactive system, eg, cyanuric chloride, tetrachlormidine etc;

Combine a diazotized aromatic amine with a coupling component containing a reactive system, or a diazonium compound containing a reactive system with a coupling component; Condense an aromatic compound containing a reactive system to an anthraquinone derivative, in particular, 1-amino-4-bromoanthraquinone-2-sulfonic acid (bromaminic acid); and

For phthalocyanine dyes, which do not carry a suitable nucleophilic group for the condensation with the reactive system, it is necessary to introduce a bridging group, eg, a sulfonamide, to act as the nucleophile.

**6.3 Reactive Dyes for Cellulosic Materials**

**6.3.1 Cellulosic Materials**

Cellulose (qv) is a carbohydrate. It consists of (1-4) - \( \beta \)-D-glucan and is considered as a polyalcohol with three hydroxyl groups per unit of glucopyranose. As a consequence, any group that is capable of forming a covalent bond with alcoholic hydroxyl groups is a potential reactive system to be used in a dye molecule for cellulosic fiber. However, certain criteria must be met in order for this reactive system to be of practical use.

The most important criterion is that the dye can be applied in an aqueous medium. In this instance, there are two competing reactions. One is the reaction of the dye and the fiber, and the other is the reaction (hydrolysis) between the dye and water. In principle, it is possible to dye cellulosic fibers in an aqueous alkaline medium with water-soluble dyes.
dyes under alkaline conditions the hydroxyl groups in the cellulose molecules are partially ionized and can act as nucleophilic heagent.

The reactive system of the dye molecule can then react either with cell O or OH. It has been shown that the dissociation constant for cellulose is higher than that of water, thus cell-O reacts faster than OH- with the reactive group of the dyestuff. This preference of dye fiber interaction has been attributed to the higher nucleophilicity of the aliphatic hydroxyl groups of cellulose. In order for the hydroxyl anion of cellulose to attack the reactive system of the dye, they must be in proximity, i.e., the dye molecules must be adsorbed into the fiber. This property, known as substantivity, is the second fundamental condition that must be fulfilled before a dye-fiber interaction can take place.

Another important criterion is that the covalent bond formed between the dye and the fiber must be sufficiently stable to resist subsequent after treatments. In other words, the dye- fiber interaction must be relatively irreversible. In addition, the dye must have a suitable shelf-life, and be nontoxic and economical to produce.

Reactive systems can be classified into several groups depending upon the reaction mechanism.

**6.3.2 Reactive Systems Based on Nucleophilic Substitution**

This generally involves a base-catalyzed addition of a nucleophilic functional group of the cellulose to the electrophilic center of the reactive groups followed by the subsequent displacement of a suitable leaving group. This mechanism applies particularly to heterocyclic aromatic compounds containing labile leaving groups. Shown below is the reaction scheme of a dichlorotriazinyl functional group with cellulose (e.g., Procion M dyes)

![Reaction Scheme](image)

An excellent discussion has been presented of the mechanisms of the reaction of reactive dyes with cellulosic fiber. This nucleophilic substitution reaction mechanism also applies to other similar heterocyclic aromatic compounds such as monochloro-s-triazine (6) derivatives (procion 1-I and H-E type and Cibacron); 2,4, 5-trihalopyrimidine (eg, (7)) (drimarene K, R, X and Z type, Reactone, Levafox EA and PA); 2,4-dichloropyrimidine (8) (Reactofil); 3,6-dichloropyridazine (9)
(Solidazol); 1-H-4, 5-dichloro-6-pyridazinone (3) (Primazin P); 2,3- dichloropyrimide (2) (levafix E, Cavalite); 1,4-dichlorophthalazine (5) (Solidazol, Elisiane); and 2-chlorobenzothiazole (10) (Elisiane).

The reactivity of the heterocyclic aromatic systems can be altered by making suitable substitutions in the ring:

The hetero-atoms in the aromatic ring are important in that they affect the electronegativity of the system; an increase in the number of hetero-atoms favors nucleophilic exchange, and consequently, the reactivity of a triazine derivative is higher than that of a pyrimidine derivative; and

Replacing the halogen with an electron-attracting group will increase the reactivity, whereas an electron-donating group will decrease the reactivity, eg. Replacement with an amine, such as in the case for Procion H and Cibacron dyes, reduces the reactivity.

An important substitution in the pyrimidine system is the replacement of the chlorine atom at the 5-position with an electronegative group such as -N02, -CN, -CQOH, etc. IC claimed that substituting a nitro group in the 5-position of the pyrimidine ring enhanced the reactivity to such an extent that the dye could be applied to cellulose under much milder conditions than trichloropyrimidyl derivatives. However, this was not suitable for practical application because the dye-fiber bond was weakened by the over-activation of the nitro group making the resulting dyeing deficient in wash fastness. Dyes containing a cyano group in the 5-position possess high reactivity and afford satisfactory dyeings.

When a carboxyl group is substituted into the 5-position of the pyrimidine ring, the reactive system can be attached to the chromophore through an amide bridge. This results in another group of dyes, called Reactofil, which possess reactivity towards cellulose of the same order as that of a dichlorotriazinyl dye.

In general, the reactivity of N-heterocyclic reactive groups increases in the order of chloropyrimidine < monochloro-s-triazine < dichloroquinonoxaline < dichloro-s-triazine. Nucleophilic substitution at a saturated carbon is demonstrated in β-substituted ethylamine derivatives. The reaction proceeds via an ethyleneimine intermediate that exhibits high reactivity towards nucleophilic substitution reactions. For cellulosic fiber, the leaving group at the β-position is generally a sulfato group. The neighboring group

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participation of the nitrogen is essential for the easy formation of the three-member ethyleneimine ring.

6.3.3 Reactive Systems Based on Nucleophilic Addition

The mechanism of this reaction generally consists of two steps. The first step is a base-catalyzed elimination of a labile group (e.g., -\(\text{OSO}_3\)H and Cl) generating a reactive double bond, followed by a 1,2 trans addition of the functional group of the cellulosic fiber to the double bond. Two commercially important groups of dyes react according to this mechanism (1) Remazol, a vinyl sulfone derivative \((\text{dye-}\text{SO}_2\text{CH=CH}_2)\); and (2) Primazin, an acrylamide derivative \((\text{dye-NH-CO-CH=CH}_4)\). Venkataraman and co-workers have illustrated the reaction mechanism of cellulose with \(\beta\)-sulfatoethyl sulfone groups, the precursor of vinyl sulfone (Remazol), according to the following scheme.

\[
\text{Dye-SO}_2\text{CH}_2\text{CH}_2\text{OSO}_3\text{Na} + \text{NaOH} \rightarrow \text{dye-SO}_2\text{CH}=\text{CH}_2 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}
\]

\[
\text{Dye-SO}_2\text{CH}_2=\text{CH}_2 + \text{cell} - \text{OH} \rightarrow \text{OH} - \text{dye-SO}_2\text{CH}_2\text{CH}_2 -\text{O- cell}
\]

The electron withdrawing nature of the bridge sulfonyl group activates the amethylene hydrogen, thus facilitating the 1,2 elimination of a base. This property has the intrinsic disadvantage that the dye - fiber bond formed in dyeings of vinyl sulfone dyes are less fast to boiling dilute sodium carbonate solution than are dyeings of ch dyes. By substituting effect is reduced and the dyeings exhibit better alkali fastness. By analogy, 3-chloropropinylamides are the precursors of acrylamide. A base elimination of hydrogen chloride provides the reactive acrylamide form. However, this type of dyes (Primazin) has only limited use in dyeing cellulosic fibers and is mainly used for wool dyeing.
6.3.4 Reactive System Based on Both Nucleophilic Addition and Substitution

Several patents have been issued to Farbweke Hoechst covering dyes with 2, 2, 3, 3-tetrafluorocyclobutane-1-carboxamide groups. The fluorine atoms on C-2 are activated by the carbonyl group on C-1 resulting in high reactivity of such dyes. The probable course of the reaction is shown below:

The first step is the base-catalyzed elimination of HF followed by nucleophilic substitution of the fluorine atom remaining on the double-bonded carbon by cellulose anions.

6.3.5 Dyes that React with Fibers under Acid Conditions

All the reactive dyes mentioned above are applied to cellulosic fiber under alkaline conditions. The Calcobond dyes introduced by American Cyanamid Company are applied under acidic conditions. The reaction system is methylolated nitrogen. The dye-fiber reaction is promoted by acid and heat and is believed to proceed according to the following mechanism

\[
\begin{align*}
\text{Dye-NHCH} + \text{H dye} & \rightarrow \text{NHCH} + 2 \text{H} \\
\text{Dye-NHCH} + \text{cell} & \rightarrow \text{OH} + \text{H dye} - \text{NHCH} + \text{H}
\end{align*}
\]

Many dyes containing methylol groups attached to the chromophore in different ways. The advantages mentioned for this type of dyes are

- They can be used together with disperse dyes, which are generally unstable in alkaline medium, to dye cotton and polyester blends;
- The reactive system is similar to many textile-finishing agents and therefore, can be applied together in a single operation.

However, these dyes have failed to achieve much practical significance in dyeing of cellulosic fibers because they are incompatible with conventional reactive dyes and the
cotton will lose up to 50% in tensile strength under the high temperature acidic fixation step.

6.3.6 **Polyfunctional Fixing Agents That Form Covalent Bonds with Both the Dyestuff and the Substrate**

Another approach to reactive dyeing is the linking of dyestuff molecules containing nucleophilic groups (e.g., NH$_2$ and OH) with the nucleophilic hydroxyl anion of cellulose by means of a colorless polyfunctional component capable of reacting with both dye and fiber. Many different compounds have been disclosed in the patent literature as bridging compounds. Most of these suffer the disadvantage of having too low an affinity for cellulosic fiber and are only suitable for pad-dyeing and printing purposes. The most important polyfunctional reactive system is 1, 3,5-triacryloylhexahydro-s-triazine (triacryloformal). This forms the basis of the Basazol range of dyes (BASF).

![Chemical structures](image)

The colour yields of ordinary reactive dyes are usually not higher than 60-85% because of some hydrolysis in the dyebath. Colour yields of about 90%, however, have been obtained with 1,3,5-triacryloformal (11) as the bridging compound. The reasons for this high yield are: (1) the carbonyl group has strong activating effect; and (2) contrary to the aromatic triazines, the activity of the substituents is not significantly altered after one or more of them have reacted.

6.3.7 **Dyes Containing Several Reactive Groups**

Conventional reactive dyes for cellulosic fibers suffer an obvious drawback in that only ca 70% of the dye is fixed onto the fiber, the remainder of the dye undergoes hydrolysis in the dyebath. There has been a continuous search for dyes that will exhibit high fixation efficiency. There are two possible methods to accomplish this goal:

- Use a reactive group that is not easily hydrolyzed; and
- Incorporate two or more reactive groups in a dye molecule to increase the chance of fixation.
The latter method appears to have been the one mainly used in developing high fixation dyes. The high fixation dyes with multireactive groups are based upon statistical probability. That is, with two or more reactive groups there is better chance of fixation to the fiber. Furthermore,

If one of the groups is hydrolyzed, the remaining groups may still react with the fiber. It must be stressed, however, that the presence of two or more reactive groups in a dye molecule does not necessarily provide high fixation. Other properties such as solubility, substantivity, and diffusibility are also determining factors.

The reactive groups of the dye can be linked as a reactive packet with another group that does not carry a second chromophore (dye-NH-R₁–B–R₂ and R₂ = reactive groups; B = bridge). Another type of reactive group is a bridge that contains two chromospheres (dye-NH-R₁,B-R₂–HN-dye)

Many patents have appeared covering dyes with two or more reactive groups. The favoured group in such dyes is chlorotriazines. Two important groups of high fixation reactive dyes, Procion HE and Procion Supra, have achieved commercial importance. Procion Supra dyes are intended, primarily for use in textile printing applications but may also be employed in continuous dyeing processes.

6.4 Classification of reactive dyes

Reactive dyes can be classified into different groups as follows:

- **Reactive dyes containing a cyanuric chloride nucleus.**

  Procion H.

  Cibacron

  Monochlorotriazine reactive dye

  X= aromatic or aliphatic amine or dye with a free amino group attached to the chlorine, or a heterocyclic residue.
Procion

Dichloro triarine reactive dye

- **Reactive dyes containing a chloro pyrimidine nucleus**

Dichloropyrimidine

Trichloropyrimidyl type

Reaction

drimazene Z.
• **The vinyl sulfone reactive type.**

Remazol

- SO₂ - CH = CH₂
- SO₂ – CH-CH₂ –SO₃H

Vinyl sulfone reactive dyes.

**Reactive dye containing an epoxy group**

The widely useful of these systems remains however the b-Suiphatoethylsulphonyl system. A manufacturing disadvantage to this type of dye is the need to synthesis an intermediate containing the reactive group and then uses this in the dye preparation rather than simply to attach the reactive system to one of the wide variety of chromophores containing an amino group, as can be done in the case of chioroheterocyclic dyes

**Pyridazone**

**Dichloroquinoxaline**

**Levafix**
Acrylamide

\[ D - \text{NH} - \text{CO} - \text{CH} = \text{CH}_3 \]

primazine

- **Methylolated Nitrogen**

\[ D - \text{NH} - \text{CH} - \text{OH} \]

Calcobond

Most of the newer systems have lower reactivity than the dichlorotriazynl amono dyes. The other reactive groups are as follows

- 1, 4-Dichlorophthalazine-6-Carbonyl
- β-Chloroethylsulphonyl
- β-Sulphatopropionamid

Reactive systems based on nucleophilic substitution and or addition. Ch dyes and most of above groups react with celluloe by a process of nucleophillic subsitution while vinyl sulphone dyes react with cellulose by nucleophilic addition.

- **Reactive dyes containing a cyanuric Chlorid nucleus**

Cyanuric chloride contains three labile chlorine atoms which can be replaced in sucession to an amine salt or a hydroxy compound. A simple dye containing a cyanuric chloride can be represented as follows

Dye represents a chromopore or a colouring molecule such as Azo, Anthraquinone or phthalocyanaine with a solubilising group SO\(_3\)H. X represents a chlorine atom or some other inactive radical, which may confirm a solublising group. If x is chlorine then two chlorine atoms are free for reaction with cellulose, wool and other natural and synthetic fibres. The ordinary procion of I.C.I. contains two chlorine atoms of sufficient reactivity to combine with hydroxyl or amino groups of polymers.
The dichloro triazine dyes have sufficient reactivity with water, and must be applied from a cold bath and mild alkali. So dyes if this class is known as cold dyeing type.

If x is something else other than chlorine then it is a monochiorotriazine type. The Cibacron dyes of Ciba and the Procion H dyes of I.C.I. belong to this type. They have only one chlorine atom available for reaction with the fibre. The mono chloro triazines are less reactive towards water and can be applied from a bath at higher temperatures without undergoing hydrolysis. However, above 60° they are found to hydrolyse. In addition these dyestuffs require a more alkaline solution before reaction. They can be applied as cold bath dyeing but careful conditions are required. Otherwise they are unstable.

Both the mono chloro and dichiorotriazine reactive dyes can be applied by the padding or exhaustive methods. However the drawback of these dyes is that they are not fast to bleaching as well as resin finishing. Fibres dyed with reactive dyes cannot be employed on a finishing bath.

Examples

The structures of these dyes have been investigated by Pancherstik et-al. Cyanuric chloride reactive dyes with a metal complex are useful and they give a fast shade. The metal is held on to the dye by coordinate covalent bonds.

Monochlorotriazinyl dyes are sufficiently stable to withstand long periods of storage, but dichlorotriazinyl dyes are liable to hydrolyse with loss of hydrogen chloride. It was found that the stability of dichlorotriazinyl dyes in dry storage could be greatly improved by addition of a buffer such as a mixture of potassium dihydrogen phosphate and disodium hydrogen phosphate; hydrolysis is evidently accelerated by presence of acid. The highly reactive dichlorotriazinyl dyes are usually more suitable for dyeing and less reactive monochlorotriazinyl dyes for printing.

Procion dyes are highly soluble in water and the solubility is conferred on the molecule by the presence of sulphonic acid groups. If cotton is padded or printed with a neutral solution of a Procion dye and then dried, the colour can be removed almost
completely from the fabric by water washing. If however, the impregnated fabric is treated, with alkali a large proportion of the dye is fixed and is resistant to soap boiling.

6.4.1 Vinyl Sulfone Reactive Dyes

Reactive dyes having a vinyl sulfone group have good fastness and were first introduced by Bayer in Germany. They form a bond with the fibre. Substituted aromatic compounds having β sulfato ethyl sulphonyl group can easily be prepared by etherification of the corresponding sulfone with H₂SO₄.

\[
R-SO_2 \text{ (CH}_2\text{ )}_2\text{OH} \quad \rightarrow \quad R-SO_2\text{ (CH}_2\text{ )}_2\text{-O-SO}_3\text{H}
\]

On neutralisation they become water-soluble. Excess alkali gives quantitative formation of vinyl sulfonyl compound.

\[
R-SO_2\text{- (CH}_2\text{)}_2\text{-OSO}_3\text{H} + \text{OH} \quad \rightarrow \quad R-SO_2\text{-CH-CH}_2\text{-OSO}_3\text{ RSO}_2\text{-CH-CH}_2
\]

The vinyl sulfone formation can be explained by assuming that the weakly basic sulphate ion is formed easily, once a proton is removed the α-methylene group. At high temperatures the vinyl sulfones hydrolysis to form hydroxy vinyl sulfones. This can react further giving the either and the vinyl sulfonyl ether undergoes cleavage giving β-hydroxy ethyl sulfones.

The hydroxy compound can react with primary, secondary and tertiary amines. They also react with proteins which are good photographic gelatine coatings. Wool treated with 3,4-sulfato ethyl sulfone in a neutral bath at the boil absorbs quantitatively. The fixation is fast to washing.

Fixation on cotton of diazo amino compounds containing a β-sulfato ethyl sulfonyl groups occurs at 80-85° from a weak sodium alkali bath in the presence of sodium sulphate. The diazo amino compound attached to the fibre can be cleaved to get a diazo compound with a small amount of mineral acid and azo dyes may then be produced on the fibre with various coupling agents. The fastness of these dyes is very good.
In neutral aqueous solutions, the Remazol dyes do not undergo chemical reaction and can so be boiled without hydrolysing. Neutral solutions are stable at room temperatures. Vinyl sulfone forms a covalent bond with cellulose.

![Chemical structure of Remazol dye](image)

The bond in Remazol is an ether linkage, stable to acid and neutral bath but cleavage with alkalies. They can be used to materials, which are resin treated which is a unique thing. Vinyl sulphone dyes are suited to the dyeing of either nitrogenous or cellulosic fibres.

In commercial dyes, the vinyl suiphonyl group rarely used, because the vinyl suiphone is normally made front the sulphate compound, so that its use in the dye would add an extra step in manufacture. Secondly the higher solubility of the sulphato esters is advantageous in dyeing and printing applications.

**6.4.2 Tetrachloro Pyrimidine Dyes**

Sandoz and Geigy Ltd. independently found a new reactive nucleus in tetrachloropyrimidine. It is different from cyanuric chloride in that one of the nitrogen is replaced by C-Cl and so all the carbon atoms are not equal. It has also been established that the 4th or the sixth carbon atom reacts first. So dyes with a free amino group react with it giving rise to a reactive dye.

![Chemical structure of Tetrachloro Pyrimidine dye](image)

Sandoz claim that their dyes (Drimarene Z) have the following advantages.
a. Stability to alkali at low temperature
b. High stability and low salt sensitivity. They can be stored without deterioration.
c. Reactivity at high temperature. A system of low reactivity is required for printing dyes to ensure good paste stability but it should also be reactive enough for maximum yield to be obtained with reasonable steaming time. With Drimarene Z dyestuffs the steaming time is 8-12 minutes, which is about the same as that for vat dyes.
d. Stable chemical link with the fibre. The reactive system should be such that the dye fibre linkage should be stable at the boil. This is exactly the case with Drimarene Z dyes.
e. Removal of unreacted dye. This is important for not all the dye reacts with the fibre. The removal of the dye unreacted is easy.
f. High brilliancy is also found in these dyes.
g. They have a very good wet fast because of the stable chemical linkage. The wet fastness to print and stability to resins differ from individual to individual.

6.5 Chemistry of tetrachioropyrimidines

Tetrachioropyrimidines contains reactive halogen atoms in the 2,4- & 6 position. The chlorine in the 5 positions is very stable and cannot be exchanged with other groups easily. The most reactive of the other 3 is exchanged for the chromophore. It is the chlorihe in the 4 or 6 position which is equivalent.

In these dyes, two reactive halogen atoms are available, but under the fixation conditions generally only one of them is believed to react with cellulose. It is generally assumed that the chlorine in the 2 positions is involved.
6.6 Reactive Dyes based on Epoxides

Epoxides are used to form a permanent bond with the cellulose polymers in resin finishes. An epoxide as part of the dyestuff molecule would render the combination with certain polymers possible. Acid or bases catalyze them.

A typical epoxide molecule would be

![Epoxide molecule diagram]

An epoxide with phthalocyanine would give a good epoxide phthalocyanine reactive dye. These have excellent fastness for cellulose, wool and synthetics.
Other types of Reactive Dyes

There are quite a number of other kinds of reactive dyes, which form stable linkages with polymers etc. They are the chlorinated pyridines, chlorosulfanamides, and other chloro compounds. Reactive dyes with the hydroxy alkyl group are the roter dyes.

Hence it is seen that reactive dyes have given us many kinds of combinations and many more are yet to come.

Major Factors influencing the Dyeing Behaviour of Reactive Dyes are:

- The chemical reactivity of reactive dyes.
- Influence of diffusion and affinity in reactive dyeing of cellulose.
- Reaction between reactive dyes and cellulose.
- Variation of reactive system in reactive dyes.
6.8 Reactivity of different types of Reactive Dyes

Procion M dyes, which have as the reactive centre a dichloro S-triazine group, are the most reactive and therefore the dyeing can be carried out at room temperature. Only one of the two chlorine atoms of the cyanuric chloride nucleus can be replaced at room temperature while the other requires temperatures above 60°C for the reaction. It can be seen therefore that dyes based upon monochloro-S-triazine reactive group (Procion H. Cibacrons) would require higher temperature for fixation. These dyes are quite stable under alkaline conditions at room temperature and are therefore admirably suited for printing, and for dyeing by the pad-bake and pad steam methods. In contrast, the highly reactive Procion M dyes are amenable to easy cold pad-batch method of dyeing; they are unsuitable for printing.

An ideal reactive dye will be one which has high reactivity with cellulose and at the same time having good stability in alkaline solutions or pastes. Generally, the greater the reactivity of the dye, the greater is its instability in alkaline media. Levafix E dyes, which are based on halogenated quinoxaline ring (2-3-dichloroquinoxaline-6-carboxylamide), combine in them these opposing properties well. They are almost as reactive as Procion M dyes, and are quite stable under alkaline conditions.

Drimarenes, which are based on tetrachloropyrimidine are excellent for printing as they have high storage stability under alkaline at room temperature, but react rapidly with cellulose during steaming. The reactivity of vinyl sulphone dye lies between those of monochloro and dichlorotriazinyl dyes. Vinyl suiphone dyes have good stability under neutral and acidic conditions but poor stability under alkaline conditions.

6.9 Application

Reactive dyes are possessing high moderate or low reactivity. A highly reactive dye, which combines with the fibre rapidly or hydrolyses in water in a short period of time, requires only weak alkali such as sodium bicarbonate. A low reactivity product requires a strong alkali like sodium hydroxide. A moderately reactive dye requires an alkali such as soda ash.

6.10 Purification of Reactive Dyes

Reactive Dyes of the tetrachloropyrimidine and cyanuric chloride have registered a steady increase. Productions of these dyes were not fully investigated Normal purifying with salt and polar solvents affect the reactive group. The method by Rose also does not come handy as the use of polar solvents and fairly high temperature are involved. Generally the dye was dissolved in Dimethyl formamide and brought out with chloroform. They successfully purified reaction red 2B of the tetrachloropyrimidine and Procion Brilliant red H.7 G.S. of the cyanuric chloride type. They could also purify other similar dyes.

6.11 Advantage and Limitations of Reactive Dyes

The reactive dyes give even a better performance than most of the non-reactive dyes. Their advantages over the other dyes are as follows:

a. Their advantages over vats.
i. Improved surface appearance and penetration;
ii. Avoidance of reduction and oxidation processes, and
iii. Lower cost.
iv. Better range of shades

b. Their advantages over azoics are:
   i. Better rubbing fastness
   ii. Reproducibility of matchings
   iii. Better range of shades

c. Their advantages over pigments are
   i. Better workability and less scumming of reserved portions,
   ii. Much better penetrations and much better rubbing fastness even at higher concentrations, and
   iii) Absence of adverse effect in final, handle.

d. Their advantages over rapid fasts and rapidiogens in printing are
   i. Brighter prints and better (softer) handle.
   ii. No acid - steaming for fixation.

6.12 Fabric Preparation

Reactives are generally used on higher value cloths, which are normally mercerised. The colour build-up of reactives depends on the degree and efficiency of mercerisation. Thus the same strength of dyes used on differently mercerised cloth will give different depths and variations in shade, this impairs reproducibility of matchings.

6.13 Washing off

A large quantity of reactive dyestuff (10-40%) gets hydrolysed and hence remains unfixed and the difficulties associated with this residual dye which if not removed completely will tend to run during subsequent washing and will cause a lot of consumer dissatisfaction and/or possibly stain the while portions. Hence a thorough washing and soaping is absolutely necessary. This leads to a higher level of water consumption. The vinyl sulphone group gives much less difficulty. In the first place the quantum of unfixed dye is in the region of 10-15%; as against 30-40% in the case of cold brands. Also the unfixed dye does not stain the adjoining portions during washing.

Some of other disadvantages are
   i. Poor chlorine fastness
   ii. High printing cost and
   iii. Limited stability of printing paste (with alkali)
PRACTICAL WORK AND EVALUATION
The major objective of the project is to check the effect of quality of water from different areas of Pakistan on quality of reactive dyed cellulosic textile material with respect to evenness, chroma, and depth, washing fastness and rubbing fastness.

7.1 Experimental requirement

- Water
- Water testing requirement.
- Fabric
- Dye stuff
- Dyeing working area.
- Dyeing machine.

7.1.1 Water

The ground water is collected from four industrial areas, Faisalabad, Multan road, Kotlakhpat, Rawind manga road.

Location

- Faisalabad near Nishatabad (Nishat Textile Mills).
- Multan road near High Noon Textile Mills.
- Kotlakhpat Mr. Denim Textile Mills.
- Raiwind Manga road Master Textile Mills.

Water is collected in neat and clean transparent bottles. The bottles are labeled with the location of water. From each bottle two liter of water is filled in separate bottles and labeled with their location for water testing.

7.1.2 Water Testing Requirement

There are very little facilities in Pakistan for water testing. Water testing is performed in the chemistry department of PCSIR laboratory by relevant staff. They didn’t share testing method and procedure with us. The water sample bottles are provided to them and they delivered test reports of each sample after one month.

7.1.3 Fabric

It is decided to perform project on single jersey knitted fabric due to its good absorbency and simple structure. The fabric is arranged from Shahkam Textile Mills with following specification:

- Yarn counts 20 single.
- Yarn source Sapphire Textile Mills.
- Knitting Shahkam Textile Mills.
7.1.4 Dye stuff

The dye stuff selection for such a research is very critical red, yellow and navy dyes are selected. sumifix supra red EXF, sumifix supra yellow EXF and sumifix supra navy EXF are arranged from Lahore office of Sumitomo Chemical .sumifix supra dyes are bifunctional having vinyl sulphone as well as mono chloro triazinyl groups. Sumifix supra range is selected due to its medium affinity and good buildup. These dyes are very good for exhaust process and widely used for the dyeing of knitted goods in Pakistan industry.

7.1.5 Dyeing working area

It is necessary to have suitable laboratory for research work in dyeing area. The dyeing work is completed in fabric dyeing lab of Shahkam Textile Mills. The lab is equipped with modern infrared pot dyeing machine, sample dryer, light box, spectrophotometer and other necessary requirements; the technical staff of the lab has relevant experience training and cooperative attitude.

7.1.6 Dyeing machine

Ahiba Nuance Top Speed II is used for dyeing of samples. The machine is manufactured and marketed by Data Color. It is a rotary dyeing machine with infrared heating and water cooling .it is programmable having constant speed and movement of dye bath and substrate. It provides accurate temperature and time.

7.2 Water testing

Water testing is performed to analyses different parameters of water like pH, hardness, carbonates, bicarbonates, TDS .etc. The water testing is carried out with PCSIR chemistry department and they delivered the complete test reports after one month of submission of the samples. The report is given in table 7.1.
### Table 7.1

<table>
<thead>
<tr>
<th></th>
<th>Faisalabad</th>
<th>Kotlakhpat</th>
<th>Multan Road</th>
<th>Raiwind</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>pH</strong></td>
<td>7.7</td>
<td>7.3</td>
<td>7.7</td>
<td>7.6</td>
</tr>
<tr>
<td><strong>Conductivity at 25°C (µs/cm)</strong></td>
<td>4056</td>
<td>690</td>
<td>741</td>
<td>1364</td>
</tr>
<tr>
<td><strong>Total dissolved solid (ppm)</strong></td>
<td>2839</td>
<td>483</td>
<td>519</td>
<td>955</td>
</tr>
<tr>
<td><strong>Total hardness as CaCO₃</strong></td>
<td>506</td>
<td>200</td>
<td>270</td>
<td>232</td>
</tr>
<tr>
<td><strong>Calcium Hardness</strong></td>
<td>168</td>
<td>108</td>
<td>120</td>
<td>108</td>
</tr>
<tr>
<td><strong>Magnesium Hardness</strong></td>
<td>338</td>
<td>92</td>
<td>150</td>
<td>124</td>
</tr>
<tr>
<td><strong>Calcium as Ca++</strong></td>
<td>67</td>
<td>43</td>
<td>48</td>
<td>43</td>
</tr>
<tr>
<td><strong>Magnesium as Mg++</strong></td>
<td>81</td>
<td>22</td>
<td>36</td>
<td>30</td>
</tr>
<tr>
<td><strong>Total alkalinity as CaCO₃</strong></td>
<td>580</td>
<td>260</td>
<td>250</td>
<td>600</td>
</tr>
<tr>
<td><strong>Bicarbonate</strong></td>
<td>580</td>
<td>260</td>
<td>250</td>
<td>600</td>
</tr>
<tr>
<td><strong>Carbonate</strong></td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td><strong>Bicarbonate as HCO₃</strong></td>
<td>708</td>
<td>317</td>
<td>305</td>
<td>732</td>
</tr>
<tr>
<td><strong>Carbonate as HCO₃</strong></td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td><strong>Chlorite as Cl</strong></td>
<td>88</td>
<td>43</td>
<td>78</td>
<td>71</td>
</tr>
<tr>
<td><strong>Sulphate as SO₄</strong></td>
<td>400</td>
<td>60</td>
<td>80</td>
<td>150</td>
</tr>
<tr>
<td><strong>Sodium as Na⁺</strong></td>
<td>792</td>
<td>82</td>
<td>77</td>
<td>277</td>
</tr>
</tbody>
</table>
7.3 Dyeing process

Dyeing is carried out in “AHIBA NUANCE TOP SPEED II” dyeing machine.

7.3.1 Dyeing plan

The dyeing is performed in each water sample with Sumifix supra red, yellow and navy EXF dye stuff. Each dye stuff is applied with depth (practical concentration) 0.5%, 1%, 2%, 3% and 5%.

7.3.2 Solution formation

The concentration of each dye solution is kept 0.5%. The solution is prepared in the same water in which dyeing is done. No dye solution is used after 24 hours of its preparation, due to dye hydrolysis.

7.4 Dyeing procedure

The dyeing parameters are shown in table 7.2.

<table>
<thead>
<tr>
<th>Depth of shade</th>
<th>Fabric weight (g)</th>
<th>L:R</th>
<th>Temp °C</th>
<th>Salt gm/l</th>
<th>Soda gm/l</th>
<th>Caustic soda gm/l</th>
<th>Time (Min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5%</td>
<td>10</td>
<td>1:10</td>
<td>60</td>
<td>20</td>
<td>8</td>
<td>-</td>
<td>60</td>
</tr>
<tr>
<td>1%</td>
<td>10</td>
<td>1:10</td>
<td>60</td>
<td>30</td>
<td>15</td>
<td>-</td>
<td>60</td>
</tr>
<tr>
<td>2%</td>
<td>10</td>
<td>1:10</td>
<td>60</td>
<td>50</td>
<td>20</td>
<td>-</td>
<td>60</td>
</tr>
<tr>
<td>3%</td>
<td>10</td>
<td>1:10</td>
<td>60</td>
<td>60</td>
<td>20</td>
<td>2</td>
<td>60</td>
</tr>
<tr>
<td>5%</td>
<td>10</td>
<td>1:10</td>
<td>60</td>
<td>70</td>
<td>20</td>
<td>3</td>
<td>60</td>
</tr>
</tbody>
</table>

The other dyeing details are shown in figure 7.1, figure 7.2, and figure 7.3.
Fig 7.1

Pale shade

Fig 7.2.

Medium shade
Deep shade

7.4.1 Neutralization and sampling
After dyeing cold wash is done then neutralize with 2gm/l acetic acid solutions at 60°C, then two hot washes are done at 90°C. Finally soaping is done with 2gm/l soaps solution at 80°C.

7.4.2 Dyeing and conditioning
After soaping samples are dried in oven and conditioning of dried samples is done in conditioning cabinet at 18°C for four hours.

7.5 Fastness testing
The washing and rubbing fastness are mostly commonly demanded by the customer. These are performed to evaluate the effect of water quality on fastness properties.

7.5.1 Washing fastness
- Washing fastness is determined by test procedure ISO 105 C02.

This method is used for determining the resistance of the color of textile to the action of soap solution as used is washing by hand.

a. Apparatus and Reagent
Suitable washing device.
Soap solution containing 5g soap per liter.
Two white clothes 5*4 cm. place the two pieces of white cloth respectively above and below the specimen.

The specimen is 10*4 cm, in this way the 5*4 cm of the specimen remains uncovered.
Gray scale for assessing change in color.

b. ISO Test No.1 Procedure

- Places the specimen in the container and add the necessary amount of soap at previously heated to 40±2 C° to give a liquor ratio of 50:1.
- Treat the composite sample at 40±2 for 30min.
- Rinse the composite specimen twice in cold distilled water and then in cold running water, and squeeze it. Remove the stitching and dry the sample in air at the temperature not above 60 C°.
- Assess the change in color of the uncovered portion of the sample and the staining of undyed cloth with the gray scale.

c. ISO Test No.2 Procedure

- Place the composite sample in the container and add 5-g/l soap solutions.
- Treat the composite sample at 50±2 C° for 45 min.
- Rinse the composite specimen twice in cold distilled water and then in cold running water, and squeeze it. Remove the stitching and dry the sample in air at the temperature not above 60 C°.
- Assess the change in color of the uncovered portion of sample and the staining of the white clothe with gray scale.

d. ISO Test NO.3 Procedure

- Place the sample in the container and add 5-g/l soap and 2g/l carbonate.
- Treat the composite sample at 60±2 C° for 35min at the liquor ratio of 50:1.
- Rinse the composite specimen twice in cold distilled water and then in cold running water, and squeeze it. Remove the
stitching and dry the sample in air at the temperature not above 60 C°.

- Assess the change in color of the uncovered portion of sample and the staining of the white clothe with gray scale.

e. **ISO Test NO.4 Procedure**

- Place the sample in the container adding 10 balls (of stainless steel approximate 0.6cm in dia.) and add 5-g/l soap and 2g/l carbonate.
- Treat the composite sample at 95±2 C° for 30min at the liquor ratio of 50:1.
- Rinse the composite specimen twice in cold distilled water and then in cold running water, and squeeze it. Remove the stitching and dry the sample in air at the temperature not above 60 C°.
- Assess the change in color of the uncovered portion of sample and the staining of the white clothe with gray scale.

f. **ISO Test NO.4 Procedure**

- Place the sample in the container adding 10 balls (of stainless steel approximate 0.6cm in dia.) and add 5-g/l soap and 2g/l carbonate previously heated to 95±2 C° at the liquor ratio of 50:1.
- Treat the composite sample at 95±2 C° for 4 hour.
- Rinse the composite specimen twice in cold distilled water and then in cold running water, and squeeze it. Remove the stitching and dry the sample in air at the temperature not above 60 C°.
- Assess the change in color of the uncovered portion of sample and the staining of the white clothe with gray scale.

g. **Standard**

- For Reactive dyes the acceptable limit for change in shade from gray scale is 3-4.

### 7.5.2 Rubbing fastness

Rubbing fastness is determined by test procedure AATCC 8\165
This method is used for determining the resistance of the colors of textile to rubbing off and staining other materials. Two tests are made one with the dry rubbing and the other with the wet rubbing.
a. Apparatus and Reagent

- Crock meter or its equivalent.
- White bleached cotton lawn or similar cloth free from starch or other finishes, cut into 5-cm squares.
- Gray scale for assessing staining.
- Two pieces of the specimen are required, not less than 22*5 cm for dry rubbing and for wet rubbing. One specimen of each pair has the long direction parallel to warp yarns, the other parallel to the weft yarns.
- Distilled water.

b. Procedure

i. Dry rubbing
Place the white dry cloth over the end of the finger of the testing device, rub it in to and fro in a straight line along a track 10 cm long on the dry specimen, 10 times in 10 second, with a downwards force of 900gm. Test warp and weft directions separately.

ii. Wet rubbing
Repeat the test with a fresh dry specimen and white cloth that has been wetted with water and squeezed to a take up of 100%. Dry the cloth at room temperature. Assess the staining of the cloth with the gray scale. Standards are given below.

<table>
<thead>
<tr>
<th>For Reactive</th>
<th>For Sulphur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry rubbing</td>
<td>Dry rubbing</td>
</tr>
<tr>
<td>Wet rubbing</td>
<td>Wet rubbing</td>
</tr>
<tr>
<td>3 – 4</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Effect of water quality on Reactive dyeing of cellulose Textiles
Evaluation

The major objective of the project is to check the effect of quality of water from different areas of Pakistan on quality of reactive dyed cellulosic textile material with respect to evenness, hue, chroma, and lightness, washing fastness and rubbing fastness. The evaluation consists of:

- Evaluation of water testing report.
- Evaluation of dyed samples.

7.6 Evaluation of water testing report

Water testing report consists of testing results of Faisalabad, Multan road, Kotlakhpat, Raiwind Manga road water samples. The report is very clear. Faisalabad water is contaminated with TDS (Total Dissolved Solid), Total hardness, Calcium hardness and Magnesium hardness as Calcium carbonate.

Total alkinity, bicarbonate, carbonate as calcium carbonate for all the water samples is within the limit. Faisalabad water is also contaminated with chloride as Cl\(^-\), sulphite as SO\(_4\)\(^-\), sodium as Na\(^+\), and potassium as K\(^+\). Due to access of TDS, hardness, Chlorides, Sulphates, and metal ions. This water is not suitable for boilers. It causes the scaling of boiler walls and steam pipes. The presence of these impurities also causes the scaling of dyeing machine. Other problems associated with these contaminations are whiteness on dyed textile material, precipitation of soap and dyeing auxiliaries and unevenness of dyeing results the scope of this project is to just check the effect of water quality on reactive dyed cotton goods which will discuss in next section.

7.7 Evaluation of dyed samples

The dyed samples are dyed for following:

- Dyeing characteristics.
- Fastness properties.

7.7.1 Dyeing characteristics

The dyeing samples are evaluated for dyeing characteristics, hue, Chroma and lightness.

- Surface properties

Evenness and whiteness are absorbed by placing the dyed samples and comparing them with each other in Data Color light box. The surface of all the samples is commercially
satisfactory. Faisalabad sample is slightly uneven but that is acceptable, Multan road, Kotlakhpat and Raiwind Manga road samples having very good surface properties.

b. Fastness properties
To evaluate the dyed samples for hue, lightness and chroma the samples dyed in Multan road water are selected as standard to compare with samples dyed in water form other locations. The samples are compared visually as well as with the help of spectrophotometer.

7.8 Visual evaluation
Red, navy and yellow samples in 0.5%, 1%, 2%, 3% and 5% depth are compared. Samples are evaluated with each other according to their color and percentage category. e.g. navy samples with 1% concentration dyed in different location water are compared with each other. In visual evaluation there was not a considerable difference. So it is decided to proceed for instrumental color evaluation through spectrophotometer.

7.9 Instrumental color evaluation
For instrumental color evaluation, spectrophotometer is used. In each color and percentage category samples dyed with Multan road, are taken as standard. The samples dyed with other locations water are compared with Multan road samples through spectrophotometer. The comparison results for lightness (DL), hue (DH), Chroma (DC) are given in table 7.3, table 7.4, and table 7.5.
### Lightness (DL) Value

**Dye Name:** Sumifix Supra RED EXF  
**Standard water:** Multan road (Highnoon Textile Mills)

<table>
<thead>
<tr>
<th>Concentration (%)</th>
<th>Faisalabad</th>
<th>Raiwind</th>
<th>Kotlakhpat</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>-0.16</td>
<td>-0.36</td>
<td>-0.06</td>
</tr>
<tr>
<td>2</td>
<td>-0.20</td>
<td>0.07</td>
<td>-0.32</td>
</tr>
<tr>
<td>5</td>
<td>0.64</td>
<td>-0.14</td>
<td>0.46</td>
</tr>
</tbody>
</table>

**Dye Name:** Sumifix Supra Yellow EXF  
**Standard water:** Multan road (Highnoon Textile Mills)

<table>
<thead>
<tr>
<th>Concentration (%)</th>
<th>Faisalabad</th>
<th>Raiwind</th>
<th>Kotlakhpat</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.2</td>
<td>-0.1</td>
<td>-0.29</td>
</tr>
<tr>
<td>2</td>
<td>0.28</td>
<td>0.32</td>
<td>0.03</td>
</tr>
<tr>
<td>5</td>
<td>-0.46</td>
<td>-0.23</td>
<td>-0.55</td>
</tr>
</tbody>
</table>

**Dye Name:** Sumifix Supra Navy EXF  
**Standard water:** Multan road (Highnoon Textile Mills)


<table>
<thead>
<tr>
<th>Concentration (%)</th>
<th>Faisalabad</th>
<th>Raiwind</th>
<th>Kotlakhpata</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.36</td>
<td>-0.23</td>
<td>0.65</td>
</tr>
<tr>
<td>2</td>
<td>0.80</td>
<td>-0.23</td>
<td>0.74</td>
</tr>
<tr>
<td>5</td>
<td>0.19</td>
<td>0.34</td>
<td>1.30</td>
</tr>
</tbody>
</table>

Table 7.3

**Hue (DH) Value**

**Dye Name:** Sumifix Supra RED EXF  
**Standard water:** Multan road (Highnoon Textile Mills)

<table>
<thead>
<tr>
<th>Concentration (%)</th>
<th>Faisalabad</th>
<th>Raiwind</th>
<th>Kotlakhpata</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>-0.02</td>
<td>0.04</td>
<td>-0.17</td>
</tr>
<tr>
<td>2</td>
<td>0.34</td>
<td>-0.04</td>
<td>0.20</td>
</tr>
<tr>
<td>5</td>
<td>-0.60</td>
<td>0.33</td>
<td>-0.37</td>
</tr>
</tbody>
</table>

**Dye Name:** Sumifix Supra Yellow EXF  
**Standard water:** Multan road (Highnoon Textile Mills)

<table>
<thead>
<tr>
<th>Concentration (%)</th>
<th>Faisalabad</th>
<th>Raiwind</th>
<th>Kotlakhpata</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.39</td>
<td>0.15</td>
<td>-0.01</td>
</tr>
<tr>
<td>2</td>
<td>0.51</td>
<td>0.85</td>
<td>0.32</td>
</tr>
<tr>
<td>5</td>
<td>-0.73</td>
<td>0.08</td>
<td>-0.63</td>
</tr>
</tbody>
</table>

**Dye Name:** Sumifix Supra Navy EXF  
**Standard water:** Multan road (Highnoon Textile Mills)

Effect of water quality on Reactive dyeing of cellulose Textiles
### Chroma (DC) Value

<table>
<thead>
<tr>
<th>Dye Name:</th>
<th>Sumifix Supra RED EXF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard water:</td>
<td>Multan road (Highnoon Textile Mills)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Concentration (%)</th>
<th>Faisalabad</th>
<th>Raiwind</th>
<th>Kotlakhpat</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.28</td>
<td>0.24</td>
<td>-0.01</td>
</tr>
<tr>
<td>2</td>
<td>-0.20</td>
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<table>
<thead>
<tr>
<th>Dye Name:</th>
<th>Sumifix Supra Yellow EXF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard water:</td>
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</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Concentration (%)</th>
<th>Faisalabad</th>
<th>Raiwind</th>
<th>Kotlakhpat</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>-0.53</td>
<td>0.21</td>
<td>0.38</td>
</tr>
<tr>
<td>2</td>
<td>0.25</td>
<td>-0.04</td>
<td>0.39</td>
</tr>
<tr>
<td>5</td>
<td>0.71</td>
<td>0.81</td>
<td>0.54</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
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<th>Sumifix Supra Navy EXF</th>
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<tbody>
<tr>
<td>Standard water:</td>
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<tr>
<td>5</td>
<td>0.71</td>
<td>0.81</td>
<td>0.54</td>
</tr>
</tbody>
</table>
7.10 Interpretation of Instrumental Color Evaluation Results

- Lightness \( DL \)
- Hue \( DH \)
- Chroma \( DC \)
- Total difference \( DE \)

### 7.10.1 Formula for chroma, Hue, lightness and Total difference

\[
\begin{align*}
\text{Yellow} & : +b \\
\text{Green} & : -a \\
\text{Red} & : +a \\
\text{Blue} & : -b
\end{align*}
\]

\[
\begin{align*}
\text{Batch} & : \text{Yellow} + \text{Green} \\
\text{Standard} & : \text{Yellow} + \text{Red}
\end{align*}
\]
\[ C_{\text{batch}} = \sqrt{a_b^2 + b_b^2} \]

\[ C_{\text{stand}} = \sqrt{a_s^2 + b_s^2} \]

\[ DC = C_{\text{batch}} - C_{\text{stand}} \]

\[ DL = L_{\text{batch}} - L_{\text{stand}} \]

\[ H_{\text{stand}} = \tan^{-1} \frac{b_{\text{stand}}}{a_{\text{stand}}} \]

\[ H_{\text{batch}} = \tan^{-1} \frac{b_{\text{batch}}}{a_{\text{batch}}} \]

\[ DH = H_{\text{batch}} - H_{\text{stand}} \]

\[ DE = \sqrt{(DL)^2 + (Da)^2 + (Db)^2} \]

- DL compares the lightness and darkness of the value. If DL is positive the batch is lighter than standard. If the value of DL is negative the batch is darker than standard.
• DH expresses the hue. Its positive and negative values have different meaning for different colors.

• DC expresses the chroma. If DC is positive, batch will be bright than standard and if DC is negative the batch will be duller then standard.

• DE expresses the total difference. It is always positive. It tells the over all pass/fail result usually if it below than 1 the batch is considered ok with standard.

7.11 Lightness (DL)

The tables 7.3 show the comparison of lightness values DL for dyed samples taking Multan road sample, as a standard .It is evident that there is no definable difference in the values of lightness according to the quality of water.

E.g.: consider the samples dyed with Faisalabad water incase of samples dyed with Sumifix supra red EXF. The shade with 0.5% and 2% concentration are slightly darker than standard and shade with 5%concentration is reasonable lighter than standard. but in case of samples dyed with Sumifix supra yellow EXF, the shade with 0.5% and 2% concentration are slightly lighter than standard but shade with 5% concentration is reasonable darker than standard .In case of sample dyed with Sumifix supra yellow EXF, the shades with 0.5% and 2%concentration are lighter than standard so it is concluded that quality of water has no definite effect on lightness of shade.

7.12 Chroma (∆C)

The table 7.4 Show the comparison of chroma values DC for dyed samples taking Multan road sample as a standard evident that there is no definable difference in the values of lightness according to the quality of water.

E.g.: consider the samples dyed with Faisalabad water incase of samples dyed with Sumifix supra red EXF. The shade with 0.5% and 2% concentration are slightly brighter than standard and shade with 5%concentration is reasonable duller than standard. but in case of samples dyed with Sumifix supra yellow EXF, the shade with 0.5% and 2% concentration are slightly duller than standard but shade with 5% concentration is reasonable brighter than standard .in case of sample dyed with Sumifix supra navy EXF, the shades with 0.5% and 2%concentration are duller than standard so it is concluded that quality of water has no definite effect on lightness of shade.

7.13 Hue (DH)

It is clear from the study of hue table 8.2 that there is no definable effect of water quality on the hue of a shade.
e.g.: the samples dyed in Faisalabad water with Sumifix supra red EXF have negative hue for 0.5% shade. Positive hue for 2% shade and negative hue for 5% shade but in case of samples dyed with Sumifix supra yellow EXF, the shades have +ve hue for 0.5 and 2% concentration and –ve hue for the shade with 5% concentration and in case of Sumifix supra navy EXF, there is a +ve hue for the shades with 0.5% and 2% concentration and negative hue for shade 5% concentration.

7.14 Total difference (DE)

Total difference is very important parameter in the instrumental measurement of color. It gives overall measurement of color. It gives overall assessment of color; pass/fail of a shade with standard. Commercially if DE is less than 1, shade is considered match with standard.

When samples are compared with relevant standards (samples dyed with Multan road water). 25 samples have value of DE less than 1. It means 93% samples are commercially acceptable and only 7% are rejected. So the quality of water has very little effect on total difference DE.

7.15 Evaluation of Fastness properties

7.15.1 Evaluation of Washing Fastness
The samples dyed in different area water are tested for washing fastness. The washing fastness results are given in table 7.6, table 7.7, and table 7.8. It is clear from the tables that washing fastness is changed with the changed in depth of shade and there is no definable effect of water quality on the washing fastness of reactive dyed cotton goods from different quality water.

7.15.2 Evaluation of Rubbing Fastness
The samples dyed in different area water are tested for dry and wet crocking. The dry and wet crocking results are given below in the table 7.6, table 7.7, and table 7.8. It is evident that dry and wet crocking is changed with the change in depth of shade and there is no definable effect of water quality on the crocking of reactive dyed cotton goods from different quality water.

Fastness Test
### Washing Fastness Test

- **C1**: Dry rubbing Fastness test
- **C2**: Wet rubbing Fastness test

**Dye Name:** Sumifix Supra Red EXF  
**Standard water:** Multan road (Highnoon Textile Mills)

#### Table 7.6

<table>
<thead>
<tr>
<th>Concentration (%)</th>
<th>Faisalabad</th>
<th>Raiwind</th>
<th>Kotlakhpat</th>
<th>Multan</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>W</td>
<td>C1</td>
<td>C2</td>
<td>W</td>
</tr>
<tr>
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<td>4-5</td>
<td>3-4</td>
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<tr>
<td>1</td>
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<td>4</td>
<td>4-5</td>
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<td>4</td>
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<td>3-4</td>
<td>3-4</td>
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<td>3</td>
<td>4-5</td>
<td>3</td>
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</table>

**Dye Name:** Sumifix Supra Yellow EXF  
**Standard water:** Multan road (Highnoon Textile Mills)

#### Table 7.7

<table>
<thead>
<tr>
<th>Concentration (%)</th>
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<th>Multan</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>W</td>
<td>C1</td>
<td>C2</td>
<td>W</td>
</tr>
<tr>
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**Dye Name:** Sumifix Supra Navy EXF  
**Standard water:** Multan road (Highnoon Textile Mills Table)
Table 7.8

<table>
<thead>
<tr>
<th>Concentration (%)</th>
<th>Faisalabad</th>
<th>Raiwind</th>
<th>Kotlakhpate</th>
<th>Multan</th>
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</thead>
<tbody>
<tr>
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<td>W  C₁   C₂</td>
<td>W  C₁    C₂</td>
<td>W  C₁   C₂</td>
<td>W  C₁   C₂</td>
</tr>
<tr>
<td>0.5</td>
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<td>4 -5  4-5  4</td>
<td>4 -5  5  4-5</td>
<td>4  5  4-5</td>
</tr>
<tr>
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<td>4  5   4</td>
<td>4   5   4</td>
<td>4  4-5  3-4</td>
<td>4  4-5  3-4</td>
</tr>
<tr>
<td>2</td>
<td>4  5   4</td>
<td>4  4-5  3-4</td>
<td>4  4-5  3-4</td>
<td>4  4-5  3</td>
</tr>
<tr>
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<td>4  4-5  3-4</td>
<td>4  4-5  3</td>
<td>4  4-5  3</td>
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<tr>
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<td>3  4-5  2-3</td>
<td>2-3  4-5  2</td>
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</table>

7.16 Conclusion

The results obtained from the research are,

- The Faisalabad water is very much contaminated with TDS (Total Dissolved solid), Hardness, Metal ions and Chloride. The water from different areas of Lahore is less contaminated.

- Faisalabad water will cause scaling in boiler and boiler pipes.

- Experimental results and evaluations do not support the hypothesis that water quality has definable effect on the Hue, Chroma, Lightness and Total Color difference of reactive dyed cotton goods.

- Experimental results and evaluations do not support the hypothesis that water quality has definable effect on the washing fastness and crocking of reactive dyed goods.

7.17 Future research
The area that is focused in the research has bright chances for future research. The following research work can be conducted.

- Comparison of lab results with the production results related to the effect of quality of water on reactive dyeing and printing of cotton.
- Comparison of lab results with production results related to the effect of water on disperses dyeing and printing of polyester.
- Artificial adjustment of pH, Alkalinity, TDS (Total dissolved solid) and Hardness of distilled water by the addition of chemicals and effect of these parameters on dyeing and printing of Textile materials.
- Determination of most suitable parameters of water (pH, Alkalinity, TDS and Hardness etc.) for dyeing and printing.
8 References

Venue Engaged

1. Fabric textile (PVT) Limited, Lahore
2. Highnoon Textile (PVT) Limited, Lahore
3. Crescent Textile Mills, Faisalabad
4. Comfort Textile Mills, Lahore
5. Shahraj Textile Mills, Lahore
6. Shahkam Textile Mills
7. PCSIR Labs Lahore

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    d. ref/12/11473.pdf
    e. ref/08/07099.pdf


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      i. /edu/waterquality.html

Effect of water quality on Reactive dyeing of cellulose Textiles 105