INVESTIGATION INTO COTTON KNIT DYEING WITH REACTIVE DYES TO ACHIEVE RIGHT FIRST TIME (RFT) SHADE

BY

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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF

M. SC IN TEXTILE ENGINEERING

DAFFODIL INTERNATIONAL UNIVERSITY

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Preface

I hereby declare that the work which is being presented to Daffodil International University in this thesis entitled, **“Investigation into cotton knit Dyeing with Reactive Dyes to Achieve Right First Time (RFT) Shade”** is original work of my own, has not been presented for a degree of any other university and all the resource of materials uses for this thesis have been duly acknowledged.

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Md. Ibrahim Hossain Date of Submission

Acknowledgement

At first, I praise the almighty Allah that he makes me enable to complete the research work successfully.

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I am grateful to my all colleagues for their encouragement for this research work. Specially, I convey my gratitude and love to my parents who inspire me lot to do the job successfully**.**

The Author

Abstract

The present situation of dying process in Knit sector is well established & successful. But there are new challenges arising everyday which are trying to unsettle this progress. The process can be improved more if some new technology is introduced under precise condition making sure that the quality of production is not degraded. The knit dyeing process of cotton is almost entirely using Reactive Dyes & Exhaust methods, which are still undoubtedly successful.

But there are some problems which were not previously taken into consideration due to flexible market situation, now the business is very complex and competitive. So now some of them are playing vitally in the ratio of profit with quality. The first & the foremost target of any industrial production are to produce in the least time with maximum quality. At present days our knit dyeing industries are affecting with reduction of profit margin, economic crisis in countries, energy crisis etc. In such hostile condition the industries should concentrate very carefully on the duration of unit production, making the dyeing right in the minimum process steps. That’s why intense control of process should be done to get as much as close towards right-first-time dyeing. The “right first time” (RFT) approach to dyeing requires management, supervisors, and operators to focus on close measurement and follow-up of all aspects of the production system to ensure that each step is operating as specified. Goal-oriented product specifications are met on first-pass processing, so material is not held in-process for dye additions or rework dyeing. Rapid corrective action is taken when any defect is identified in the process or product. Operator and technical teams define and implement longer-term solutions to more frequently occurring breakdowns or disruptions in the process.

Fixation levels for reactive dyes, when doing deep dyeing, can be as high as 70%. Tests in several factories in Bangladesh have shown that currently fixation ranges from 40-65%. If, on average, the fixation is 50% then about 20% of the dye is essentially being wasted. If 20 kg of dye is used to dye a batch of 200 kg of fabric then 4 kg is being wasted per batch. If, on average, dye costs Tk.460 per kg then this is a loss of Tk.1840 per batch. If a factory dyes 1,000 tones of fabric each year, using 100,000 kg of dye and wastes 20% because of poor fixation, this is the equivalent of a loss of Tk. 9,200,000 per year (approximately US$ 117,949). This fixation level can increase achieving RFT shade by changing the variables (pH, time, temperature, liquor ratio, dyeing process, process parameters-different types of salt, alkali etc.), by modification the cellulose (cationization), reducing water hardness. In this experiment it was studied most of the parameters related to RFT concepts. Among them 22 points were summarized through which it can achieve the RFT shade. All these factors were discussed in details. It was also worked to utilize the 3M (Man, Machines and materials). For this dyeing workers were trained to not using more or less dyes, chemicals, machines were ensured accurate parameters and raw materials quality were tested in every lot. Among the 22 RFT factors the water hardness effect on reactive dyes fixation was worked more. For this experiment there was used three reactive dyes namely, Dychfix Red 3BXF, Dychufix Yellow 3RXF, Dychufix Navy Blue 2GLXF. Their fixation efficiency was observed by using at different dosing the chelating agent Liang710. It was also studied the change in color fastness due to using at different dosage of sequestering agent. The result was compared among the sample dyed without chelating agent and sample dyed with chelating agent.

Introduction

Right First Time shade means to match the shade of dyed fabric with the required shade at first time without facing or facing minimum dyeing faults. In other word RFT shade is matching the dyed fabric shade with required without topping and re- dyeing.

Actually it was very difficult to achieve the RFT shade in any dyed fabric manufacturing industries. Because there are a lots of factors related in the manufacturing process of dyed fabrics. Such as raw materials (water, dyes, chemicals, and grey fabric etc.), Process parameters, machines maintenance, manpower skill, utility support etc. All of these need to very control for about dyeing at RFT.

To achieve the right first time shade into knit dyeing at first it was found out the existing reasons behind dyeing faults & long process time of dyeing .Then reproducibility of lab to bulk was analyzed. It was studied of the combination selection of dyes. Water hardness was analyzed in both in-house laboratory and outside standard laboratory. A sequestering agent was selected to work by analyzing of different companies sequestering agent. An optimum dosage was also selected by laboratory research work. The raw materials testing system was developed. All the digital electrical measuring balances were calibrated. Digital temperature gun, pH meter, Hradness meter, peroxide killing test kit etc. was provided. It was also developed to provide computerized auto dyeing recipe making system. The soda dosing and color dosing system was developed for the light, deep & critical colors according to cycle time and the affinity of dye stuffs. There was also ensured the minimum dyeing breakdowns and the maximum utility support. The R & D department was involved to work with the dyes, chemical analysis continuously to develop the fabric quality & to reduce the dyeing cost. Then it was trained the Operator & Helper working in the dyeing floor & dyes chemical store about the technical operation, process, dyes chemicals handling. Finally there was developed the optimum good housekeeping in all over the floor.

Cellulose is a linear polymer of 1,4-β-D-glucose units linked together by valence bonds between the carbon atoms number 1 of one glucose molecule and number 4 of another molecule. The degree of polymerisation of cellulose molecule may be as high as 10000. Cotton fibres also contain waxes, pectins, organic acids and inorganic substances which produce ash when fibre is burnt [1].

The dye molecule contains specific functional groups that can undergo addition or substitution reactions with the OH, SH, and NH2 groups present in textile fibers. The dyeing with reactive dyes is performed in the presence of an alkali such as Na_2CO_3 and caustic soda. The ionization of OH group in cellulose fibres is accelerated with an increase in pH value, which facilitates their reaction with reactive dyes. On the other hand, reactive dyes also react with water and are increasingly hydrolysed, which is unfavorable for dyeing. In practical dyeing condition e.g. the kind and amount of alkali, temperature and time, so that to minimize the hydrolysis of dyes and maximize the reaction of reactive dyes with cellulose fibres and water taking place in the presence of alkali. [2].

Fixation is invariably achieved in the presence of aqueous alkali. Under these conditions, nucleophilic cellulosate ion, Cell-O-, is in competition with hydroxide ion, OH-, for reaction with the electrophilic reactive group(s) of the dye [3]. It is shown that the dye fixation to the fabric is controlled by a solid–liquid interfacial process; however, the rate of this reaction is governed by the availability of sites for the adsorption of dye molecules on the fabric surface [4].

Reactive dyes fixation mechanism can be explained by the intermolecular force acting among the dye stuffs and the application media. Water Hardness has a great impact on the fixation level of reactive dyes. If the dye bath water contain metal ions like Ca^{++}, Fe^{++}, Mg^{++} , then the dye stuffs will react with the this metal ions and create ionic bond. Calcium and magnesium ions reduce the solubility of anionic dyes causing them to aggregate or even precipitate on the fiber. Aggregated and precipitated dyes cannot migrate or diffuse they remain on the fiber surface as particular deposits. A chemical compound which possesses two (or more) chemical groups, which can surround a metal ion, resulting into a complex is called chelate. These chelates are more stable then the simple salts formed with acid (i.e acetic or formic acid) such simple salts formed with acids are usually highly soluble and useful way of demineralising cotton before dyeing [5].

The most undesirable impurities in Fibre, Common salt, Glauber's salt, Caustic Soda and Soda ash are the di- and tri-valent e.g., Ca++, Mg ++ Cu ++, Fe+++ etc. These ions increase hardness of the process bath and generate iron oxides in the bath. Calcium and Magnesium reacts with alkali and precipitates as a sticky substance on the textile material, which creates patchy dyeing and discoloration of the fibre.

Also the dye stuffs make H-bond reacting with the H^+ available in the dye bath water. Hence it will cause for Hydrolysis of reactive dyes. This cannot be avoid, because H-bond is negative inherent reaction, which occurs at the same time of creating Covalent bond with $Cell^+$ of the cellulosic fibre. This will be a part of cellulose as the covalent bond is very stronger than ionic, H-bond and vander walls force. And the amount of dye molecules take part in the covalent bond with the fire is the total amount fixation of reactive dyes. Among this bonds van walls force is avoidable with increasing the temperature during dyeing. H-bond cannot be avoided. Covalent bond is our only target to fix up the maximum amount of dye molecules on the substrate from the dye bath solution. But the ionic bond can be eliminating using chealting or sequestering agent.

Sequestering agents work by a mechanism of complex formation, also termed chelation. The sequestering/chelating agent has groups at appropriate locations in the molecule to form one or more chelate rings with the metal ion. The complex thus formed remains soluble as well as stable under given conditions. These chemicals usually contain nitrogen, such as amines and substituted amines, and oxygen in the form of carboxyl, phosphate or hydroxyl groups. They form molecules in which the ions are held securely (sequestered) that they can no longer react.

CHAPTER – 01

OBJECTIVES

Objectives

1. To investigate how to dye cotton knit fabric with reactive dyes at RFT
2. To utilize the 3M(Man, Machine and Maerials)
3. To increase the reproducibility of lab and bulk
4. To improve the fixation (%) of reactive dyes using chelating agent
5. To analyze the fixation (%) of primary colors (Red, Yellow, Blue)
6. To analyze the fixation(%) of combined colors
7. To compare the color fastness properties of different dyes at different dyeing steps
8. To reduce the dyeing Faults
9. To reduce the dyeing process time
10. To improve the dyeing quality
11. To minimize the dyes fixation loss per year
12. To study the cost effectiveness for RFT shade achievement

CHAPTER – 02

LITERATURE REVIEW

1. Cotton

Cellulose (Latin word cellula, “little cell”) is a complex carbohydrate. In plants, cellulose is normally combined with woody, fatty or gummy substances. Photoinitiated biosynthesis results in the main product group of saccharides (particularly cellulose and starch) besides proteins, fats and oils. Payen suggested that the cell walls of a large number of plants were constructed of the same substrate to which he gave the name of cellulose [6] [7] [8]

Cotton fibre is one of the most important natural textile fibres of plant origin and accounts for about one third of the total world production of textile fibres. Cotton fibres grow on the surface of the seed of cotton plant. Cotton fibre contains 90–95% cellulose which is an organic compound with the general formula $(C_6H_{10}O_5)n$. Cotton fibres also contain waxes, pectins, organic acids and inorganic substances which produce ash when fibre is burnt. Cellulose is a linear polymer of 1,4-β-D-glucose units linked together by valence bonds between the carbon atoms number 1 of one glucose molecule and number 4 of another molecule. The degree of polymerisation of cellulose molecule may be as high as 10000. The hydroxyl groups OH protruding from the sides of the molecule chain link neighbouring chains together by hydrogen bond and form ribbon-like microfibrils which are further arranged into larger building blocks of the fibre. Cotton fibre is partly crystalline and partly amorphous; the degree of crystallinity measured by X-ray methods is between 70 and 80% [9]. Natural cellulose fibers carry a small negative charge ($\zeta_{plateau}$ = -11 mV) due to the presence of some carboxylic acid groups from oxidation at the primary hydroxylic sites [10].

1.1 Molecular structure of cellulose

Cellulose is composed of a large number of repeating units of 1,4-D-glucopyranose as shown in the following figure.

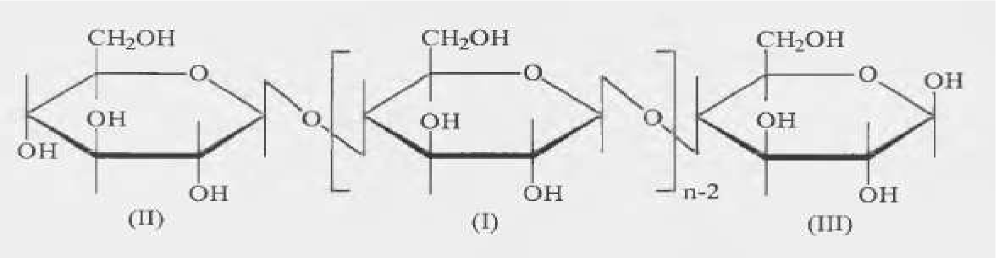


Fig 1: Molecular structure of cellulose.

The distinguishing features of the polymer chain are the main sequence of repeating intermediate units (I), the non-reducing end group (II), the reducing end group (III) and the glycosidic linkage. Each intermediate unit contains three alcohol groups, two of which are secondary alcohols and one primary alcohol. The reducing end group is a cyclic hemiacetal, which shows the characteristics of both an alcohol and an aldehyde under appropriate conditions as shown in the following Figure [8].

Fig 2: Cyclic hemiacetal group showing both an alcohol and aldehyde characteristics

1.2 Repeat unit of cellulose

The current consensus regarding cellulose crystallinity (X-ray diffraction) is that fibers are essentially 100% crystalline and that very small crystalline units imperfectly packed together cause the observed disorder.

The density method used to determine cellulose crystallinity is based on the density gradient column, where two solvents of different densities are partially mixed. Degree of Crystallinity is, then, determined from the density of the sample, while densities of crystalline and amorphous cellulose forms are known (1.505 and 1.556 respectively). Orientation of untreated cotton fiber is poor because the crystallites are contained in the micro fibrils of the secondary wall, oriented in the steep spiral (25-30°) to the fiber axis.

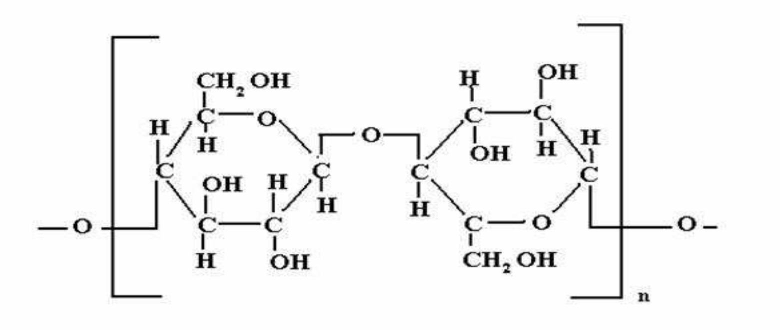


Fig 3: Chemical Structure of cellulose [11]

1.3 Morphology of cotton

The seed hair o f cotton consists o f three parts as illustrated in Figure 1.2. When looking at a cotton-fibre cross-section, it shows a lumen or central canal (S3), the secondary thickening (S2) which is cellulose and the primary wall (Si) or cuticle which forms a protective layer containing pectin, proteins, waxes and mineral matter. In the development of the secondary wall, cellulose is deposited in the form of fibrils. The fibrils in turn consist of micro fibrils which contain polymer chains that are well packed and almost identically oriented and thus are crystalline. The fibrils in the fibre are formed in layers which are associated with the daynight cycles experienced during growth. The fibrils are arranged spirally around the axis of the fibre, the direction o f the spiral reverses from a left to right direction and vice versa, many times along the length o f the fibre [12] [8].

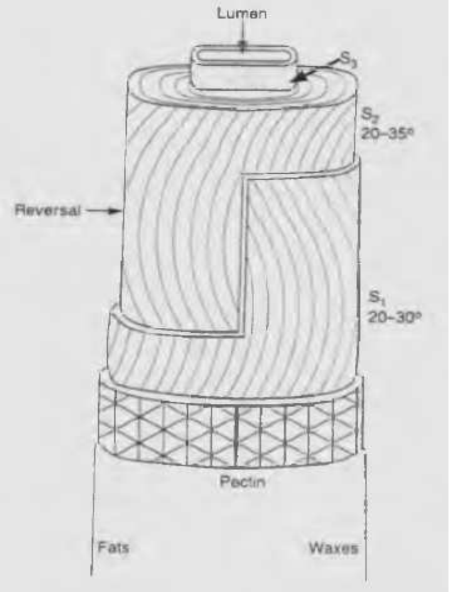


Fig 4: Morphological structure of the cotton fibre

1.4 Supramolecular structure of cellulose

Native cellulose is a highly crystalline material which contains crystalline fibrils o f varying degree o f complexity and undetermined length. The fibrils are placed in the fibre in such a manner that they may be interspersed with material in which the chain molecules are not as well ordered as in the crystalline region. The same molecular chain may occur in both crystalline and non-crystalline regions of the fibre, along different portions of its length. The overall arrangement o f chain molecules in a fibre, the supra molecular structure, may also be explained in two concepts; crystalline and fine structure. Several key features o f the cotton cellulose molecule give rise to important structural and mechanical characteristics in the fibre itself [13].

♦ It is ribbon-like with an approximately rectangular cross-section.
♦ It is relatively flexible, through rotation about the bridging oxygen links between the glucose rings.
♦ It features a high concentration o f hydroxyl groups along its edges.
♦ It has directionality.

The disordered regions are important to facilitate dyeing, since the penetration o f dyes and other chemical reagents is possible mainly through disordered regions. Molecules that are located at the surface of the crystallite areas are also accessible to chemical interactions and therefore size and distribution of crystallites play an important role in determining the accessibility o f fibres. The morphology of a cotton fibre is illustrated in Figure 1.2. In addition to the form and structure of the fibre, the morphology of cellulose includes factors of fine structure such as fibrils and micelles, accessible and non-accessible regions [14].

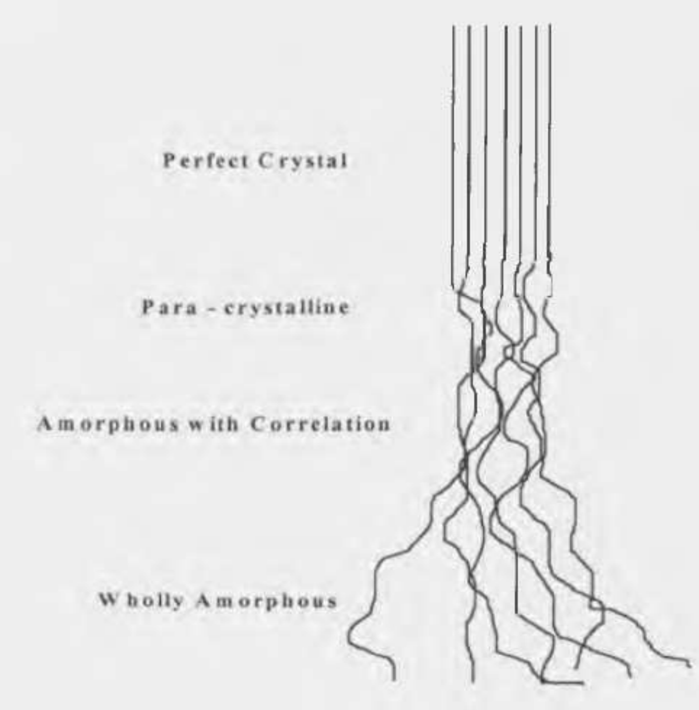


Fig 5: Relative degrees of order in the packing of chain molecules

All the different cellulosic fibres encountered in dyeing, including cotton, mercerized cotton, viscose rayon, linen, ramie, hemp and jute, have uniquely different morphologies derived from the same basic cellulose material. Thus, chemical behavior of these fibres towards water and dyes will be similar but the overall behavior will be determined by several variables depending on the morphological structure o f the fibres such as characteristics o f the outer and inner layers, the ratios o f crystalline to amorphous cellulose and the size and distribution o f the crystallite regions. [8]

2. Water

Water is the chemical substance with chemical formula H_2O: one molecule of water has two hydrogen atoms covalently bonded to a single oxygen atom. Water appears in nature in all three common states of matter (solid, liquid, and gas) and may take many different forms on Earth: water vapor and clouds in the sky, seawater in the oceans, icebergs in the polar oceans, glaciers in the mountains, fresh and salt water lakes, rivers, and aquifers in the ground.

As water and its quality play a very important role in wet processing, let us have a brief look into the quality of water required for wet processing, with an emphasis on reactive dyeing. We get water from various sources, like river, ponds, shallow wells and deep bore wells. According to the source of water, it contains many dissolved and suspended impurities. The water from a running river contains many dissolved salts (solids) like Sulphates, Chlorides, silicates, Carbonates and Bicarbonates of heavy earth metals like Calcium, Magnesium, Iron, Aluminums, and Sodium etc. The ratio of these salts varies according to the source of water.

Water is an important ingredient in the recipes of textile wet processing. Due to inadequate availability of good quality surface water, many units are compelled to use ground water. The quality of ground water is not always as good as surface water, and it could contain soluble calcium and magnesium salts, leading to hardness. This hardness can be corrected by using a water softening plant, which can remove these metal salts and replace them with sodium salts, but these softening plants may not take care of other metal salts of Cu2+, Ni2+, Fe3+, Cr3+, etc, if present in raw water, and these metal salts can cause problems in textile wet processing

The quality of textile products is affected by the water quality. Chlorine, iron and treatment chemicals have a major effect on dyeing process. Shade variation can be caused by chlorine contamination of water. This can cause color loss for many classes of dyestuff. Shade variation also be caused by metal such as iron, copper and other metals. These metals are known to affect many dyes, especially reactive dyes. Trace metals can change the shade of reactive colors, for example, the colors of azo dyes are reduced by metallic salts. The most common metals affecting shade variqtion of textile goods in water are aluminium, copper, manganese and iron.[15] [16].

2.1 Sources of water

As you know, the earth is watery place. Estimates vary, but somewhere between 70 and 75% of the earth’s surface is water covered. But water also exists in the air as water vapor and in the ground as soil water. Water is used in very large quantities, so it must be cheap. Natural water mainly obtained from the following sources:

- Mains supply
- Surface water
- Sub-soil or ground water
- Rain water
- Sea water [17]

2.2 Importance of water

It has the great importance regarding to its usage. It used as 88% in agriculture, 7% in industries and 5% in domestic uses. The importance of water to the textile wet-processing industries cannot be stressed enough. It is not just something to dissolve the dye in or float the textile around in; it is one of the most important substances used. It is certainly the one that the industry uses most of. In textile industry, water plays a vital role, it used as 52% in dyeing, 1% in finishing, 6% in cooling and 41% in preparation (Preparatory processes). It is observed that, there is need of about 50 liter water to dye 1 kg fabric [17].

2.3 Minimum standard water quality for dye house

In "Wet-processing sector" of Textile field, the role of water is not negligible. It uses very large volumes of water to carry out the processes associated with it. In this area it is utilized from preparation to the finishing processes. Therefore, a very special care is taken while using the processing water, so that it may not create any problem during processes and required target is achieved without any difficulty. The following are considered to be the essential requirements for textile wet processing.

Table 1: Minimum standard quality of water for a dye house

Parameters	**Permissible Concentration**
1. Color	Colorless
2. Smell	Odorless
3. pH	Neutral (7-8)
4. Hardness	25 PPM of $CaCO_3$
5. Solid deposits	50mg/l
6. Organic substance	10mg/l
7. Inorganic salt	500mg/l
8. Iron (Fe)	0.1mg/l
9. Copper (Cu)	0.005mg/l
10. Nitrate (NO_3)	50mg/l
11. Nitrite(NO_2)	5mg/l
12. Manganese (Mn)	0.02mg/l
13. Silica	3.0mg/l
14. Dissolved Solids	65-150mg/l
15. Suspended Solids	1.0mg/l
16. Filterable	50mg/l
17. Alkalinity to pH	30-65 $CaCO_3$

2.4 Water properties

Water has the physical and chemical properties that make it so unique and necessary for living things. When we look at water, taste and smell it, it could be more boring. Pure water is virtually colorless and has no taste or smell but the hidden qualities of the water make it a most interesting subject [17].

2.4.1 Chemical Properties of Water

The hydrogen atoms are "attached" to one side of the oxygen atom, resulting in a water molecule having a $+^{ve}$ charge on the side where the H_2 atoms are, and the $-^{ve}$ on the other side, where the oxygen atom is. Since opposite electrical charges attract, water molecules tend to attract each other, making H_2O "sticky". As the diagram shows, the side with the hydrogen atoms (positive charge) attracts the oxygen side (negatives charge) of different water molecule. Water is called the "Universal solvent", because it dissolves more substances than any other liquid. This means that whatever water goes, either through the ground or through our bodies, it takes along valuable chemicals, minerals and nutrients. Pure water has a natural pH of 7, which is neither acidic nor basic [17].

2.5 Impurities of water

There are many salts and other particles are dissolved in water or scattered in the water from the rock touching to the ground, when water float through glaciers to rivers and canals. There are two main types of impurities which are present in the water, which are as follow;

- Physical impurities
- Chemical impurities

2.5.1 Physical impurities (insoluble): The impurities which are due to the scattered particles present in the water like sand, clay and other particles. Those impurities are;

- Turbidity
- Color

2.5.2 Chemical impurities (soluble): The impurities which are due to the dissolved particles in the water are known as chemical impurities or soluble impurities. In these impurities most important are:

- Hardness
- Metals
- Chlorides
- Carbon dioxide

2.6 Hard water

Water is said to be hard when it contains high concentration of Calcium and Magnesium salts. Hard water is that water which contain with a charge of +2, especially Ca+ and Mg+. These ions do not pose and health threat but they can engage in reactions, leave insoluble mineral deposits. Water is said to be hard when it does not easily form lather with ordinary soap, but does after so much soap is consumed. Hard water reacts with soap ($C_{17}H_{35}CO_2Na$) to give a precipitate of ($C_{17}H_{35}CO_2Ca$) instead of good lather. While soft water would rapidly give the good lather with soap. Hard water is undesirable because it may lead to greater soap consumption, scaling of boilers, causing corrosion and incrustation of pipes and also making food tasteless. The acceptable level for textile wet processing purposes is around 40 ppm $CaCO_3$[17].

2.6.1 Metals

The most trouble making metals are iron, manganese and copper. They may create trouble in altering the shade and fastness of some dyes and to catalyze processes such as bleaching of the textiles. The acceptable level of metals is:

Fe = 0.1 PPM
Mn = 0.05 PPM
Cu = 0.01 PPM

2.6.2 Chlorides

Ground water contains high concentration of chlorides particularly when bore holes are sunk into the salt-bearing rocks. It may also be high in rivers because of the discharge of sewerage. The chloride content is not trouble making in textile wet processing. So, its acceptable level is 250 PPM but their concentration should be fairly constant throughout the water.

2.6.3 Carbon Dioxide

The ground water contains high concentration of dissolved carbon dioxide gas. It may create trouble in steam raising boilers as corrosion. The maximum acceptable level of carbon dioxide is 50 PPM.

2.6.4 Causes of hard water

There are some causes of hard water which are given below;

- Geology
- Mining
- Industrial discharge
- Sewerage out flow

When our sewerage goes into the rivers and canals then this salt goes to the water and causes the hardness of water. The range of soft water is as below [17].

Table 2 : The range of soft water

Hardness rating	Concentration of Calcium Carbonate (mg/L)	Concentration of Calcium Carbonate (grains/US gallon)
Soft	0 to <75	0 to <5.2
Medium hard	75 to <150	5.2 to <10.5
Hard	150 to <300	10.5 to <21
Very hard	300 and greater	21 and greater

2.6.5 Problems due to hard water in textile wet processing

- Hard water consumes larger amount of soap in washing purpose.
- Hard water can be cause of scaling in boilers for producing steam.
- It may cause of deposits on goods which are difficult to remove.
- Solubility of dyes is affected in the process of dyeing.
- Hard water to be used in processing can cause the wastage of heat.
- If hard water is also used for drinking purpose for long period, it may cause stomach diseases in the workers of the industry [17].
- If calcium and magnesium are not sequestered, there is the strong possibility of their combining with natural “soaps” which have been generated during the alkaline scouring process, to form waxy substance. These have been referred to as “Lime soap deposits” they can deposit not only on the substrate itself but also on the surface of machinery.
- Calcium and magnesium ions reduce the solubility of anionic dyes causing them to aggregate or even precipitate on the fiber.
- Aggregated and precipitated dyes cannot migrate or diffuse they remain on the fiber surface as particular deposits.
- In the bleaching of cotton with peroxide, pinhole marks in fabric and hosiery, lower tensile strength in the case of yarn, and poor spinnability of bleached cotton fibre are the result of iron and copper impurities. Sometimes, pinhole marks may not be seen but DP values would be lower, though whiteness remains the same. Also, the presence of calcium can rapidly decompose hydrogen peroxide.
- In reactive dyeing, precipitation of dyestuff could take place due to the presence of calcium, leading to dye spots and poor colour yield, and affecting reproducibility.

- In washing off of reactive dyestuffs, poor wash fastness and wet rub fastness result from the presence of calcium.

2.7 Hardness of water

Hardness may be due to the minerals dissolved in water. Those minerals are Carbonate, bicarbonate, sulphates or chlorides of Calcium or Magnesium. The acceptable level for textile wet processing purposes is around 40 ppm CaCO3. There are two types of hardness:

- Temporary hardness
- Permanent hardness [17].

2.7.1 Temporary hardness

Soluble salt of Bi carbonate of Ca & Mg is called Temporary Hardness. The presence of bicarbonates of Calcium and Magnesium in water is called temporary hardness. When the water containing these salts are heated to boil,

$$HCO_3^{-} == H_2O + CO_2$$

The temporary hardness is due to the presence of $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$. The above salts get precipitated in alkaline medium and a turbidity will be formed. If these Calcium and Magnesium salts are converted to water soluble Sodium salts, then the precipitation will not be there. The process of changing the basic radicals viz., Ca++ and Mg++ in to Na+ is taking place in the ion–exchange type water softening plants.

2.7.2 Temporary hardness salts

- Calcium Carbonate ($CaCO_3$) - Known as limestone, rare in water supplies. Causes alkalinity in water.

- Calcium Bicarbonate [$Ca(HCO_3)_2$] - Forms when water containing CO_2 comes in contact with limestone. Also causes alkalinity in water. When heated CO_2 is released and the calcium bicarbonate reverts back to calcium carbonate thus forming scale.

- Magnesium Bicarbonate [$Mg(HCO_3)_2$] - Similar to calcium bicarbonate in its properties

- Magnesium Carbonate ($MgCO_3$) - Known as magnesite with properties similar to calcium carbonate.

2.7.3 Permanent hardness

If the sulphates, chlorides and nitrates of calcium or magnesium are present in water then water is said to be permanent hard. This hardness can not be removed by simple boiling and therefore such water requires some special treatments to make it soft [17].

2.7.4 Permanent Hardness Salts

- Calcium Sulfate ($CaSO_4$) - Know as gypsum, used to make plaster of paris. Will precipitate and form scale in boilers when concentrated.

- Calcium Chloride ($CaCl_2$) - Reacts in boiler water to produce a low pH as follows: $CaCl_2 + 2HOH ==> Ca(OH)_2 + 2HCl$

- Magnesium Sulfate ($MgSO_4$) - Commonly known as epsom salts, may have laxative effect if great enough quantity is in the water.

- Magnesium Chloride ($MgCl_2$) - Similar in properties to calcium chloride.

Fig 6: Digital water Hardness test meter

3. Chelating agent

Chelating and sequestering agents have had considerable applications for many years. These materials usually form complexes or coordination compounds by reaction of their negatively charged donor groups with polyvalent metal ions such Ca++, Mg ++ Cu ++, Fe+++ etc. The most undesirable impurities in Fibre, Common salt, Glauber's salt, Caustic Soda and Soda ash. These ions increase hardness of the process bath and generate iron oxides in the bath. There are several classes of chelating agents including the EDTA (ethylenediamine tetra acetic acid) type and the aldonic (sugar) acid group. An aldonic acid is any of a family of sugar acids obtained by oxidation of the aldehyde functional group of an aldose to form a carboxylic acid functional group. Gluconic and citric acid are examples of the latter. The choice of chelating agent depends to a great extent upon the conditions under which it is applied for example, the EDTA family is effective in acid, neutral, or alkaline media whereas the sugar acids function best with which this note concerned [18].

The present invention relates to a novel composition of matter having utility in the sequestering or complexing of metal ions particularly calcium and / or magnesium ions. More particularly, the present invention is unique combination of water soluble aminopolyacetate demonstrating improved chelating properties. Sequestering agent are employed in a number of applications such as builders in detergent formation to eliminate interfering effects caused by dissolved metal salts, particularly calcium or magnesium salts. Sequestering agents are also employed in other applications requiring control of metal ion content in aqueous solution such as waste water treatment, potable water conditions, micro-nutrient solubilization, gas conditioning, photographic development processing catalysis of chemical processes, finishing and conditioning of textile, etc. [19].

3.1 Invention of chelating agent

The present invention is an improved sequestering agent comprising of a mixture of from about 2% to 20% by weight of iminodiacetic acid or water soluble salt thereof (IDA) and from about 80% to 98% by weight of nitrilotriacetic acid or water soluble salt thereof (NTA). Iminodiacetic acid, $HN(CH_2CO_2H)_2$, often abbreviated to IDA, is an polyamino carboxylic acid. It is discovered that the sequestering agent corresponding to the above defined range of composition provides improved sequestration or chelation, particularly of calcium and magnesium ions in aqueous solution, over the performance of each component of the composition individually, thereby resulting in a synergistic addition of chelating properties. Equally surprising is the fact that addition to a composition of large amounts of IDA than called for by the present invention deleteriously affects the performance of the sequestering agent. [19].

A preferred application of the present sequestering agent is as a detergent builder in combination with additional components such as surfactants, thereby providing an improved detergent, particularly suited for use in water containing dissolved calcium and/ or magnesium ions. [20].

One of the most important sugar based chelating agent issodium gluconate, which has found an extensive use as a chelating agent in the dairy, detergent, brewing, leather and textile industries. Medicinally it is used as a carrier for calcium and iron intreatment of deficiencies of these elements. Gluconates are prepared commercially by enzymatic transformation of D – glucose with glucose oxidase (EC 1.1.3.4 - D – glucose: oxygen oxidoreductase) or by catalytic air oxidation of glucose.

Higher members of the series such as sodium glucohaptonate can be prepared by addition of sodium cyanide to glucose followed by hydrolysis. Lactobionic acid and its amides were less effective as chelater for iron then were corresponding gluconic acid compounds. The EDTA and Lactosyl urea were ineffective under this condition. The presence of an additional carboxyl groups, as in saccharic acid or sodium mucate, afforded no benefits over gluconic acid in the amount of ferric chloride complexes. Amides formed by reaction of glucono or Lactobiono-Lactone with 2-methyl-2 aminopropanol were slightly superior in chelating power to their parent acids [21].

3.2 Advantages of chelating agent/sequestering agent

- Prevention of pinhole formation due to catalytic oxidation caused by iron during bleaching (chelates iron / heavy metals).
- During dyeing, it prevents spots, shade change and unevenness by chelating heavy metals and dispersing impurities.
- Improved rinsing due to the scale inhibition (effective at low concentration such as its presence in rinse bath).
- Improve the fixation level of reactive dyes.

During fabric preparation sequester also provides iron chelating to prevents fabric / yarn damage and provides additional stabilizing effect on the hydrogen peroxide [19].

3.3 Use of sequestering agent in dyeing

The three main stages in which sequestering agents are used are:
1. Pretreatment
2. Dyeing
3. After treatment

3.4 Classification of sequestering agent

The five main classes of sequestrant used in the textile industry are:
1. Aminocarboxylic acid base products
2. Phosphates and Phosphonates
3. Hydroxy carbroxylates
4. Polyacrylates
5. Sugar acrylates [19].

3.4.1 Aminopolycarboxilic acid sequestering agent

In aminopolycarboxylates, it is assumed that one molecule of sequestering agent complexes with one ion of metal. Depending upon the pH of the medium, i e acidic, neutral or alkaline, the preferential sequestering order or each product could change.
Some of the characteristics of some of these sequestering agents are summarized as below:

3.4.1.1 Features of EDTA

One of the oldest known, and most widely used “textile sequestrant “ EDTA is cheap and forms strong complexes with a broad spectrum of metal ions. Weight for weight comparison shows significantly inferior sequestering capacity to that of polyphosphonic acid.

Good sequestering agent for Ca/ Mg at high pH values(but only in the absence of oxidizing agents). But for the ferric ion (Fe+++). The sequestering action is excellent at low pH values but begins to decrease at pH 6. At higher pH values, EDTA becomes completely ineffective at controlling Fe+++. Never likely to provide protection for localized “pinhole damage” in peroxide bleaching. The failure of EDTA to sequester iron above pH 8 renders it useless as a peroxide bath sequestrant / stabilizer – unless it is used in combination with a second sequestrant which can bind iron in the pH range 11 – 13.

EDTA can demetalise many metal containing dyes, usually resulting in a drastic shade change. EDTA is not suitable as a dyebath sequestrant. Beware of red, Bordeaux and burgundy shades turning a very dull blue (almost purple). EDTA is hardly soluble in acidic pH, and is often used, therefore, in the form of a sodium or ammonium salt. It is good sequestering agent for calcium and magnesium at alkaline pH but no sequestering agents on Fe3+ at alkaline pH. It is not stable with oxidizing agents. It has low solubility in acidic medium. [19].

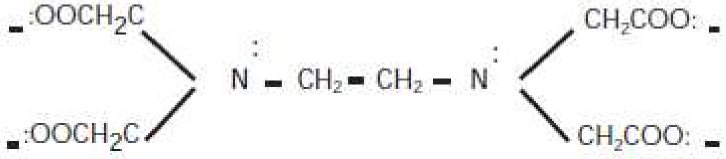


Fig 7 : Ethlene diamine tetra acetate ion [19].

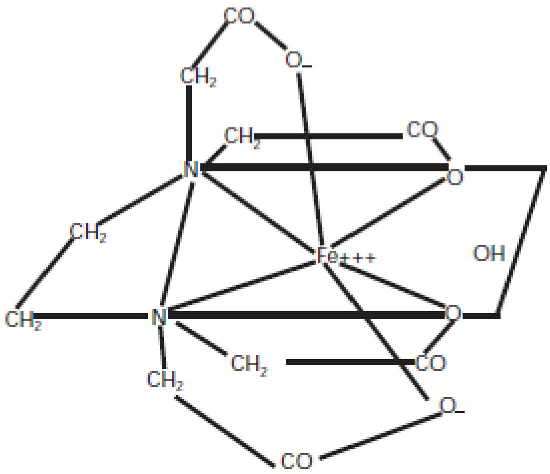


Fig 8 : EDTA Ferric Chelate [19].

3.4.2 Features of Polyphosphonate sequestrants

Very high sequestering capacity for Ca and Mg from pH 5 – 13; And for Cu / Fe from pH 1 – 13. The resultant sequestrant – metal complexes are generally highly soluble, and not easily precipitated (even in the presence of Rock salts and Sea salts which are known to contain very high levels of alkaline earth metal impurities). By contrast, aminopolycarboxylic acids are more easily precipitated; and have higher limits of effectiveness over a narrower pH range.

Improve dyestuff solubility, by deflocculating and disaggregating effects.Avoid dye spotting problem.

Polyphosphonic acids (rather like aminopolycarboxylic acid) do not readily biodegrade in a laboratory activated sludge test. However, in more realistic die – away river tests, these substances are rapidly degraded in the presence of sunlight and ferric ions. These are also degraded in the soil. They do not bio-accumulate on aquatic species and are readily eliminated by fish.

Polyphosphonates can be eliminated from water by classical treatment with aluminum sulphate or lye treatment. Due to their low concentration and strong adsorption on sewage sludge and on sediments, mobilization of heavy metals into the aquatic environment is low. [19].

However, they are not always resistant to precipitating condition and also often easily stripped of the metal ion by a dyestuff molecule, obviously, this is the opposite of the effect required [22]. One of the main class of sequestrant is polyphosphate. Another most commonly used sequestrant of textile industry is EDTA, which is considered as most stable complex, because the metal atom is enclosed in a 5 or 6 member ring. These sequestering agents are divided in two broad classes:

- Inorganic polyphosphates such as sodium hexa meta phosphate (SHMP), sodium polyphosphate, sodium tri polyphosphate, sodium tri meta phosphate, sodium pyrophosphates
- Phosphonated amino polycarboxylates such as EDTMP, DETMP, ATMP, HEDP, DTPMP

Compared to popular amino polycarhoxylic acid based sequestering agents, these phosphonates based sequestering agents have a high chelation ratio. Apart from better chelation value or better chelation ratio, these phosphonates also have better iron chelation than EDTA and NT

Phosphates of aminopolycarboxylic acids or phosphonates are derivatives of phosphorous acid and are characterised by a C-P bond, which has stronger hydrolytic stability than the P-O-P bond of polyphosphates. This type of sequestering agent has emerged as a major class of sequestering agent, since these possess more features than mere chelation.

3.4.3 Hydroxy carboxylates sequestering agent

Organic compounds that have several hydroxylic groups often have the property of preventing precipitation of bi and trivalent metal cationis in an alkaline medium. Some of the well known products in this category are: Citric acid, Tartaric acid, Gluconic acid and Oxalic acid.These are less important sequestering agents, compared to aminocarboxylic acid or phosphonates. Gluconic acid/sodium gluconate has been found to be an effective chelating agent for iron under alkaline conditions.

3.4.4 Polyacrylates sequestering agent

Polyacrylates are effective dispersants, with mild chelation values and protective colloid properties. The chelation values of polyacrylates have no demetallising effect on metal containing dyestuffs. They are completely non foaming.

They are very suitable as dyebath conditioners, soaping agents and washing aids. Being non surface active agents they are easily rinsable and thus reduce the quantity of water required for removing their traces from the substrates, unlike all surfactants. The typical chelation values offered by polyacrylates do not come close to the chelation values offered by amino polycarboxylates or the phosphonates. This problem has been overcome by development of sugar acrylates.

3.4.5 Sugar acrylates sequestering agent

Sugar acrylates have sequestering values as high as amino polycarboxylates or the phosphonates. They are biodegradable, effective components in cellulosic fabric pretreatment during desizing, scouring, bleaching and mercerising. These products are characterised by good chelation values from the acidic to the alkaline range and from temperatures of 45 to 115°C. They also exhibit no demetalising effect on metal-containing dyestuffs and are non-foaming. They are ideally recommended in pretreatment for desizing, scouring and bleaching and as dyebath conditioners during the cellulosic dyeing.

3.5 Chemistry of sequestering agent

In dyeing with metallised reactive or direct dyes containing metal ions, the sequestering agent should not demetallise the dyestuff, i e. remove metal ions from dye molecules, which will lead to shade change. Let us review the chemistry of various types of sequestering agents and the conditions under which these are most effective. Sequestering agents work by a mechanism of complex formation, also termed chelation. The sequestering/chelating agent has groups at appropriate locations in the molecule to form one or more chelate rings with the metal ion. The complex thus formed remains soluble as well as stable under given conditions. These chemicals usually contain nitrogen, such as amines and substituted amines, and oxygen in the form of carboxyl, phosphate or hydroxy groups.

3.6 The factors should be consider before selecting a sequestrant

- Different sequestering power. (i.e, the strength of the sequester - metal complex)
- Different specific sequestering power for individual metal.
- Sequestering power not only depends on the specific sequestrant / metal pairing, but also on pH and temperature.
- Different sequestering capacities.
- Sequestering capacities which are metal ion specific.
- Difference in the spread of pH over which a particular sequestrant will combine with a particular metal ion.
- That not all sequestrants are stable to high temperatures.
- That not all sequestrants are stable to oxidation or hydrolysis.
- That some sequestrants will de-metallise/pre-metallise dyes.
- That some sequestrants can affect the shade reproducibility of some dyestuffs (the effects can be very dye-sequestrant specific).

That some sequestrant does not satisfy the environmental and toxicological requirements of every market. [19].

4. Textile raw materials testing procedure

To achieve a RFT shade we should consider the quality of all raw materials, right from the processing of fabric or yarn to all the dyes and chemicals. Because if there are changes in quality of raw materials (Dyes, chemicals and auxiliaries) it will cause for a unmatched shade. The basic parameters (pH, hardness, specific gravity, viscosity, purity, strength, solubility etc.) should be checked and compared with TDS for new arrival raw materials and compare with previous standard quality for old raw materials. Some of the raw materials testing procedures are given below:

4.1 Basic chemicals testing procedure

Industrially the following chemicals are known as basic chemicals. These should test randomly.

- Caustic Soda
- Soda ash
- Acetic acid
- H_2O_2
- Glauber's salt

4.1.1 Purity testing procedure of Sodium Hydroxide (NaOH)

Preparation of indicators

Pheophthalein indicator : Dissolve 1 gm of indicator in L of alcohol
Methyl Orange indicator: dissolve 1 gm of indicator in 100 ml distilled water.

Procedure

- Weigh 1 gm sample of NaOH flakes
- Dissolve in 50 ml distilled water and cool
- Transfer 25 ml of the solution into a 250 ml conical flax
- Warm at 80'c for 2 minutes before titration
- Add 1 to 2 drops phenolphthalein indicator
- Titrate with 1N HCl from pink to colorless end point and record volume of titer as B
- Transfer another 25 ml of the solution into a 250 ml conical flax.
- Add 1 to 2 drops Methyl Orange indicator and titrate with 1NHCl from yellow to light salmon. Record volume of titer as A

$$\text{Now purity \% of } Na_2CO_3, \text{ in NaOH} = \frac{(A-B) \times \text{M.wt of NaOH} \times 100}{\text{Wt. of sample}}$$

Where,
B = volume of titer using Phenophthalein
A = volume of titer using Methyl Orange
N = Normality of HCl used in titration
M.wt of NaOH = 40amu/1000 = 0.04
Wt. of sample = 25 ml x 1 gm/50 ml = 0.5 gm

Again,

$$\text{Purity \% of NaOH (Alkalinity)} = \frac{B \times N \times \text{M.wt of NaOH} \times 100}{\text{Wt. of sample}}$$

So,

$$\text{Total Alkalinity} = \frac{(A + B) \times \text{M.wt of NaOH} \times 100}{\text{Wt. of sample}}$$

4.1.2 Purity test procedure of Sodium Carbonate (Na_2CO_3)

Preparation of 1N HCl

- Weigh 42 ml of HCl (36.46 gm/mol) or 83.3 ml of HCl (12N) and dissolve in litre distilled water.
- Allow the solutions to cool before using

Procedure

- Weigh 1 gm sample of Sodim carbonate (Na_2CO_3)/Soda Ash
- Dilute to 50 ml with distilled water
- Titrate with 1N HCl using Methyl Orange indicator
- Record the volume of HCl used until the solution changes from light yellow to salmon. Make two trials for accuracy.
- Calculate the purity (%) of Soda ash using the following formula:

$$\text{Purity (\%) of } Na_2CO_3 = \frac{(N \times V) \times \text{M.wt of } Na_2CO_3 \times 1oo}{\text{wt. of sample}}$$

where,
N = Normality of HCl used in Titration
V = Volume of HCl used in titration
M.wt of Na_2CO_3 = 106amu/2000 = 0.053
Wt. of sample = 50 ml x 1 gm/50 ml = 1 gm

4.1.3 Purity testing procedure of Acetic Acid (CH_3COOH)

Preparation 0.1N NaOH

- Weigh 4.17 gm NaOH flakes
- Dissolve in 1000 ml distilled water
- Allow the solution to cool before using

Procedure

- Weigh 5 gm sample of Acetic acid
- Dilute to 50 ml with distilled water
- Pipette 25 ml from the diluted solution
- Take 1ml from the solution for titration
- Add 2 drops of Phenophthalein indicator
- Titrate with 0.1 N NaOH until a pink end point. Make 2 trials for accuracy
- Find the purity of Acetic acid using the following formula:

$$\text{Purity (\%) of } CH_3COOH = \frac{(N \times V) \times \text{M.wt. of } CH_3COOH \times 100}{\text{Wt. of sample}}$$

Where,
N = Normality of NaOH used in titration
V = Volume of $KMnO_4$ used in titration
M.wt of CH_3COOH = 60amu/1000 = 0.06
Wt. of sample = 1 ml x 5 gm/1000 ml = 0.1 gm

4.1.4 Purity testing procedure of Sodium Sulphate/ Glauber's Salt ($Na_2SO_4.10H_2O$)

Procedure

- Weigh 5 gm sample of Na_2SO_4 into a beaker
- Dilute to 500 ml with distilled water
- Pipette 25 ml from the diluted solution in a 250 ml conical flask
- Add 10 ml of HCl (6N) and shake
- Add 50 ml distilled water and shake

- Add 10 ml $BaCl_2$ (10%) and sake
- Then boil the solution for 5 minutes
- Take a filter paper and record the wt. of empty filter paper
- Filter the solution and collect sediment ($BaSO_4$) on filter.
- Dry the filter paper, take weight at room temperature.
- Find the purity (%) of Na_2SO_4 using the following formula:

$$\text{Purity (\%) of } H_2O_2 = \frac{\text{(Wt. of } BaSO_4 \text{ (Sediment) x M.wt of } Na_2SO_4 \text{ / M.wt. of } BaSO_4 \text{ x 100}}{\text{Wt. of sample}}$$

Where,
M.wt of Na_2SO_4 = 142
M.wt of $BaSO_4$ = 133.4
Wt. of sample = 25 ml x 5 gm/500 ml = 0.25 gm

4.1.5 Purity testing procedure of Hydrogen peroxide (H_2O_2)

Preparation of 10% Sulfuric Acid

- Measure 90 ml distilled water in conical flask.
- Then slowly add 10 ml of 98% Sulfuric acid.
- Cool the solution before using.

Preparation of 0.1N $KMnO_4$

- Weigh 3.89 gm of $KMnO_4$ and dissolve in 1000 ml distilled water. Warm and stir until the crystals are dissolved.
- Heat to just below boiling point for 30 minutes.
- Cover the solution with a watch glass and allow standing overnight.
- Filter the permanganate solution and store in brown reagent bottle.

Procedure

- Weigh 5 gm sample of Hydrogen peroxide
- Dilute to 1000 ml with distilled water
- Pipette 25 ml from the diluted solution
- Add 25 ml 10% Sulfuric acid
- Titrate with 0.1 N Potassium permanganate up to pink end point. Record the result of two trials.
- Find the purity of Hydrogen peroxide using the following formula:

$$\text{Purity (\%) of } H_2O_2 = \frac{\text{(N x V) x M.wt. of } H_2O_2 \text{ x 100}}{\text{Wt. of sample}}$$

Where,
N = Normality of $KMnO_4$ used in titration
V = Volume of $KMnO_4$ used in titration
M.wt of H_2O_2 = 34amu/2000 = 0.017
Wt. of sample = 25 ml x 5 gm/1000 ml = 0.125 gm

4.2 Dyeing auxiliaries testing procedure

4.2.1 Quality of surfactants (like wetting, scouring agents) testing procedure

Solid Content

Weigh accurately 10 grams of the material to be tested in a pre-weighed porcelain crucible; let the weight be "A" grams. Dry the crucible in a high temperature electrical over at 95C for 2 hours. Take out the crucible and re-weigh it; let the weight after drying be "B" grams.

$$\text{Then the solid content of the material} = \frac{100 \times (\text{B-Empty Crucible wt})}{(\text{A-Empty Crucible weight}).}$$

Wetting Time

Various methods have been used for testing wetting agents. A simple test is to determine the number of seconds required for a 1-inch square piece of No. 6 canvas to sink in a 1 per cent solution of the wetting agent at 22 to 23 C.

Ionic Nature

Ionic nature of a wetting agent may be decided by a very simple test. Dissolve 2 grams of the wetting agent in 100 ml of distilled water. Call this as Solution 'A'.

Anionic

Take about 10 ml of this solution (A) in a 20 ml test tube. Add 10 drops of 2N Hydrochloric acid in to this and shake well. If a white cloud or precipitate is formed, then the surfactant tested is Anionic in nature.

Cationic

Take about 10 ml of the solution (A) in a 20 ml test tube. Add 10 drops of 2N sodium hydroxide solution and shake well. If a White cloud or precipitate is formed, then the tested product is Cationic in nature.

Non-ionic

If no precipitate or cloud is formed either with acid or alkali, then the material tested is Non-ionic in nature.

Amphoteric

Amphoteric wettings will make a very slight white precipitate with acids and the precipitate will not settle down to the bottom or the test tube even after few hours. It will remain in suspension.

Cloud Point

The non-ionic surfactants exhibit a property called cloud point. Upon slowly raising the temperature of 2 grams per liter of solution (prepared using distilled water), at a particular temperature the clear solution becomes cloudy. That temperature is called the cloud point of that non-ionic wetting agent. After the cloud point temperature it is said that the nonionic products do not exhibit its intrinsic properties, such wetting, scouring, rewetting, emulsifying etc. So if a wetting agent's cloud point is 70C, then it should be understood that above 70C, it should not used as wetting agent. For example if you are doing scouring and bleaching at 90C, then a 70C cloud point wetting agent is not suitable for this purpose. Most of the non-ionic wetting agents have the cloud of more of less 70°C.

Foaming Test

Formation of foam during processing especially in jet and soft-flow type of machineries is a big headache for the dyer. So in these machines people prefer only no-foaming or very low foaming wetting agents only. Compare two wetting agents by making .01% solution, in two 500 ml measuring jars. Shake the jars for about 3 minutes and keep them intact for some time. Compare the height of the foam. Lower the height better the wetting agent.

4.2.2 Testing procedure of residual peroxide on the fabric

Preparation of Titanyl Chloride solution:

- 100 ml titanium (IV) chloride (50%w/v) are added drop wise, with stirring to 200 ml of conc hydrochloric acid (SG 1.18). The reaction should be carried out in a fume cupboard as the reaction is exothermic and hydrogen chloride gas is given off. It is essential that each drop is added slowly and the reaction mixture is constantly stirred with a magnetic stirrer.

- When all the titanyl chloride has been added, the solution is heated to boil and, after boiling for approximately one minute, 800 ml of dilute hydrochloric acid (2 parts conc hydrochloric acid 10 1 part water) is added. On cooling the reagent is ready to use.

- Procedure for textiles: Spot 2 – 3 drips of the titanyl chloride solution onto the fabric, and wait for 15-20 seconds for reaction, if any to occur. If no colour develops, there is no peroxide. If yellow – orange colour develops then you may compare the colour with the stripes on the scale L and determine the intensity of peroxide present.

4.2.3 Quality testing procedure of cationic dye fixing agents

Solid Content: Take approximately 3 gram of the sample and weigh it accurately in a glass dish. Place it in the oven for 4 hours at 110C. After cooling in the decicator, weigh the dish accurately.

$$\text{Solid content \%} = \frac{\text{Dry weight x100.}}{\text{Actual weight}}$$

Free Formaldehyde content

Take about 2.0 grams of the sample in a glass dish and weigh it accurately. Then dissolve it in 25 ml of distilled water in a 250 ml beaker. Pour 25 ml of neutralized sodium Sulphite solution and 10ml of 1.0N HCl. Immediately titrate with 0.5N NaOH using Thymothaline as the indicator. End point will be indicated by the appearance of light blue color. Also take the blank reading. Free formaldehyde % = Difference x 0.5 x 3/ weight.

Actual fixing test

Do fixing test of dyed fabric using the recommended concentration. Test the treated fabric for a) tone change, b) wash fastness and c) crocking.

4.3 Quality testing procedure of dye stuffs

Dyes are main important materials to dye a fabric. In general we face a problem of shade variation in batch to batch dyeing. There may be lots of reasons to responsible for this. But dyes lot to lot quality plays a vital rule in this shade variation. Especially this happens due to the differences between the previous and new lots of dyes. Practically we observed by testing there are 10-15% strength differences with previous one. This difference may be more/less than the standard. So this should be tested randomly from every new lot and form several drums also. Generally the following parameters should check of dyes:

- Strength difference
- Dye solubility
- Fixation%
- Impurities in dyes

4.3.1 Strength difference testing procedure of dyes

It is nothing but to dye a specific shade% of any dye following the available lab dyeing procedure. Generally 2% shade is preferred to dye for easy evaluation. For this it should keep record of standard shade% dyed sample of every dyes of each company used in dyeing. This record also should store in the spectrophotometer. When any new lot of dye comes it can dye in 2% shade and compare with the recorded standards. The best evaluation can get from the spectrophotometer CMC report. The difference can also evaluate on visually.

4.3.2 The solubility testing procedure of a dyestuff

Requirements for this solubility test:

1) Whatman filter paper,
2) a good digital micro-balance,
3) an electric oven,
4) distilled water,
5) measuring flaks 500 ml capacity.
6) 250 ml drying crucible

Procedure:

1. Weigh accurately 100 grams of the dyestuff and note the exact balance reading as A grams.
2. transfer this dyestuff in to a 500 ml clean beaker
3. Slowly add hot distilled water (60°C) and make it in to a paste and dilute it further with cold distilled water.
4. Transfer the dissolved portion of the dyestuff liquor in to the 500 ml standard measuring flask (SMF).
5. To the un-dissolved semi-solid mass of dyestuff remaining in the beaker add further quantity of distilled water and dissolve it. Again transfer the dissolved dye in to the standard measuring flask. Repeat the process until about 400ml of water is added into the SMF. Now make the remaining quantity of dyestuff in the beaker in to a slurry by adding further water and transfer the whole slurry in to the SMF flask
6. Make up the volume of water to 500ml in the SMF.
7. Shake well for about 10 minutes.
8. Weigh a whatman filter paper blank - let the weight be B grams. Filter the dissolved dye-liquor through a pre-weighed whatman filter paper-1 - do not add any water during filtration. make use of the solute only for all transfers.
9. After filtering dry the filter paper at 110C for 3 hours. cool it in a decicator and weigh the paper along with the content. Let the Weight be C grams.
10. Then the un-dissolved dyestuff in the filter paper (D) = C - B grams
11. The the solubility of the dyestuff (S1) = (A -D)/500 x 1000 grams per liter.
12. To counter check this value, measure 100 ml of the clear dissolved dyestuff solution and transfer in to a 250 ml pre-weighed drying crucible. Evaporate and dry it at constant temperature of 95°C for 3 hours.
13. Check for drying in to powder mass and cool the crucible, weigh it. Find the weight of dissolved dyestuff - x grams.

14. So 100 grams of the solution contain x grams of dyestuff - calculate for 1000 ml. let it S2.

Evaluation:
Compare S1 and S2 - if the difference is very small then average out the two readings or repeat until you get both readings are very close.

4.3.3 Fixation% measurement procedure of dyes

It is described at 13.5.9 in this paper.

5. Light

Visible light (commonly referred to simply as light) is electromagnetic radiation that is visible to the human eye, and is responsible for the sense of sight[23]. Visible light is usually defined as having a wavelength in the range of 400 nanometers (nm), or 400×10^{-9} m, to 700 nanometres – between the infrared, with longer wavelengths and the ultraviolet, with shorter wavelengths [24-25]. These numbers do not represent the absolute limits of human vision, but the approximate range within which most people can see reasonably well under most circumstances. Various sources define visible light as narrowly as 420 to 680 [26-27] as broadly as 380 to 800 nm.[28-29]. Under ideal laboratory conditions, people can see infrared up to at least 1050 nm [30] for children and young adults ultraviolet down to about 310 to 313 nm [31- 32].

5.1 Mechanism of light's production

All light comes from atoms. It is produced by atoms that have gained energy either by absorbing light from another source or by being struck by other particles. An atom with such extra energy is said to be excites by giving up its extra energy. It can emit (Give off) Light. But light can also be described as a small particle called a photon. Each photon moves on straight line much as a pool ball does [33].

5.2 Properties of visible light

Primary properties of visible light are:

- intensity,
- propagation direction,
- frequency or wavelength spectrum and
- polarization,

While its speed in a vacuum, 299,792,458 meters per second, is one of the fundamental constants of nature. Visible light, as with all types of electromagnetic radiation (EMR), is experimentally found to always move at this speed in vacuum. In common with all types of EMR, visible light is emitted and absorbed in tiny "packets" called photons, and exhibits properties of both waves and particles. This property is referred to as the wave–particle duality. The study of light, known as optics, is an important research area in modern physics. In physics, the term light sometimes refers to electromagnetic radiation of any wavelength, whether visible or not [34-35].

5.3 Electromagnetic spectrum and visible light

Electromagnetic spectrum

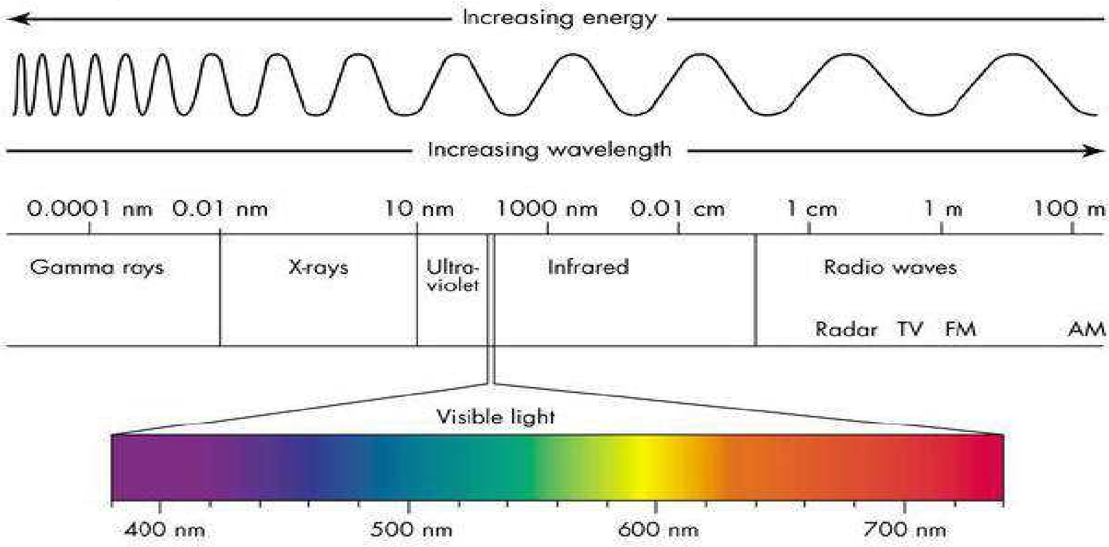


Fig 9: Electromagnetic spectrum with light highlighted

In the above picture, we can see that visible light is very small fragment of Electromagnetic spectrum (a form on energy described in terms of wavelength and amount of energy).

- Wave lengths of light between 400nm and 700nm are the range of light energy where 99% of human color response occurs; it is called as the visual range and is commonly referred to as the visual spectrum.

- If there is no light there is no Color for example if you close your eyes your eyes sensors do not detect visible wave- Length thus your brain perceives the black color.
- The white light is composed of seven colors (The colors of Rainbow)
- In the below, the RED shirt has absorbed all other lights (Wavelength) except the red light which is reflected all by the shirt. Thus we see the red shade this function is done by the red dyes and pigments in the fabric. That is why when we have different dyes, we have different tones of colors.
- The wavelength of color light is measured in nanometers.
- The numbers shown below here are the number of nanometers between each wave of light [33].

Table 3: The range of visible light

SL No.	Light	Wavelength (nm)
1	Ultra – Violet	Below 380
2	Violet	380-450 nm
3	Blue	450-490 nm
4	Green	490-560 nm
5	Yellow	560-590 nm
6	Orange	590-630 nm
7	Red	630-780 nm
8	Infra-red	Above 780 nm

Above the range of visible light, ultraviolet light becomes invisible to humans, mostly because it is absorbed by the cornea below 360 nanometers and the internal lens below 400. Furthermore, the rods and cones located in the retina of the human eye cannot detect the very short (below 360 nm.) ultraviolet wavelengths, and are in fact damaged by ultraviolet. Many animals with eyes that do not require lenses (such as insects and shrimp) are able to detect ultraviolet, by quantum photon-absorption mechanisms, in much the same chemical way that humans detect visible light.

The distance between each wave of light is very small; there are one billion nanometers in one meter. So the waves of light are extremely small but they make all the colors difference. It is that different in wavelengths of light that the human eye detects as different color **[**33].

6. Color

6.1 Definition of color

There is a famous saying that color does not exist, Color is in our mind.

Figure 10: Color is in human mind

There are many ideas of what color is. Artists believe color is an expression, Scientists believe color is a substance of some kind and philosophers believe that color is a creation of the mind and /or to a certain extent a sensation.
Thus the topic of color is very complex because it includes many factors::

- Color is physics of light

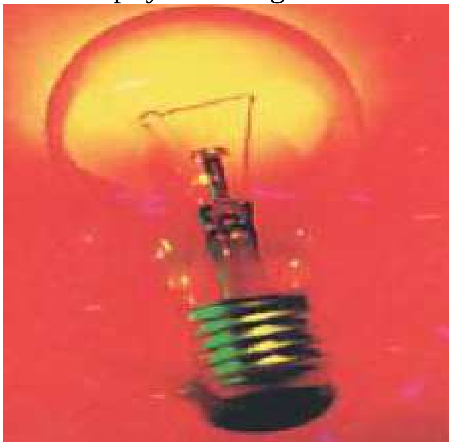


Figure 11: Color is physics of light

- Color is the chemistry and physics of the materials

Figure 12: Color is the chemistry and physics of the materials

- Color is the human response to light.

Figure 13: Color is the human response to light

- Color is the human judgment of the color response

Figure 14: Color is the human judgment of the color response

- All above together create the human sensation we call Color.

Figure 15: human sensation for color

Thus, the color can be defined as follows:

- Color is actually the light which comes through light source (Sun Bulb Tub light etc.) is reflected by the object (Shirt Fabric Yarn, Any material) and which is sensed by our eye. Therefore color is not a physical thing. It is just a light. Coming from the object.
- My Favorite definition of color is: the color of an object is not contained within the object. The color is the result of the light which strikes the object and is reflected by it.
- Color is formed from an interaction between light, object, and the viewer (Eye). It is light that has been modified by an object in such a manner that the view or such as the human perceives the modified light as a distinct color. All three elements must be present for color to exit [33].

6.2 Three elementary things of color

In order to see Color, we need three things:

1. An object
2. Light
3. Eye

This is also called Triplet of color. It is the biology (eye) the reflected light enters your eye and stimulates vision cells. These cells are composed of rods and cones. The rods are only active in the dark and in dim light. In normal Daylight you see exclusively with the cones and they distinguish color. Three types of cones differentiate the various colors. These are RED, GREEN, And BLUE cones. There are about 120 million rods and about 6 to 7 million cones in the human eye.

6.3 Causes for materials to appear colored

When light hits the object some of it will reflect off the surface. The rest enters the material normally do three things:

- Light can scatter by the material and thus you do not see the tight color. This property is applied on carpet fiber whose cross section is designed such a way that most light is scattered and you do not see the dirt & soil on carpets. This gives soil hiding properties carpet fiber.
- Light is perfectly reflected by the dyes and colorants on the surface and you see the right color appearance.
- Light is scattered, reflected and also pass through (refracted) the material and come out the other side we call these materials transparent materials such as a grass of

water. This is important when a shade assessment is performed by eye of by spectrophotometer. Otherwise the background color will affect the color of fabric [33].

6.4 Causes of a color seems specific

Colored light travels in the form of electromagnetic waves. Different colors have different wavelengths, and different cones response to the different wavelengths. So when a particular wavelength is sensed by cones, they give a message to brain which recognize that color. There are some other wave lengths which we cannot see for example ultraviolet and infra red rays.
First, it is the physics. Light strikes the object and is reflected.

- Reflection Diffusion , And scattering of light
- The nature /Type of light and its properties
- The object ‘s physical properties

Second, it is the biology (eye), the reflected light enters our eye and stimulates vision cells. These cells are composed of rods and cones. The rods are only active in the dark and in dim light. In normal Daylight you see exclusively with the cones and they distinguish color. Three types of cones differentiate the various colors. These are red, green, and blue cones. There are about 120 million rods and about 6 to 7 million cones in the human eye [33].

Short- Cones:	Blue light	400nm
Medium –Cones	Green Light	500nm
Long –Cones	Red light	700nm

6.5 Color chemistry

The dyes or pigments in the colored material are responsible for absorption / reflection of light thus giving the final color. There is a very important chemical part of the dye called chromophore, who is the real responsible part for providing a particular color. There is another part of the dye called auxochrome which increase ht intensity of a color [33].

6.5.1 Chromophore

A chromophore is the part of a molecule responsible for its colour. The colour arises when a molecule absorbs certain wavelengths of visible light and transmits or reflects others. The chromophore is a region in the molecule where the energy difference between two different molecular orbitals falls within the range of the visible spectrum. Visible light that hits the chromophore can thus be absorbed by exciting an electron from its ground state into an excited state.
In biological molecules that serve to capture or detect light energy, the chromophore is the moiety that causes a conformational change of the molecule when hit by light.

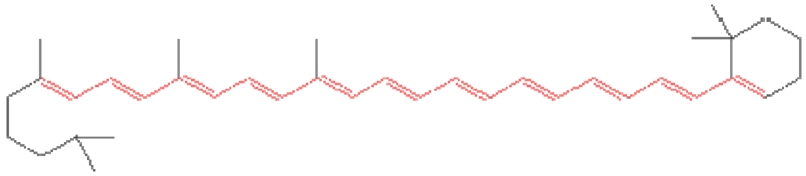


Figure 16: Chemical structure of beta-carotene.

The eleven conjugated double bonds that form the chromophore of the molecule are highlighted in red.

Some of these are metal complex chromophores, which contain a metal in a coordination complex with ligands. Examples are chlorophyll, which is used by plants for photosynthesis and hemoglobin, the oxygen transporter in the blood of vertebrate animals. In these two examples, a metal is complexed at the center of a tetrapyrrole macrocycle ring: the metal being iron in the heme group (iron in a porphyrin ring) of hemoglobin, or magnesium complexed in a chlorin-type ring in the case of chlorophyll. The highly conjugated pi-bonding system of the macrocycle ring absorbs visible light. The nature of the central metal can also influence the absorption spectrum of the metal-macrocycle complex or properties such as excited state lifetime [36] [37] The tetrapyrrole moiety in organic compounds which is not macrocyclic but still has a conjugated pi-bond system still acts as a chromophore. Examples of such compounds include bilirubin and urobilin, which exhibit a yellow color.

6.5.2 Auxochrome

An auxochrome is a functional group of atoms attached to the chromophore which modifies the ability of the chromophore to absorb light, altering the wavelength or intensity of the absorption.

Important chromophores are :

- Azo(-N=N-)
- Carbonyl (C=O)
- Methine (-CH=)
- And nitro (NO2)

Important auxochromes are :

- Hydroxyl(OH)
- Amino(NR2)

Dyes are aromatic compounds their structure includes aryl rings which have delocalized electron systems. These are responsible for the absorption of electromagnetic radiation of varying wavelengths depending on the energy of the electron clouds. Choromophres are atomic configuration which can alter the energy in delocalized system. They are composed of atoms joined in a sequence composed of alternating single and double bonds. If the atoms with double bonds are not adjacent, They are other termed isolated double bonds and exist independently of other bonds in the same molecule. If adjacent atoms have double bonds, they are termed conjugated double bonds and the bonds interact with each other.

Figure 17: Conjugated double bonds in a carbon series.

In summary, Chromospheres are atomic configuration that contains delocalized electrons. Usually they are represented as nitrogen carbon oxygen and sulphur that have alternate single and double bonds. If the energy incorporated in to the electron cloud is change then the wavelength of the radiation to absorb will also change. If this change in the wavelength to be absorbed is sufficient to cause any absorption at all within the visible range then the compound will be colored [33].

In addition, given that humans can perceive over 2.8 million different hues [38]. It has been suggested that the number of possible color combinations is virtually infinite thereby implying that predictive color harmony formulae are fundamentally unsound [39].

A triadic color scheme adopts any three colors approximately equidistant around a color wheel model. Feisner and Mahnke are among a number of authors who provide color combination guidelines in greater detail [40]. It is important to note that while color symbolism and color associations exist, their existence does not provide evidential support for color psychology or claims that color has therapeutic properties [41].

6.6 Color theory

In the visual arts, color theory is a body of practical guidance to color mixing and the visual effects of a specific color combination. There are also definitions (or categories) of colors based on the color wheel:

- primary color,
- secondary color and
- tertiary color.

Although color theory principles first appeared in the writings of Leone Battista Alberti (c.1435) and the notebooks of Leonardo da Vinci (c.1490), a tradition of "colory theory" began in the 18th century, initially within a partisan controversy around Isaac Newton's theory of color (Opticks, 1704) and the nature of so-called primary colors. From there it developed as an independent artistic tradition with only superficial reference to colorimetry and vision science [33].

6.7 Types of color mixing

It is important to remember that there are two types of color mixing:

- Additive color mixing
- Subtractive color mixing

6.7.1 Additive color mixing

This is applied to mixing of lights only, like color television, computer monitor, film projectors, etc. this is not applied in textile dyeing, printing or other coloration process. The additive color system is what computer monitors and TV screens user any color source that emits the light itself. If we look very closely at our screen we will see that it is built up of tine red green and blue dots. Take same drop of water and place it on your screen and see the red green blue dots, experience this. In the additive system we get white when the three primary colors are present 100% **.** As the name suggests the lights are added to get new colors. When you project light you are sending out frequencies of light that add together to form a certain color beam [33].

In additive color mixing the primary color are:

- Red
- Green
- Yellow

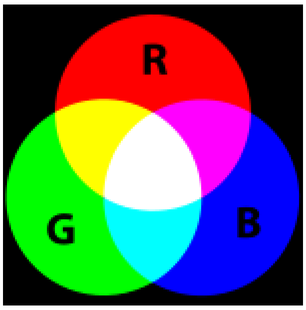


Figure 18: Additive color mixing

And the secondary color are:

- Cyan

- Magenta
- Yellow

If we mix all three colors we get, White color

6.7.2 Subtractive color mixing

This color mixing is briefly applied to industries, dyes, pigments, dyeing, printing, painting, etc. The color we see on fabric, yarn, garment etc is created using a subtractive color mixing model, where the light frequencies that are not absorbs or by the object is seen as color. In other words the objects absorb or subtract all lights and send us the only light which we see as a color.

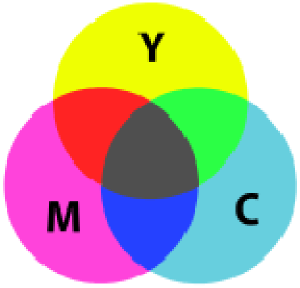


Figure 19: Subtractive color mixing

However in textile dyeing and printing industries the normal practices is to use Red, Yellow and Blue as primary colors, they are also called Trichromats. If we mix all three color we get, Black [33].

7. Human eye

The human eye is an organ that reacts to light and has several purposes. As a conscious sense organ, the mammalian eye allows vision. Rod and cone cells in the retina allow conscious light perception and vision including color differentiation and the perception of depth. The human eye can distinguish about 10 million colors [42].

Similar to the eyes of other mammals, the human eye's non-image-forming photosensitive ganglion cells in the retina receive light signals which affect adjustment of the size of the pupil, regulation and suppression of the hormone melatonin and entrainment of the body clock [43].

The eye acts much like a camera, with the lens forming the image of the scene on the light-sensitive retina. There are several kinds of light detectors, called rods and cones. The cones are grouped into three types, each responds to a portion of the spectrum, with peak responses corresponding to blue, green, and red light. The interaction of these groups is then responsible for the stimulus which is interpreted by the brain as color. This widely accepted theory on color vision is known as Trichromatic Theory.

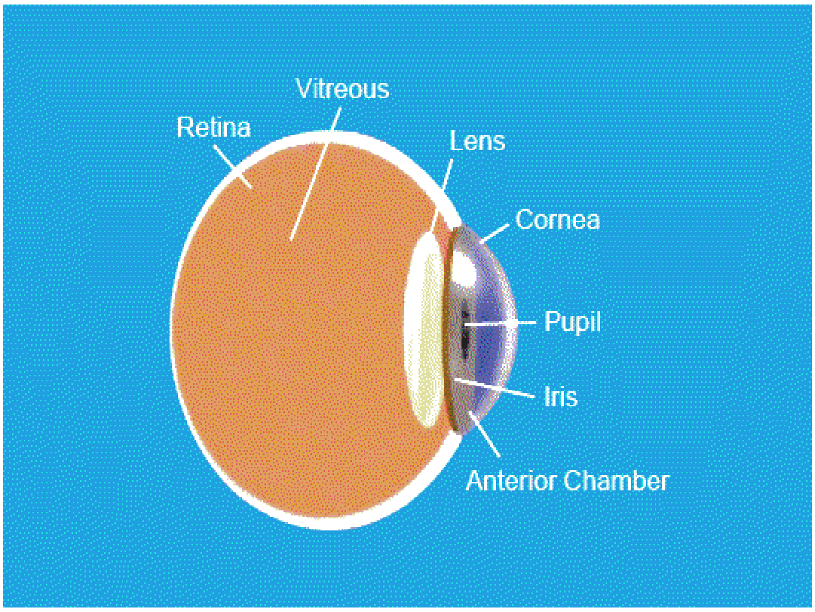


Figure 20: Human eye

7.1 General properties of human eye

The eye is not shaped like a perfect sphere, it is a fused two-piece unit. The smaller frontal unit, more curved, called the cornea is linked to the larger unit called the sclera. The corneal segment is typically about 8 mm (0.3 in) in radius. The sclerotic chamber constitutes the remaining five-sixths; its radius is typically about 12 mm. The cornea and sclera are connected by a ring called the limbus. The iris – the color of the eye – and its black center, the pupil, are seen instead of the cornea due to the cornea's transparency.

7.2 Components of human eye

The eye is made up of three coats, enclosing three transparent structures. The outermost layer, known as the fibrous tunic, is composed of the cornea and sclera. The middle layer, known as the vascular tunic or uvea, consists of the choroid, ciliary body, and iris. The innermost is the retina, which gets its circulation from the vessels of the choroid as well as the retinal vessels, which can be seen in an ophthalmoscope. Within these coats are the aqueous humour, the vitreous body, and the flexible lens. The aqueous humour is a clear fluid that is contained in two areas: the anterior chamber between the cornea and the iris, and the posterior chamber between the iris and the lens. The lens is suspended to the ciliary body by the suspensory ligament (Zonule of Zinn), made up of fine transparent fibers. The vitreous body is a clear jelly that is much larger than the aqueous humour present behind the lens, and the rest is bordered by the sclera, zonule, and lens. They are connected via the pupil.

7.3 Color blindness

Color blindness, or color vision deficiency, is the inability or decreased ability to see color, or perceive color differences, under normal lighting conditions. Color blindness affects a significant percentage of the population [44]. There is no actual blindness but there is a deficiency of color vision. The most usual cause is a fault in the development of one or more sets of retinal cones that perceive color in light and transmit that information to the optic nerve. This type of color blindness is usually a sex-linked condition. The genes that produce photopigments are carried on the X chromosome; if some of these genes are missing or damaged, color blindness will be expressed in males with a higher probability than in females because males only have one X chromosome (in females, a functional gene on only one of the two X chromosomes is sufficient to yield the needed photopigments [45].

7.3.1 Causes of color blindness

Some of the inherited diseases known to cause color blindness are:

- cone dystrophy
- cone-rod dystrophy
- achromatopsia (aka rod monochromatism, aka stationary cone dystrophy, aka cone dysfunction syndrome)
- blue cone monochromatism,
- Leber's congenital amaurosis.
- retinitis pigmentosa (initially affects rods but can later progress to cones and therefore color blindness).

About 8 percent of males, but only 0.5 percent of females, are color blind in some way or another, whether it is one color, a color combination, or another mutation [46].

7.3.2 Ishihara color test

The Ishihara color test, which consists of a series of pictures of colored spots, is the test most often used to diagnose red–green color deficiencies. A figure (usually one or more Arabic digits) is embedded in the picture as a number of spots in a slightly different color, and can be seen with normal color vision, but not with a particular color defect. The full set of tests has a variety of figure/background color combinations, and enable diagnosis of which particular visual defect is present. The anomaloscope, described above, is also used in diagnosing anomalous trichromacy.

7.3.2.1 Example of an Ishihara color test plate.

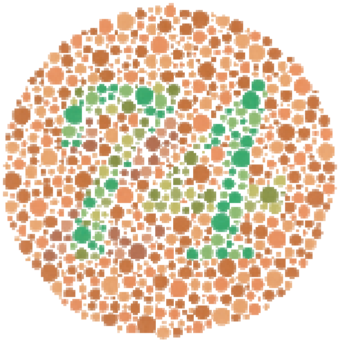


Figure 21: Example of Ishihara test (74).

Here the numeral "74" should be clearly visible to viewers with normal color vision. Viewers with dichromacy or anomalous trichromacy may read it as "21", and viewers with achromatopsia may not see numbers [33].

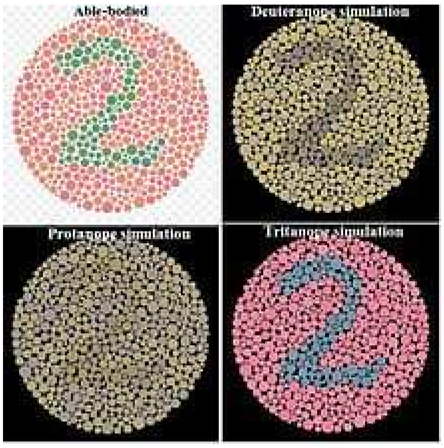


Figure 22: Example of Ishihara test (2).

An Ishihara test image as seen by subjects with normal color vision and by those with a variety of color deficiencies

8. Metamerism

When two objects have the exact color match in one light, But have different of color in second light. It is called metamerism and pair is called mesmeric match. This thing is very easy to see, but hard to understand.

8.1 Types of metamerism

There are four types of metamerism:

8.1.1 Illuminant metamerism

This is the most common type of metamerism which is experienced when different light s are used. Thus color pair matches in one light but do not match in 2nd light. This is a big issue in dyeing and printing when dyer changes the dyestuff.

8.1.2 Observer metamerism

Every individual perceives color slight differently. Thus a pair of shirt seem marched to one person but could be mismatched by the other.

8.1.3 Geometric metamerism

Identical color appear different when viewed at different angles, Distances, light positions etc . It can be argued that one reason men and women often perceive color differently is that the distance is on between woman ‘s eyes average slightly less than a man ‘s and that slight different angle of stereoscopic viewpoint also falls under the category of geometric metamerism.

8.1.4 Field size metamerism

A pair which is good match from a distance (Small field of view), Do not match when viewed neat the pair (Large field of view) [33].

8.2 Measuring of metamerism

The best-known measure of metamerism is the Color Rendering Index (CRI), which is a linear function of the mean Euclidean distance between the test and reference spectral reflectance vectors in the CIE 1964 color space. A newer measure, for daylight simulators, is the MI, CIE Metamerism Index [47].

which is derived by calculating the mean color difference of eight metamers (five in the visible spectrum and three in the ultraviolet range) in CIELAB or CIELUV. The salient difference between CRI and MI is the color space used to calculate the color difference, the one used in CRI being obsolete and not perceptually uniform.

MI can be decomposed into MI_{vis} and MI_{UV} if only part of the spectrum is being considered. The numerical result can be interpreted by rounding into one of five letter categories [48].

Table 4 : Category of metamerism index

Category	**MI (CIELAB)**	**MI (CIELUV)**
A	<0.25	<0.32
B	0.25–0.5	0.32–0.65
C	0.5–1.0	0.65–1.3
D	1.0–2.0	1.3–2.6
E	>2.0	>2.6

9. Spectrophotometer

In chemistry, spectrophotometry is the quantitative measurement of the reflection or transmission properties of a material as a function of wavelength [49].

It is more specific than the general term electromagnetic spectroscopy in that spectrophotometry deals with visible light, near-ultraviolet, and near-infrared, but does not cover time-resolved spectroscopic techniques. Spectrophotometry involves the use of a spectrophotometer. A spectrophotometer is a photometer that can measure intensity as a function of the light source wavelength. Important features of spectrophotometers are spectral bandwidth and linear range of absorption or reflectance measurement.

A spectrophotometer is commonly used for the measurement of transmittance or reflectance of solutions, transparent or opaque solids, such as polished glass, or gases. However they can also be designed to measure the diffusivity on any of the listed light ranges that usually cover around 200 nm - 2500 nm using different controls and calibrations.[1] Within these ranges of light, calibrations are needed on the machine using standards that vary in type depending on the wavelength of the photometric determination [50].

Spectrophotometer is just like an artificial Eye, this equipment can help you in several ways.

- Color pass/fall decision
- Color difference
- Color recipe formulation
- Whiteness
- Color sorting & Quality control
- Metamerism
- Reliable Spectrophotometer must do above tasks with great repeatability and with accuracy.

Source: datacolor

Figure 23: Spectrophotometer (Datacolor 600 ^{TM})

9.1 Key points about spectrophotometer

- Understand the dye/recipe formulation software
- Understand the Q.C software in your spectro.
- Do daily and periodical calibration
- Know instrument geometry (If using 2 different equipment)
- Do replace parts as per manufacturer’s recommendation
- Pay special attention on the temperature and humidity of the room where spectro is installed
- Color is often thermochromic and most colors will change with the temperature at which is made. Also color is often hydrochromic and most color s will change with the humidity at which measurement is made [33].

9.2 Design of a spectrophotometer

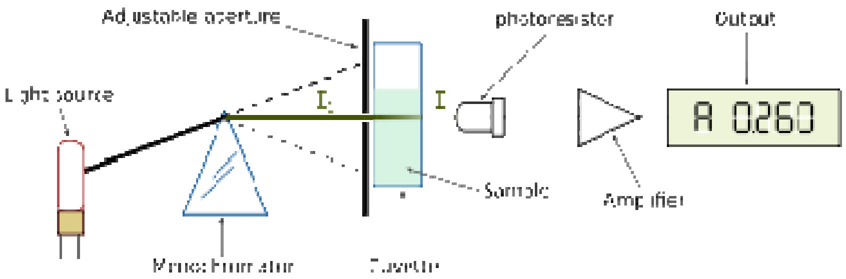


Figure 24: Single beam spectrophotometer

There are two major classes of devices: single beam and double beam. A double beam spectrophotometer compares the light intensity between two light paths, one path containing a reference sample and the other the test sample. A single-beam spectrophotometer measures the relative light intensity of the beam before and after a test sample is inserted. Although comparison measurements from double-beam instruments are easier and more stable, single-beam instruments can have a larger dynamic range and are optically simpler and more compact. Additionally, some specialized instruments, such as spectrophotometers built onto microscopes or telescopes, are single-beam instruments due to practicality.

In short, the sequence of events in a modern spectrophotometer is as follows:

1. The light source is imaged upon the sample.
2. A fraction of the light is transmitted or reflected from the sample.
3. The light from the sample is imaged upon the entrance slit of the monochromator.
4. The monochromator separates the wavelengths of light and focuses each of them onto the photodetector sequentially.

9.3 Mechanism of spectrophotometer's work

Lights fall on the object and the reflected light is measured by electronic sensors which converts their analysis in to color equation which tells us what is the color difference pass/fail results etc. Thus this instrument measures the amount of light that an object reflects (reflectance) in each spectrum and translate this to an easy language [33].

9.3.1 Measurement

Modern spectrophotometers contain monochromators and photodiodes that measure the reflectance curve of a product's color every 10 nm or less. The analysis gen rates typically 30 or more data points with which an exacting color composition can be calculated. These three element are:

1. Hue
2. Lightness
3. Chroma

9.3.1.1 Hue or shade

This refers to the color in its purest form Red , yellow, Blue , Green etc. In sample terms hue is how we see an object's color and the very first basic description of color . For example a red shirt NAVY yarn orange bed sheet etc.

9.3.1.2 Lightness or darkness

In simple terms lightness scale refers to how close the color is to black or white and how much light is reflected form the color. We know that black absorbs nearly 100% light. The scale between them is light nests & Darkness scale. The lightness scales is three dimensional and goes inside color diagram.

9.3.1.3 Chroma or saturation

Chroma is how bright a color appears or how close it is to being the pure color (Purity) . If a color has more chroma it can also be described as :

- More saturated/ Less saturated
- Stronger / Weaker
- Brighter / Duller
- More chroma /Less chroma
- More Gary / Less gray [33].

10. Dyes

Unlike most organic compounds, dyes possess colour because they 1) absorb light in the visible spectrum (400–700 nm), 2) have at least one chromophore (colour-bearing group), 3)have a conjugated system, i.e. a structure with alternating double and single bonds, and 4)exhibit resonance of electrons, which is a stabilizing force in organic compounds [51].

When any one of these features is lacking from the molecular structure the colour is lost. In addition to chromophores, most dyes also contain groups known as auxochromes (colour helpers), examples of which are carboxylic acid, sulfonic acid, amino, and hydroxyl groups. While these are not responsible for colour, their presence can shift the colour of a colourant and they are most often used to influence dye solubility. The relationships between wavelength of visible and colour absorbed [52]

10.1 Reactive Dyes

Reactive dyes cover the major part of the textile dyeing industry. They offer bright shades with a full range colour. Reactive dyes became very popular after the first Reactive dye was introduced by ICI in 1956, the first dye for cellulosic fibres which would actually react with the fibre molecules to form a covalent dye-fibre bond [53]. Because of their covalent fixation with the fibre, the dyes exhibited good wet-fastness properties [8]

The most important distinguishing characteristic of reactive dyes is that they form covalent bonds with the substrate that is to be colored during the application process. Thus, the dye molecule contains specific functional groups that can undergo addition or substitution reactions with the OH, SH, and NH2 groups present in textile fibers.

Cross and Bevan first succeeded in fixing dyes covalently onto cellulose fibers (in 1895) [54]. but their multistep process was too complicated for practical application. Early work by Schröter with sulfonyl chloride-based dyes was unsuccessful [55]. But Günther later did succeed in fixing derivatives of isatoic anhydride onto cellulose fibers [56].

Reactive dyes are so called because their molecules react chemically with the fiber polymers of some fiber to from a covalent bond between the dye molecules and fiber polymer. Reactive dye is a class of highly colored organic substances, primarily utilized for tinting Textiles that attach themselves to their substrates by a chemical reaction that forms a covalent bond between the molecule of dye and that of the fiber. The dyestuff thus becomes a part of the fiber and is much less likely to be removed by washing them are dyestuffs that adhere by adsorption. The very first fiber-reactive dyes were designed for cellulose fibers, and are still used mostly in this way.

10.1.1 General properties of reactive dyes

- Reactive dyes are anionic dyes.
- Reactive dyes are found in powder, liquid and print form.
- During dyeing the reactive group of this dye forms covalent bond with fibre polymer and becomes an integral part of fibre.
- Reactive dyes are soluble in water.
- They have very good light fastness with rating about 6.
- The dyes have very stable electron arrangement and can protect the degrading effect of ultra-violet ray.
- Textile materials dyed with reactive dyes have very good wash fastness with rating about 4-5 due to strong covalent bonds formed between fibre polymer and reactive group of dye.

- Reactive dyes give brighter shades and have moderate rubbing fastness.
- Dyeing method of reactive dye is easy. It requires less time and low temperature for dyeing.
- Reactive dyes are comparatively cheap.
- Fixation occurs in alkaline condition.
- Reactive dyes have good perspiration

10.1.2 The main advantages o f reactive dyes

- Good light-fastness dyeings
- Give full range of colours on cotton and polyamide fibres
- Good fastness properties when dyed on cotton and polyamide fibres [8].

10.1.3 Reactive dyes have some big drawbacks

- Hydrolysis of the dye giving coloured effluents
- Addition of electrolytes to increase their substantivity for cellulose
- Lengthy washing-off processes when applied to cellulosic fibres [8].

10.1.4 General structural requirements of reactive dyes

Fibre reactive dyes contain one or more reactive groups, capable of reacting with the nucleophilic groups in a fibre to produce a covalent dye-fibre linkage. Reactive dyes have the general structural requirements of a reactive group (R), a chromophore (C), a bridging group (B) and one or more solubilising group (S), as shown in Figure 25 [8].

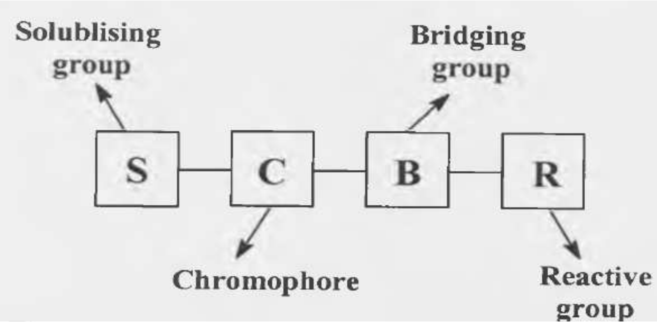


Figure 25: General structural requirements of reactive dye.

where the four different components of the reactive dyes are:

- The chromogen is as mentioned before (azo, carbonyl, anthraquinons, triphenon-dioxazine or copper phthalocyanine group). The chromophoric group is liable for color yielding

- The water solubilising group (ionic groups, often sulphonate salts), which has the expected effect of improving the solubility, since reactive dyes must be in solution for application to fibres. This means that reactive dyes are not unlike acid dyes in nature.

- The bridging group that attach the reactive group either directly to the chromophores or to some other part of the dye molecule. Frequently the bridging group is an amino, -NH-, group. This is usually for convenience rather than for any specific purpose.

- The fibre-reactive group (-Cl, -Br, -SH, -OCH, etc.) is the only part of the molecule able to react with the fibre [57]. Reactive group is the reasons of active covalent bond between fibre & dye molecule.

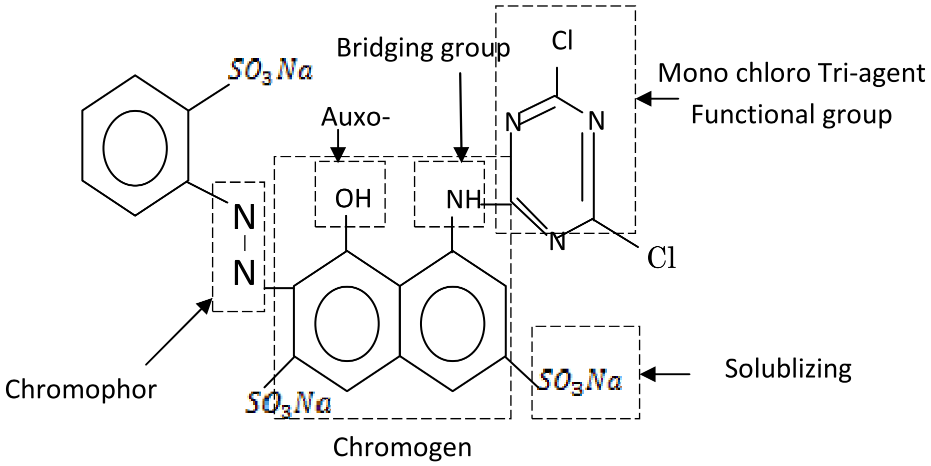


Figure 26: CI Reactive Red 1

Reactive dyes are generally divided into two basic classes according to differences in the manner in which they bind to the cellulosic fibre.

- Nucleophilic substitution reaction
- Nucleophilic addition reaction

10.1.5 Nucleophilic substitution reaction

The first class (Figure 1.16) contains dyes that react by a nucleophilic substitution mechanism (Figure 27).

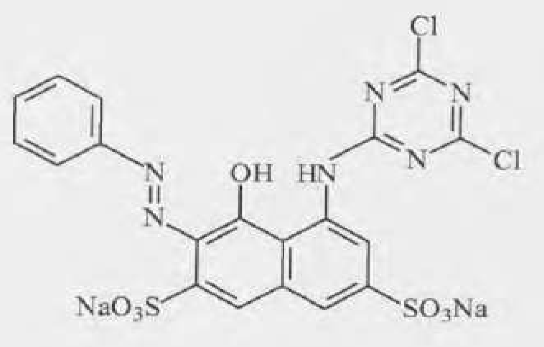


Figure 27: Chemical structure of CI Reactive Red 2 [8].

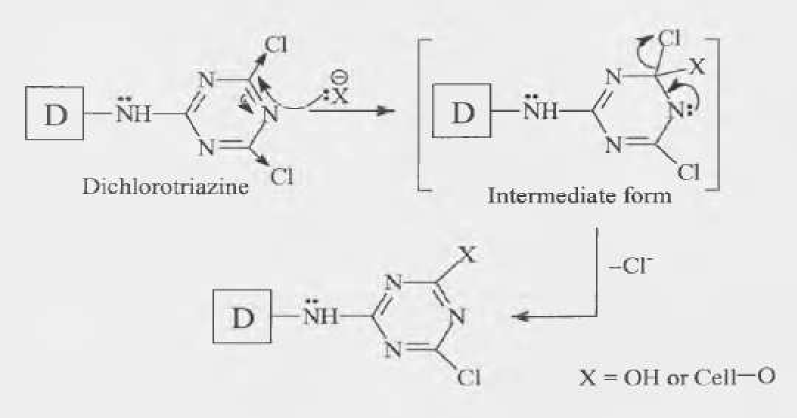


Figure 28: Nucleophilic substitution reaction occuring with cotton cellulose and hydroxyl anions

10.1.6 Nucleophilic addition reaction

The second class (Figure 1.18) involves dyes that react with a cellulosic fibre by a nucleophilic addition reaction (Figure 1.19) via an activated carbon-carbon double bond in the dye. In the case of vinylsulphone dyes the unsaturated carbon-carbon double bond is only formed from an ester of hydroxyethylsulphone during the application; the most common precursor system used in dyes of this type is the sulphonic acid ester of phydroxyethylsulphone which eliminates to produce vinylsulphone residues during the dyeing process [8].

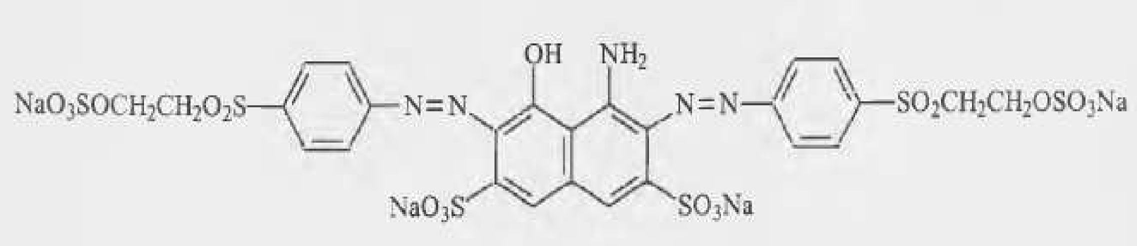


Figure 29: Chemical structure of Cl Reactive Black 5

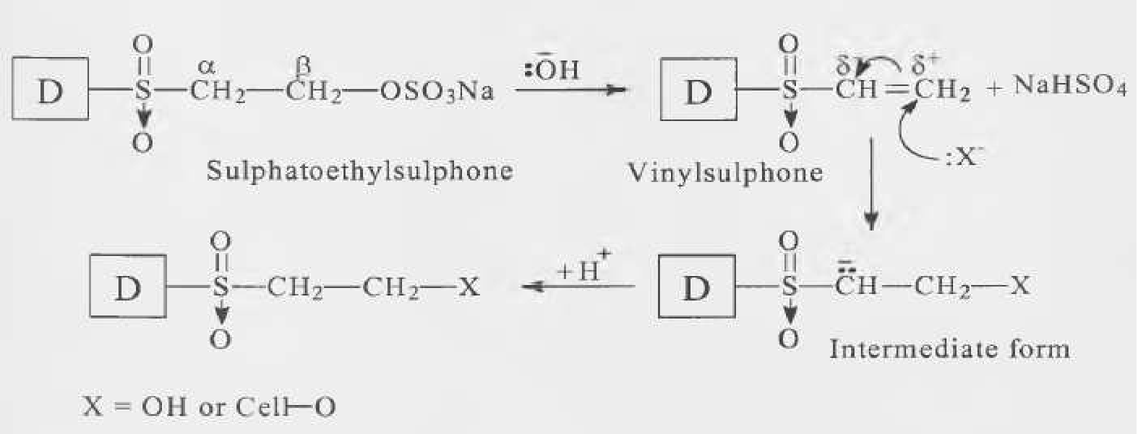


Figure 30: Nucleophilic addition reaction occurring with cotton cellulose and hydroxyl anions

10.1.7 Factors influencing the performance of reactive dyes

10.1.7.1 Molecular structure of dye

- Number of reactive groups
- Chemical nature of reactive groups
- Molecular mass (size)
- Number of sulphonic acid groups
- Ratio of sulphonic acid groups to aromatic carbons hydrophobic – hydrophilic balance
- Linear / planar structure (shape)
- Other functional groups present
- Realtive positions of functional groups (incl. reactive groups)

10.1.8 Classification of reactive dye

10.1.8.1 Classification of reactive dye on the basis of reactive groups

i. Mono-Functional Reactive dyes
ii. Bi-Functional Reactive Dyes
iii. Multi-Functional Reactive Dyes

Bi-Functional reactive dyes

The reactive groups increase the molecular wt. of dyes but not enhance any chromogenic value or strength. Such increase in molecular wt. of dye has impact on cost. They also influence the variety of important physical properties of dye, solubility, aggregation, substantivity, migration and so on.

10.1.8.2 Classification of reactive dyes on the basis of controllable parameters

i. Alkali Controllable dyes
ii. Salt controllable dyes
iii. Temperature controllable Reactive dyes

Alkali Controllable dyes

These dyes have optimal fixation temperature between 40^0 C & 60^0C. They are characterized by relatively low exhaustion in the neutral salt solution before alkali is added. They have high relatively & care should be taken to produce level dyeing. Typical example of this dye DCT, Dichlorodifluoro pyrimidine, Dichloroqinoxaline & VS d dyes.

Salt controllable dyes

Dyes in this group low optimal fixation temperature between 80^0C & boil. Such dye exhibit comparatively high exhaustion at P^H 7 that is neutral medium, so it is important to add salt a carefully to ensure level dyeing. Typical example of this class is Trichloropyrimidine, Aminochlorotriazine & bis(Aminochlorotriazine) etc.

Temperature controllable Reactive dyes

This group of dye react with cellulose above the boil in absence of alkali although this can be applied between 80^0C & boil in alkali medium. Dyes of this group has self leveling characteristics. There is no need additional auxiliaries to achieve level dyeing. Good result can be achieved by controlling the temperature only the Kayacelon React (KYK) range of bis (aminochlorotriazine) dyes belong to this group.

10.1.8.3 Classification of reactive dyes On the basis of reactivity

There are 3 types of reactive dyes on the basis of reactivity:

i) Lower reactive dyes: here pH is maintained 12-12.5 by using NaOH in bath.
ii) Medium reactive dyes: here pH is maintained 11-12 by using $NaCO_3$ in dye bath
iii) Higher reactive dyes: here pH is maintained 10-11 by using $NaHCO_3$ in dye bath.

10.1.8.4 Classification of reactive dyes On the basis of dyeing temperature & method

There are 3 types:

i) Cold brand: This type of dyes contains reactive groups of high reactivity. So dyeing can be done in lower temperature i.e. 32^o-60^oC. For example Procion M, Livafix E.
ii) Medium brand: This type of dyes contains reactive groups of medium reactivity. So dyeing is done in higher temperature i.e. 60^o-71^oC. For example Remazol, Livafix.
iii) Hot brand: This type of dyes contains reactive groups of low reactivity. So dyeing is done in higher temperature i.e. 72^o-93^oC. For example Procion H, Cibacron.

10.1.9 Dyeing mechanism of reactive dye

10.1.9.1 Cotton Preparation

The purpose o f scouring is to remove cotton waxes and other impurities such as pectin, hemi-cellulose and mineral salts from the fabric. This is usually achieved by the application of detergent and an alkali such as sodium hydroxide. Bleaching is the whitening o f the fabric and is achieved by solubilising and removing impurities from the fabric including natural and synthetic fats and waxes. The end goals of the bleaching process are to achieve a sufficiently high and uniform degree of whiteness which is stable to storage, a high and level absorption o f water, dye and other chemicals by the fabric and the fabric should not be damaged to a great degree. Bleaching has traditionally been carried out using oxidising or reducing chemicals such as hypochlorite, chlorite, hydrogen peroxide and sulphur based reducing chemicals [58].

10.1.9.2 Cellulose during dyeing

The most important properties o f cellulose according to dyeing point o f view are hydrophilicity, accessibility to water, physical behaviour in aqueous solution and chemical reactivity. The important fact is that all the different cellulosic fibres encountered in dyeing, including cotton, mercerised cotton, viscose rayon, linen (from flax), ramie (from china grass), hamp and jute, have uniquely different physical organisations (morphology) of the same basic raw material: cellulose or Cell — OH. It means, although the overall chemical behaviour of these fibres towards water and dyes will be similar, properties such as the accessibility o f the fibres to aqueous solutions o f dye molecules will be governed to a large extent by several variables. These variables are the morphological characteristics o f the fibres in both the outer and inner layers, the ratios o f crystalline to amorphous cellulose and the size and the distribution o f the crystalline regions [8].

10.1.9.3 Basic principle in dyeing with reactive dyes

- Exhaustion (E%)
- Fixation (F%)
- Washing off/Rinsing

Exhaustion (E%)

It involves the exhaustion of the dye onto the fiber in the presence of electrolyte. Exhaustion occurs during immigration of dyes to the fabric. Exhaustion means, how much dye is exhausted with fabric. In fabric dyeing maximum 60-70% dye is pick up during migration.

Fixation

Fixation is the addition of alkali to provide the chemical reaction between dye and cellulose. Fixation is necessary to fix the exhausted dye to the fabric. Performance of dyeing depends on how much dye is fixed with the fabric. Fixation started by the soda dosing. Generally soda dosing is performed for 40 min at gc. The dyeing with salt, soda and dye sum for 50 min at 60◦ C.

Fixation is invariably achieved in the presence of aqueous alkali. Under these conditions, nucleophilic cellulosate ion, Cell-O-, is in competition with hydroxide ion, OH-, for reaction with the electrophilic reactive group(s) of the dye [59]. It is shown that the dye fixation to the fabric is controlled by a solid–liquid interfacial process; however, the rate of this reaction is governed by the availability of sites for the adsorption of dye molecules on the fabric surface [60].

Washing off/Rinsing

It needs to wash dyed fabric after dyeing process. Washing is performed for removing of unfixed & hydrolyzed dye from the material in order to achieve the desired results dyes.

11. Intermolecular bonds

Intermolecular bonds play a critical role in providing necessary strength to the fibres and in fixation of dye molecules in the fibre structure. There are four types of bonds that can be formed between the monomers in the fibre polymers and between dye molecule and the molecule of the fibre polymer. Typically the strength of the bond is characterized by the energy of interactions between the atoms involved. This energy can be calculated using methods of quantum mechanics (Atkins, 1994) and usually is given in kJ per 1 mol, where 1 mol is the amount of substance that contains the same number of atoms or molecules as there are atoms in exactly 12 g of carbon-12,
C 12 . This number is known as Avogadro's constant, N A = 6.02214179(30) × 1023

11.1. Van der waals bond

Van der Waals bonds are formed due to the intermolecular forces between two chemically inert molecules. These include electrostatic attractive forces between polar molecules, dipoles of various natures and repulsive forces between the atomic nuclei. The van der Waals bonds are characterised by low energy of up to 8.5 kJ/mol. One of the examples of van der Waals bonds are those between carbon and nitrogen atom in the CN group of polyacrylonitrile (PAN).

11.2 Hydrogen bond

Hydrogen bonds are formed by attractive interaction between a hydrogen atom, H and another two atoms in the form A–H…B, where A and B are electronegative atoms. There are three elements which form the most effective hydrogen bonds, i.e. N, O and F. The hydrogen bonds are stronger than the van der Waals interactions but weaker than both ionic and covalent bonds. Examples of hydrogen bonds in fibre polymers include (i) bonds between CO and NH groups in polyamide and protein fibres and (ii) between hydroxyl groups OH within and between neighboring chains of cellulose molecules. The latter bonds facilitate the formation of microfibrils in cellulose fibres which define their strength.

11.3 Ionic bond

Ionic bonds are formed as a result of a complete transfer of electrons between two atoms. This happens, for example, in the formation of NaCl when a sodium atom (Na) donates one electron to a chlorine (Cl) atom. The energy of ionic bonds can be calculated using the Born–Lande equation (Johnson, 2002) or Born–Haber cycle. This energy in some typical salts is as follows: NaCl – 787 kJ/mol; KCl – 717 kJ/mol; CaCl – 2255 kJ/mol.

11.4 Covalent bond

Covalent bonds are formed between two neighbouring atoms sharing a pair of electrons like, for example, in the molecule of hydrogen H 2 . These bonds can be non-polar in the case of equally shared electrons (Cl 2), or polar if the electrons are shared unequally (HCl). There are two theories describing the formation of covalent bonds. The valence-bond theory assumes that the bond is formed by two overlapping atomic orbitals of two atoms each containing one unpaired electron whereas the molecular orbital theory does not consider the shared electrons as belonging to any individual atom but rather distributed in molecular orbitals over the entire molecule. The covalent bonds are the strongest of the bonds mentioned.

12. Right First Time (RFT)

The concept of right-first-time (RFT) processing in exhaust dyeing became established in the late 1970s and early 1980s. Originally it was termed ‘no addition’ dyeing if the dyeing was found to be on shade at the colour assessment stage, or ‘blind dyeing’ if colour assessment was carried out after the batch had been removed from the dyeing machine. Elimination of an inspection stage made a significant saving in itself. Both techniques were based on achieving a high percentage of bulk dyeings that did not need colour correction or reprocessing. The original benefits were seen as cost savings and increased productivity in the coloration process. However, the introduction of concepts such as just-in-time (JIT) production and quick response (QR) resulted in major financial savings by minimising stock holding by the retailer. RFT processing became an essential means of achieving these objectives. This has become even more necessary now that long supply chains have been established between the sources of raw materials and the retailer.

In dyehouses "Right First Time Dyeing" had been a proven boon to Textile chemical processing industry. It helps to eliminate extra expense on re-dyeing, re-shading and reproducing the color. This paper deals with dye selection criteria, process involved while dyeing, assigning dye uptake, machineries developed, type and principles of reactive dyeing and benefits involved in right first time dyeing. In dyehouses processing, cellulosic fibers with reactive dyes, much progress has been made in the quest for zero defect production by the innovative introduction of controlled coloration technique that has supported the dyeing performance. Exhaust dyeing using reactive dyes quantify dye migration properties, the degree of process control to achieve shade reproducibility and level dyeing performance. The concept of Reactive Dye compatibility Matrix (RCM) will allow to identify dyes with similar properties and used in combination to support right first time production. It can also be used as a diagnostic tool when optimizing application techniques. Hence this becomes an important factor for industries to produce a value added product at a higher profit so that both the manufacturers and consumers are satisfied [61].

To improve the financial performance i.e. to increase profit margin by decreasing the working capital and to withstand intemadonal competitiveness one has to focuss attention on the need for right first time production. This demands the elimination of wastes at all stages of the textile production chain. The trends thus are towards lower ratios to increase productivity throi^gh reduced fillings draining, heating and cooling fibres and to reduce chemicals. The Reactive dye compatibility (RCM) can be used to achieve this. Understanding RCM will allow dyes with similar properties to be identified and used in combination to support tight first time production. Dye selection criteria are based on accurate and consistent standardisation of dyes is the principal requirement for optimized dye house efficiency and right first time production [61].

Exhaust dyeing of cellulose with reactive dyes is a complex process. It involves the exhaustion of dye onto the fibre in the presence of electrolyte and then the addition of alkali to promote the chemical reaction between dye & cellulose. During the "Right First Time" production in the exhaust application of reactive dyes to cellulose the following will affect the dye regularity.

- Hardness in the dye bath
- Bicarbonate in the dye bath [61]

12.1 Benefits of RFT dyeing

RFT production in textile dyehouses has a dramatic effect upon the efficiency, production capacity, and delivery schedules as well generating greater sales turnover and profitability. The impact of RFT dyeing on the dyehouse performance may be measured in terms of three parameters, namely:

- The cost of non-conformance
- The additional profit generated by improved production efficiency through conformance to requirements; and
- The cost of quality [62].

12.2 Cost of non-conformance

The batchwise dyer incurs severe financial penalties if RFT processing fails and a significant proportion of batches are wrong-first-time (WFT). A single colour correction adds between 24 and 36% to the cost of the initial dyed batch, depending on the dye/substrate system and the stage of manufacture at which dyeing is carried out. Stripping and re-dyeing can increase the initial dyeing cost by between 170 and 200%. These costs, however, are only some of the penalties incurred, since they can be equalled or exceeded by the loss in revenue and profit which occurs when machines which should be processing the next batches are occupied with corrective treatments, as shown in the following Table [62].

Table 5: Cost of non-conformance (right-first-time = 100)

Process	Cost	Productivity	Profit
Blind Dyeing	100	100	100
Small addition	110	80	48
Large addition	135	64	-45
Strip and re-dye	206	48	-375

[63].

The cost of non-conformance for a knitgoods commission dyehouse has been calculated using computer modeling techniques as long ago as 1993 and is tabulated in Table 1. Because of cost increases for machinery and equipment, labour and all utilities since 1993 the costs of non-conformance are likely to be even more detrimental to production costs and dyehouse profitability in 2012

If RFT dyeing is carried out the effect on machine and overall dyehouse productivity can be very marked, provided that there are materials to be dyed to fill the spare production capacity generated. A focus on total quality management (TQM) is required which embraces the application of controlled coloration and RFT dyeing. The cost of conforming to the required quality depends upon the following factors:

- Prevention of off-quality e.g. laboratory cost, maintenance of quality systems and procedures;
- Appraisal - fabrics examination and quality control systems;
- Reprocessing - internal and external;
- Claims / debits i.e. cost of non-conformance;
- Shading additions and re-dyes i.e. cost of non-conformance;
- Consequential - lost profit opportunity.

One of the wider consequences of the RFT dyeing approach is that it minimises the use of resources e.g. textile materials, dyes, auxiliaries, water, and energy as well as decreasing the effluent volume that requires decolorization / treatment. Thus RFT dyeing is the most sustainable approach to textile dyeing offering textile dyehouses greater sustainability, productivity and profitability, a triple win situation. The right-first-time dyeing philosophy encompasses three major approaches to production dyeing, namely:

- Standardization of dyestuffs;
- Shade reproducibility; and
- Robust dyeing processes.

Close control over the storage conditions in the dye store and over the operations of weighing, dissolving and dispersing of dyestuffs in the colour kitchen is essential. Robotized equipment for automated electronic check weighing of dyestuffs in powder form is available from many manufacturers such as Color Service, Lawer and Tecnorama, and automated dispensing of liquid dyestuffs to high accuracy is also available. Such equipment eliminates the weighing errors that can occur with manual weighing systems [63].

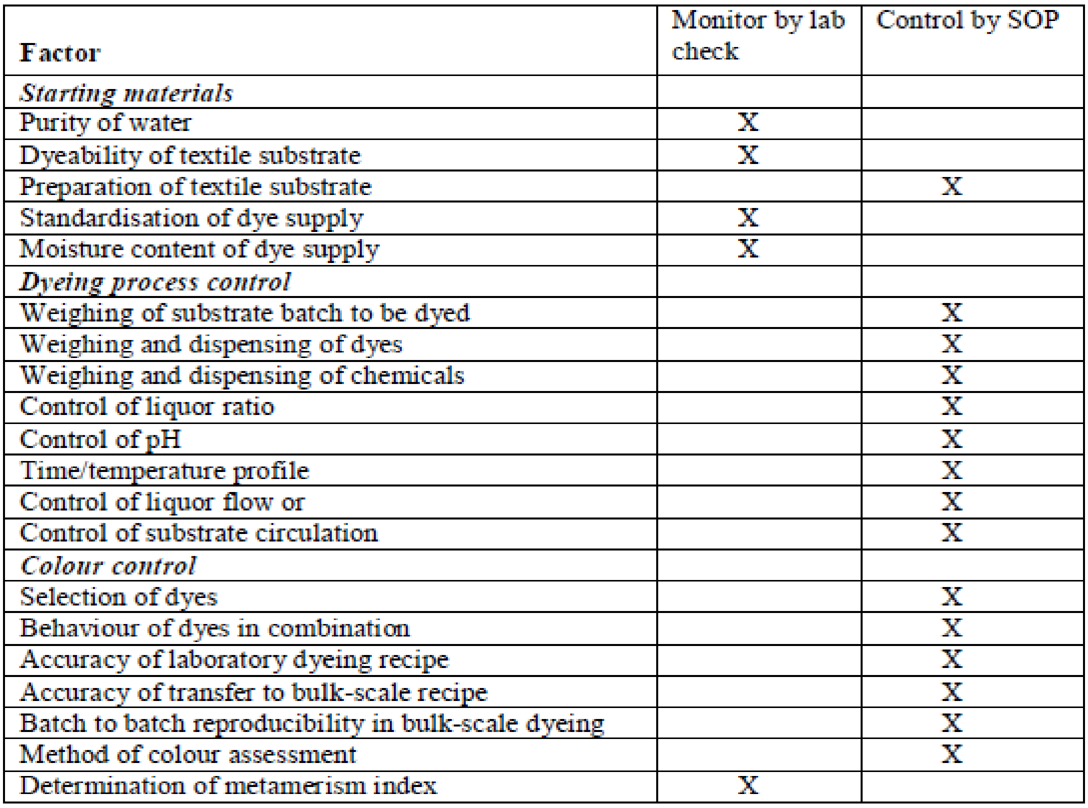
12.3 Factors for RFT processing

When reproducibility is the aim of any dyeing process, the following factors should be taken in to account. To achieve RFT processing, three objectives must be met:

- a high level of within-laboratory reproducibility and accuracy
- accurate transfer and scale-up from laboratory to bulk
- repeatability between bulk batches dyed to the same colour.

Various workers have emphasised the importance of undertaking an initial audit to identify those factors that must be brought under tighter control to meet the necessary limits of accuracy. The limits of accuracy can be defined as the practical process control limits that must be applied in the dyeing operation and in all the preceding manufacturing processes so that the sum of their effects on colour variation are equal to or less than the pass/fail colour tolerance limits. An adequate support laboratory is essential. The design, equipping, operation and procedures required include methods for achieving laboratory-to-bulk reproducibility in dyeing. Accurate laboratory dyeing is a highly cost-effective stage on the road to achieving RFT production since it has been shown that a bulk correction on a 300 kg batch costs as much as carrying out between three and twenty-five laboratory dyeings, or one sample dyeing of 3 to 10 kg, whereas a re-dyeing of such a batch costs the same as 25 to 85 laboratory dyeings, depending on the process and dyehouse infrastructure. Approximately twenty factors must be controlled in the dyeing process by the availability of standard operating procedures (SOP) or monitoring by the laboratory. These are in areas including dye selection, optimisation and standardisation; water quality; substrate dyeability, preparation and weighing; weighing and dispensing of dyes and chemicals; standardised dye application techniques and colour assessment. These factors are summarised in the following Table:

Table 6: Important factors influencing RFT production



Factor	Monitor by lab check	Control by SOP
Starting materials		
Purity of water	X	
Dyeability of textile substrate	X	
Preparation of textile substrate		X
Standardisation of dye supply	X	
Moisture content of dye supply	X	
Dyeing process control		
Weighing of substrate batch to be dyed		X
Weighing and dispensing of dyes		X
Weighing and dispensing of chemicals		X
Control of liquor ratio		X
Control of pH		X
Time/temperature profile		X
Control of liquor flow or		X
Control of substrate circulation		X
Colour control		
Selection of dyes		X
Behaviour of dyes in combination		X
Accuracy of laboratory dyeing recipe		X
Accuracy of transfer to bulk-scale recipe		X
Batch to batch reproducibility in bulk-scale dyeing		X
Method of colour assessment		X
Determination of metamerism index	X	

12.3.1 Testing prepared cotton for residual chemicals

For any cotton in an aqueous medium there are three phases which we need to concern ourselves with:

- The aqueous bath
- The surface layer
- The internal Bath.

Most testing regimes which screen for the efficiency of preparation focus upon the concentration of chemicals in last aqueous rinse before dyeing. There are three chemicals which can interfere with successful dyeing with reactive dyes if carried forward from preparation into the dye bath:

- peroxide (some dyestuff chromophores are extremely sensitive to peroxide)
- Hardness {all dyes susceptible to one degree or another)
- Alkali (which will cause premature fixation before migration and premature hydrolysis before exhaustion and fixation).

Once a prepared substrate is placed in an aqueous dye bath, the temperature will be raised to a minimum of 60 'C. Therefore, anything which is in the interior of the prepared cotton can desorb into the bath. So - it is the Internal condition of the prepared cotton which should be of prime concern.

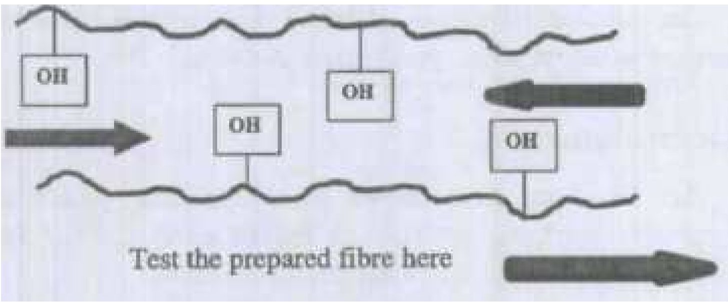


Figure 31: Internal bath of cotton

Fortunately, it is relatively easy to ensure that it is the interior of the fibre which is tested, and not simply the surface condition. This can be achieved by extraction of the prepared cotton in boiling distilled water (at the same liquor to goods ratio as that used in dyeing). The extract can be cooled to room temperature, and then measured for

- pH
- peroxide
- Hardness [61].

12.3.2 Dye selection criteria

Accurate and consistent standardization of dyes is the principal requirement for optimized dye house efficiency and right-first-time production. The external factors which influence the process have been identified and segregated into two variables:

- The Assignable variables - e.g. internal fabric pH at the start'of the dyeing, the liquor ratio, the temperature gradient, the fixation temperature, the electrolyte concentration, the addition profiles of dye, electrolyte and fixation alkali, the fixation pH and time.

- The random variables - e.g. the impurities in cotton, water supply, chemicals, and the dyes selected to reproduce the target shade [61].

12.3.3 Controlled coloration

The modern concept of controlled coloration depends on implementing all the aspects of the original RFT philosophy, discussed above. It is achieved through a combination of good management, dye and application technologies. Dye selection based on accurately standardised, robust, compatible, stable and consistent products is essential. Proper dye selection to ensure consistent laboratory-to-bulk reproducibility is very important. The dyer needs to follow systematic application methods allied to computer-aided optimised dye selection, according to substrate, equipment type and cost. The influence of dye standardisation on the likelihood of achieving RFT production has been demonstrated, based on the selection of reactive dyes for cellulosic substrates. Application methods for these dyes can be optimised to ensure RFT production using the Reactive Dye Compatibility Matrix (RCM), based on substantivity, migration and level dyeing factors. Improved dyeing machinery design, together with process control, is an additional factor in achieving RFT production. Improved machinery design extends the range of dyes within an application classification that will give RFT results. On-line monitoring of key parameters has allowed new and highly productive dyeing and washing-off procedures to be developed. This led to the development of the concept of smart rinsing which results in significant savings in time and more effective use of water, improving the degree of control of the wet processing cycle without detracting from RFT performance or product quality. In the exhaust dyeing of reactive dyes, by using optimised preparation techniques, RFT dyeing based on controlled coloration methods and smart rinsing technology, it is possible to achieve a ‘load to unload’ production concept of five hours or less. Although the continuous dyeing sector was, by necessity, the first to recognise the need for RFT processing, its achievement has received less attention. Selection of matched pairs of dyes for each fibre in the dyeing of polyester/cellulosic blends gave improved laboratory-to-bulk reproducibility with a reduction in dye inventory. A control strategy has been developed which is essentially a program to define the limits of accuracy required, to improve production efficiency in the continuous dyeing of polyester/cellulosic fabrics. It has been demonstrated that high levels of laboratory-to bulk reproducibility are achieved with the Econtrol (Monforts) continuous dyeing process based on appropriate dye selection and laboratory equipment that accurately reproduces bulk conditions.

12.3.4 Automation

RFT processing is an essential pre-requisite to the introduction of automation and robotics. The major financial savings from the concept of RFT depend on firm discipline in a manually operated or semi-automatically controlled (SAC) dyehouse. This requires defining the limits of accuracy, standardising dye selection and application techniques, using computer colour matching (CCM) methods for recipe generation and colour matching. Total automation, however, yields major savings in direct labour costs.

12.3.5 Lab to bulk reproducibility constraints

There will be differences between factors in the laboratory and on the factory floor for example: agitation of fabric and machine efficiency. There are also differences in procedures such as: the number and type of auxiliaries added; the number of wash-offs; and the vigour of washing. These differences may mean that the shade attained in the lab is different to that on the factory floor, for example more vigorous washes can lighten the shade. When differences occur the recipe is usually altered in some way, such as a dye addition, to give the correct shade. If this is done, all changes must be recorded and documented properly to reduce the need to repeat them. For example if it is regularly observed that a 10% shade addition is required when going from lab to bulk, then this can be added to the recipe from the start. This should improve the frequency of “right first time” dyeing. These variations between the lab and the factory floor mean that there needs to be strong communication between laboratory staff and staff on the factory floor. Lab Managers and Dye House Floor Managers need to establish a good relationship and work together towards following the optimal recipes created in the laboratory and reproducing them on the factory floor. Careful observation and monitoring need to take place to ensure that the correct shade is produced, and any variables are considered and compensated for during the transfer from laboratory to bulk dyeing.

Points to be considered

- Due to mechanical restrictions, matching the liquor ratios and the agitation speeds of the dye baths can be difficult, but the liquor ratios should be made as close as possible.
- The material to be dyed should be the same as that dyed in the laboratory.
- It is advisable that the test in the laboratory should be conducted with same lot of dyes as what is being used in production, particularly for the light shades.
- If manual pipetting is used for measuring the dyestuff solution:

1. Use calibrated pipettes.
2. Use Smaller volume pipettes, wherever necessary; eg. if you have to pipette 9 ml of a solution, use a 5 cc pipette for 5 plus 4 ml. For 11 ml use 2 measures of 5 cc and 1 measure of 1 cc pipette.
3. Do not use pipettes, if the tips are broken.

- Good housekeeping in laboratory for dyes storage in order to prevent them from extreme conditions of heat and moisture is also crucial.
- The dyeing auxiliaries that are used should be consistent and same as what being used in bulk.
- The quality of water should be same for both parameters.
- The temperature control of the dyeing machines should be accurate in laboratory

12.3.6 Liquor Ratio

The correct liquor ratio for the recipe must be maintained otherwise incorrect concentrations of dyes and other chemicals will be present in the dye bath and the right shade will not be achieved first time. The water gauges should be clean so that they can be easily read and should be monitored at each step during the entire dyeing process. The liquor ratio will be altered when extra water is added to mix the dyes, the salt and the alkali. This should be factored into the liquor ratio in the recipe, i.e. if a total of 1000 L is needed but 50 L of caustic soda will be added, then the volume of water initially put in the dye bath should be 950 L.

12.3.7 pH Control

The pH must be measured after the alkali (e.g. soda ash) is added to ensure that it is the same as that specified in the recipe. Different dye types require different pHs and the recipe should account for this but in general pH must be within pH 10.5-11.5

12.3.8 Time and temperature profile

Time: Allowing the correct timings for each process results in reproducialble results.

Temperature Control

Check frequently the calibration of the thermometer. Maintaining the correct temperature for every process is very important. Dyes, enzymes and some inorganic chemical treatment too require specific temperature. Maintaining the correct temperature gives better repetitive results. Different dyes require different temperatures and times for optimal dyeing. The recipes are created to ensure that the best conditions are used for each dye. It is therefore very important that these temperatures are maintained for the correct period of time. Some machines might take a longer period of time to reach the temperature required. These should be monitored and adjusted so that the required time to reach the right temperature is maintained. Records should be kept of any changes.
[64].

12.3.9 Dye ability of substrate

Prior to start dyeing - uniformity in absorbency, whiteness and pH of the fabric have to be tested and uniform conditions have to be maintained for all batches/processes.

12.3.10 Weight of substrate

Everywhere it is generally taken for granted and the weight is calculated according to the meterage or number of cheeses or number of bundles instead of actually weighing the materials ready for processing. In lab, we use RFD material for dyeing, where as in batch dyeing machines, we use only greige fabric that would be affected by up to 8 to 10% weight loss after scouring and bleaching. The correct method is to find out the actual average weight loss after scouring and bleaching and use this figure as a correction factor for predicting the recipe for dyes and chemicals.

12.3.11 Weighing of dyes and chemicals

A important phase of operation - first the recipe calculation part - recheck once or twice; second is the weighing balance calibration and its worthiness in weighing small quantities. Third phase is actual weighing. A proper supervision is a must in this phase.

12.3.12 Moisture content of substrate

In padding operations, the moisture content, temperature of fabric should be maintained uniformly as a constant. You should find out the mositure content of fabric before starting the operation (padding).

12.4 Summery

The above mentioned parameters are considered very important for Right First Time dyeing concept.

Usually, at first, test dyeing for color matching is conducted in a laboratory, and the data thus gained is important for reproducibility in practical dyeing because it is used to decide the practical dyeing conditions. It is difficult to perfectly reproduce the dyeing conditions of the laboratory in practice, but it is important to try to get them as close as possible.

Color matching equipments make real ease towards the above concept. The results of the laboratory dyeing and the practical dyeing can be measured and a coefficient for the degree of difference each time the dye is used can be calculated. If this coefficient is not constant, the reproducibility of results just within the laboratory or in the practical environment should be verified before the reproducibility of results between the laboratory and the factory is considered. If this coefficient shows a constant trend for all of the dyestuff, it can be used as a correction coefficient and crossed with the laboratory results in order to decide the practical dyeing conditions.

In the case of certain dyes that show large deviation, a dye may have bad compatibility, and a change of dye class should be considered. Most of the exhaust dyers prefer the bifunctional and vinyl Sulphone type of dyes. However, HE (High Exhaust) dyes have recently made their entrance due to various advantages over the conventional dyeing system. Nevertheless, hetro-bifunctional and vinyl Sulphone still dominates the cellulosic dyeing in exhaust system.

So it is dear that using "Rigjit First Time Dyeing" conceptsprovides broad scope of increasing the profit by reducing the after treatments. This is clear by the following flow chart In this competitive world "Only the fittest will survive". The Indian textile industry must improve its Productivity, and particularly in the Dyeing & Finishing sector; and must target the Value-Added sectors. This can be achieved mainly by introducing innovative ideas and applying chemistry to decrease the production cost and give more quality products so that the profit margin is increased. Also this type of dyeing is ecofriendly.

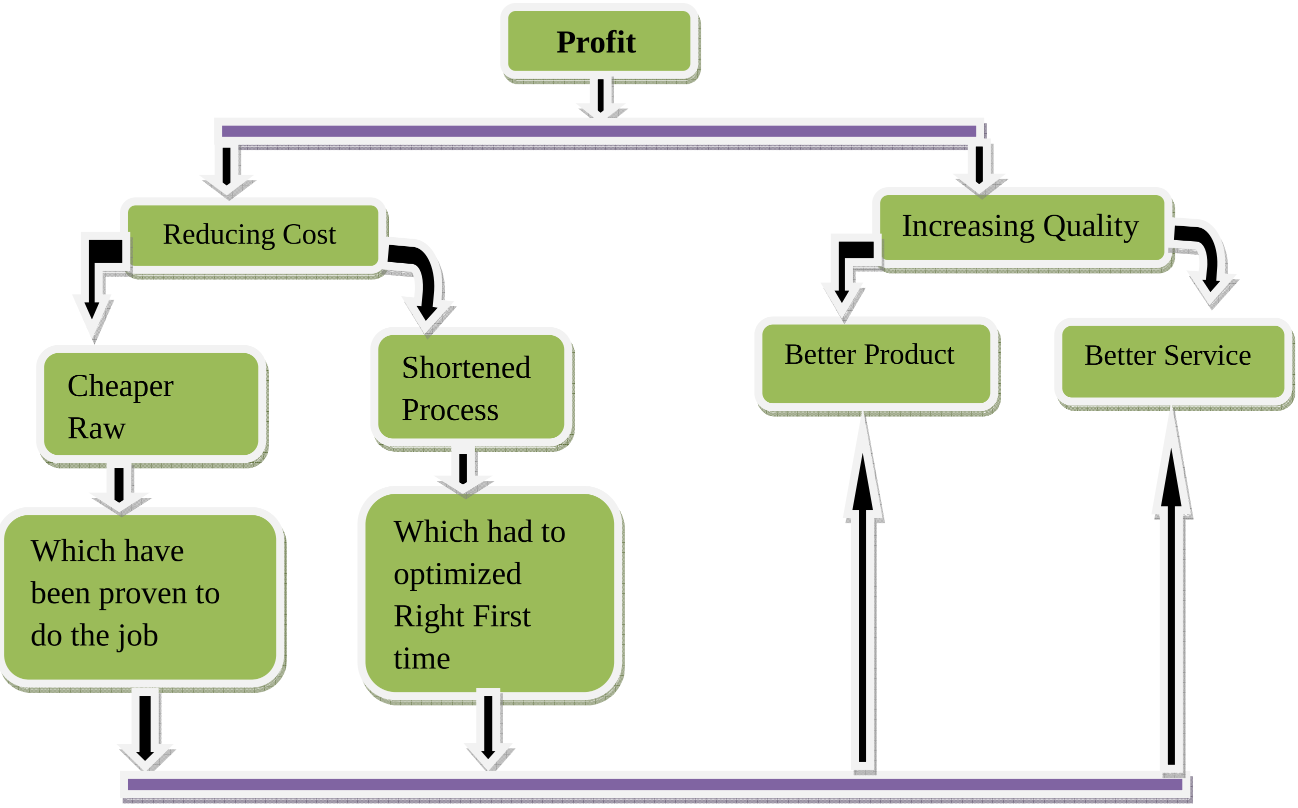


Figure 32: Strategy of profit for manufacturing unit

CHAPTER – 03
MATERIALS AND METHODS

13. Materials and methods

The materials and method or process used for this experiment are given in details below:

13.1 Fabric**:** 100% cotton Single Jersey - 180(G.S.M)

13.2 Dyes:

SL No.	Name of Dyes	Type of Dyes	Functional Group	Dyeing Temperature
01	Dychufix Yellow 3RXF-150%	Bi-Functional	VS + MCT	60’c
02	Dychufix Red 3BXF-150%	Vinyl Sulphone	VS	60’c
03	Dychufix Navy Blue 2 GLXF	Bi-Functional	VS + MCT	60’c

13.3 Chemicals and auxiliaries:

SL No.	Name of chemicals	Technical Name (usage)
01	Texsanscour CS (PCLF)	Detergent
02	Texsantifoam AF (JET)	Antifoaming Agent
03	Liang-710	Chelating Agent
04	Cetalube NFL	Anticreasing Agent
05	Eripon R (Liq.)	Soaping Agent
06	STABILIZER A pdr.	Stabilizer
07	CETATEX PC	H_2O_2 killer
08	Hydrogen Per-Oxide (H_2O_2) 50%	Bleaching Agent
09	Caustic Soda	Strong Alkali
10	Rossacid N Liquid (Green Acid)	Acid
11	GXM Ultra	Enzyme
12	ASTROLEVEL CO	Leveling Agent
13	Soda Ash Light	Mild Alkali
14	Glauber’s Salt	Electrolytes

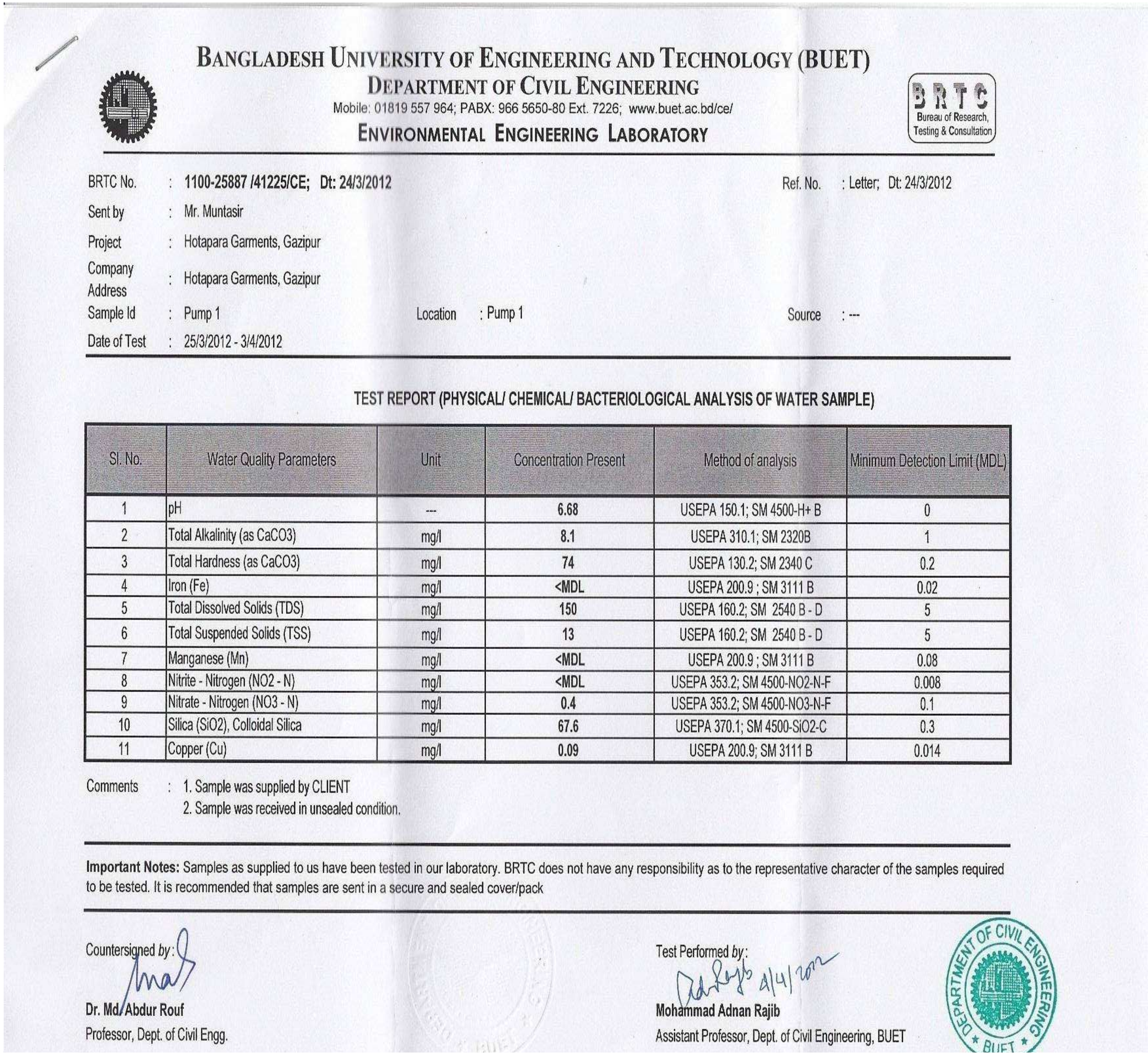
13.4 Machines:

SL No.	Name of Machine	Brand	Origin
01	Lab Dip Dyeing M/C	IRDYER	Taiwan
02	Lab Dryer M/C	RAPID	Taiwan
03	Spectrophotometer	DATA COLOR	USA
04	Light Box	VERIVIDE	UK
05	Electronic Balance Meter	SHIMADZU	JAPAN
06	Roter wash	Rapid	China
07	Q-Sun	Xenon	USA
08	Precison oven	FYICHINA	China
09	Electric pH Meter	Hanna	Romania
10	Crock Master	James H.Heal	U.K

13.5 Experimental

13.5.1 Water quality testing

Water quality is tested from BUET testing laboratory to confirm the internal testing result of water hardness accuracy with a standard laboratory with standard method. It was found there was almost close relation between our internal laboratory test report with BUET. The test report is attached below:



BANGLADESH UNIVERSITY OF ENGINEERING AND TECHNOLOGY (BUET)
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ENVIRONMENTAL ENGINEERING LABORATORY

BRTC
Bureau of Research, Testing & Consultation

BRTC No. : **1100-25887 /41225/CE; Dt: 24/3/2012** Ref. No. : Letter; Dt: 24/3/2012
Sent by : Mr. Muntasir
Project : Hotapara Garments, Gazipur
Company Address : Hotapara Garments, Gazipur
Sample Id : Pump 1 Location : Pump 1 Source : ---
Date of Test : 25/3/2012 - 3/4/2012

TEST REPORT (PHYSICAL/ CHEMICAL/ BACTERIOLOGICAL ANALYSIS OF WATER SAMPLE)

Sl. No.	Water Quality Parameters	Unit	Concentration Present	Method of analysis	Minimum Detection Limit (MDL)
1	pH	---	**6.68**	USEPA 150.1; SM 4500-H+ B	0
2	Total Alkalinity (as CaCO3)	mg/l	**8.1**	USEPA 310.1; SM 2320B	1
3	Total Hardness (as CaCO3)	mg/l	**74**	USEPA 130.2; SM 2340 C	0.2
4	Iron (Fe)	mg/l	**<MDL**	USEPA 200.9 ; SM 3111 B	0.02
5	Total Dissolved Solids (TDS)	mg/l	**150**	USEPA 160.2; SM 2540 B - D	5
6	Total Suspended Solids (TSS)	mg/l	**13**	USEPA 160.2; SM 2540 B - D	5
7	Manganese (Mn)	mg/l	**<MDL**	USEPA 200.9 ; SM 3111 B	0.08
8	Nitrite - Nitrogen (NO2 - N)	mg/l	**<MDL**	USEPA 353.2; SM 4500-NO2-N-F	0.008
9	Nitrate - Nitrogen (NO3 - N)	mg/l	**0.4**	USEPA 353.2; SM 4500-NO3-N-F	0.1
10	Silica (SiO2), Colloidal Silica	mg/l	**67.6**	USEPA 370.1; SM 4500-SiO2-C	0.3
11	Copper (Cu)	mg/l	**0.09**	USEPA 200.9; SM 3111 B	0.014

Comments : 1. Sample was supplied by CLIENT
2. Sample was received in unsealed condition.

Important Notes: Samples as supplied to us have been tested in our laboratory. BRTC does not have any responsibility as to the representative character of the samples required to be tested. It is recommended that samples are sent in a secure and sealed cover/pack

Countersigned by:
Dr. Md. Abdur Rouf
Professor, Dept. of Civil Engg.

Test Performed by:
4/4/2012
Mohammad Adnan Rajib
Assistant Professor, Dept. of Civil Engineering, BUET

13.5.2 Selection of Chelating agent:

In this experiment we worked to eliminate the ionic bond which involve from the metal ions comes from water, substrate, salt, alkali etc. These metal ions in general increase the water hardness. But it is observed that the suitable water hardness in the dye bath should below 60 ppm. Where our supplied water for dyeing was in 74-78 ppm and adding Glauber's salts and fabric it becomes 90-110 ppm.For this reason we tested first a several types of sequestering agent from different company by changing the dosing and adding the salt and leveling agent. Among them the best one, Liang-710 was selected to do the experiment. It was also analyzed and selected the dosing of 45-50 ppm by using Liang-710.

13.5.3 Water hardness testing procedure:

In the laboratory the following testing procedure was used to determine the water Hardness:

- Take 50 ml of sample water into a 250 ml conical Flask or beaker.
- Add about 1 ml. ammonium buffer solution
- Add 1 drop of insolated total hardness indicator tablet Eriochrome Black T
- Stire well until dissolved the presence of hardness is shown by a wine color or red
- Titrate with the 0.01M EDTA solution until the solution is bluish purple.

Calculation:

$$\text{Total Hardness (in terms of } CaCO_3) = \frac{\text{Burette Reading (volm. of EDTA) x 1000}}{\text{Sample amount}}$$

In house sequestering agent selection test report is shown in Table 7

Table 7: Water hardness test report of different chelating agents

SL No.	Chemical Name	Company Name	Dosing (g/l)	Total hardness (ppm)
1	Scour wet MT	Innovation world	Pump Water	80
			M/C Water	82
			MT - 0.5 g/l	60
			MT - 0.75 g/l	50
			MT - 1.0 g/l	35
2	WT	Avocet Chemicals Ltd.	Pump Water	78
			M/C Water	80
			WT - 0.1 g/l	70
			WT - 0.2 g/l	64
3	Kappa Com E12	Kap Chem Ltd.	Pump Water	80
			M/C Water	82
			E12 - 0.2 g/l	78
			E12 - 0.5 g/l	78

			E12 - 1.0 g/l	72
			E12 - 2.0 g/l	66
4	Kappa Com E12	Kap Chem Ltd.	Pump Water	78
			M/C Water	80
			Water + Ast.Co - 1.0 g/l	86
			Water + Ast.Co - 1.0 g/l + E12-1.0 g/l	90
			Water + Ast.Co - 1.0 g/l + E12-1.0 g/l + Slat-50.0 g/l	160
			Water + Ast.Co - 1.0 g/l + E12-2.0 g/l + Slat-50.0 g/l	150
5	Kappa Fos D11	Kap Chem Ltd.	Pump Water	80
			M/C Water	82
			D11 - 0.1 g/l	56
			D11 - 0.2 g/l	28
			D11 - 0.3 g/l	10
			D11 - 0.5 g/l	0
			Salt - 50.0 g/l + D11-0.3 g/l	66
			Salt - 50.0 g/l + D11-0.5 g/l	20
6	Kappa Fos D11	Kap Chem Ltd.	Pump Water	76
			M/C Water	78
			Ast.CO - 1.0 g/l + D11-0.3 g/l	10
			Ast.CO - 1.0 g/l + D11-0.3 g/l + Salt-60.0 g/l	110
7	Liang-710	Exim Chem Ltd.	Pump Water	70
			M/C Water	72
			710 - 0.2 g/l	25
			710 - 0.3 g/l	0
			Ast.CO - 1.0 g/l	68
			Ast.CO - 1.0 g/l + 710 -0.4 g/l	0
			Ast.CO - 1.0 g/l + 710 -0.4 g/l + Salt - 70 g/l	40
8	Liang-710	Exim Chem Ltd.	Pump Water	78
			M/C Water	80
			Ast.CO - 1.0 g/l + NFL- 1.0 g/l	70
			Ast.CO - 1.0 g/l + NFL- 1.0 g/l + 710 -0.3 g/l	0
			Ast.CO - 1.0 g/l + NFL- 1.0 g/l + 710 -0.3 g/l + Salt-60 g/l	50
9	Liang-710	Exim Chem Ltd.	Pump Water	72
			M/C Water	74
			710 - 0.2 g/l	20
			710 - 0.3 g/l	0
			710 -0.3 g/l + Salt-50.0 g/l	45

			710 -0.4 g/l + Salt-50.0 g/l	20
10	Leing-712	Exim Chem Ltd.	Pump Water	72
			M/C Water	74
			712 - 0.2 g/l	74
			712 - 0.5 g/l	70
			712 - 1.0 g/l	60
11	210 N	Exim Chem Ltd.	Pump Water	74
			M/C Water	76
			210N - 0.2 g/l	68
			210N - 0.5 g/l	58
			210N - 0.8 g/l	32
12	Leing-711	Exim Chem Ltd.	Pump Water	78
			M/C Water	80
			Leing-711 (Exim Chem Ltd.)	
			711 - 0.5 g/l	70
			711 - 1.0 g/l	50
13	Metaplex MIRN SQ	Innovation World	Pump Water	78
			M/C Water	80
			MERN SQ - 0.3 g/l	54
			MERN SQ - 0.4 g/l	40
			MERN SQ - 0.5 g/l	30
			Ast.CO -1.0 g/l + MIRN SQ-0.3 G/L	0
			Ast.CO -1.0 g/l + MIRN SQ -0.3 G/L + Salt -50.0 g/l	70

13.5.4 Cotton knit dyeing process (Exhaust method)

The dyeing procedure was followed of the reactive exhaust dyeing method. There were used three dyes namely, 1.Dychufix red 3BXF, 2.Dychufix yellow 3 RXF, 3.Dychufix Navy Blue 2GLXF and each color is dyed in three variables, 1.with normal water, 2.adding Chelating agent Liang-710 at 0.3 g/l , 3.adding Chelating agent Liang-710 at 0.6 g/l.

13.5.5 Pretreatment of cotton fabric

To make the 100% cotton fabric ready for dyeing, a combined scouring and bleaching process was carried out as pretreatment. Where NaOH was the main chemical for scouring with assistance of Na_2CO_3. Here both two alkalis were used to prevent the cellulose degradation. And H_2O_2 was the main chemical for bleaching. The following chemicals and auxiliaries were used for completion of pretreatment:

Table 8 : Recipe **for** pretreatment:

Sl No.	**Name of Chemical**	**Dosing**
01	Texsanscour CS (PCLF)	0.8 g/l
02	Texsantifoam AF (JET)	0.2 g/l
03	Liang-710	0.2 g/l
04	Cetalube NFL	2.0 g/l
05	STABILIZER A pdr.	0.5 g/l
06	Hydrogen Per-Oxide (H2O2)50%	2.5 g/l
07	Caustic Soda	0.8 g/l
08	Soda Ash Light	2.0 g/l
09	CETATEX PC	0.5 g/l
10	Rossacid N Liquid (Green Acid)	1.0 g/l
11	GXM Ultra	0.2 g/l

13.5.6 Pretreatment procedure:

1. Liquid Chemicals are added at 40°c for 5 minutes
2. Caustic is added at 60°c temperature for 5 minute
3. Temperature increase at 70°c
4. Hydrogen per Oxide (H2O2) is added for 5 minutes
5. Temperature increase at 95°c & continues for 60 minutes
6. Sample check (to check Absorbency, if absorbency ok)
7. Cold wash at 40°c for 5-10 minutes
8. Hot wash at 90°c for 5-10 minutes (per oxide killer hot)
9. Acetic acid is added at room temp.(for neutralization)
10. Temperature increase at 60°c for 20 minutes
11. Cold wash at 40°c & drain
12. pH check at 4.5 (For Enzyme)
13. Temperature increase at 55°c
14. Enzyme is added & run for 60 minutes at 55°c
15. Temperature increase at 80°c for 10 minutes
16. Cold wash at 40°c and drain

13.5.7 Dyeing recipe:

All the dyes were taken from 1.0% stock solution and the Glauber’s salt, soda ash were taken from 25% stock solution. 10 ml pipette was used for dye solution, 10 ml pipette for Galuber’s salt and 5 ml pipette for soda ash. A liquor ratio was followed of 1:9.

Each dye was dyed in three different steps, 1. Without adding Chelating agent, 2.adding Chelating agent at 0.3 g/l, 3. Adding Chelating agent at 0.6 g/l.

Table 9: Dyeing Recipe for Yellow 3 RXF – 150 %

Dyeing Recipe 1:	**Dyeing Recipe 2:**	**Dyeing Recipe 3:**
1. Dychufix Yellow 3 RXF-150% - 2.0% 2. Levelling Agent – Astrolebel CO - 1.5 g/l 3.Glaubers Salt – 50g/l 4. Soda Ash - 12 g/l	1. Dychufix Yellow 3 RXF-150% - 2.0% 2.Sequestering Agent – Liang 710- 0.3 g/l 3. Levelling Agent – Astrolebel CO - 1.5 g/l 4.Glaubers Salt – 50g/l 5. Soda Ash - 12 g/l	1. Dychufix Yellow 3 RXF-150% - 2.0% 2.Sequestering Agent – Liang 710- 0.6 g/l 3. Levelling Agent – Astrolebel CO - 1.5 g/l 4.Glaubers Salt – 50g/l 5. Soda Ash - 12 g/l
After Treatment: 5.Acetic Acid - 1.0 g/l 6. Wash Off Eriopon R– 0.5 g/l	**After Treatment:** 6.Acetic Acid - 1.0 g/l 7. Wash Off Eriopon R– 0.5 g/l	**After Treatment:** 6.Acetic Acid - 1.0 g/l 7. Wash Off Eriopon R– 0.5 g/l

- **Other two dyes (Red & Blue) were applied on knit using same recipes.**

13.5.8 Laboratory sample dyeing procedure:

1. Measure 5gm of knit
2. Make dyeing recipe and calculate
3. Pipette the dyes and chemicals (Sequestering agent, leveling agent, salt, soda) accurately
4. Close the dyeing pot and shake continuously
5. Insert the sample pot into dyeing machine cabinet
6. Run the Machine at 60 ‘c for 60 Minutes
7. Cold wash the sample
8. Acid wash the sample (for neutralization)
9. Take the wash off chemical (Eriopon R) into the Dyeing Pot
10. Put the sample on it
11. Start the washing machine to run at 90’c for 20 minutes
12. Cold wash the sample
13. Start the Dryer machine to dry the sample at 130’c for 160 seconds
14. Iron the sample.

13.5.9 Fixation (%) of dyes: Fixation levels can be calculated based on the absorption of visible light by dyes in solution, in dye baths and in wash baths, using a spectrophotometer. We used the Datacolor 600 ^{TM} liquid measurement instrument.

13.5.10 Integral strength measuring procedure:

1. Prepare the dye solution (leveling agent, dyes, salt, water, sequestering agent) without adding alkali.
2. Put this dye solution in to the Transmission Glass
3. Keep the transmission Glass in the e Liquid measuring instrument
4. Open the cover of the Spectrophotometer
5. Place the liquid measuring g instrument in the required area inside the spectrophotometer
6. Measure solution for a specific dye as the standard
7. Then after Bath drain again measure the integral strength of residual dye solution as the batch
8. After wash off then again measure the integral strength.

9. Calculate the fixation (%) using the following formula:

Formula to calculate the fixation %

Fixation% of dye stuff = [100 – {Color Strength (integral) % of the solution after B/D + Color Strength (integral) % of the solution after wash}]%.

F% = {100- (a+b)}%

Table 10 : Fixation (%) of Dychufix Red 3B XF

SL No.	**Dyes Name**	**Shade %**	**Salt/Soda Dosing (g/l)**	**Dyeing Step**	**Process**	**Integral Strength %**		
						B/D (a)	**wash off** (b)	**Total (**F%**)**
01	Dychufix Red 3BXF	2%	50/12	60 x 60'	Normal water	38.19	6.53	55.28
				60 x 60'	710 - 0.3g/l	36.95	8.37	54.68
				60 x 60'	711 - 0.6g/l	37.01	6.56	56.43
02	Dychufix Red 3BXF	2%	50/12	60 x 60'	Normal water	41.26	10.39	48.35
				60 x 60'	710 - 0.3g/l	36.1	9.8	54.10
				60 x 60'	711 - 0.6g/l	34.14	12.66	53.20
03	Dychufix Red 3BXF	2%	50/12	60 x 60'	Normal water	42.31	10.09	47.60
				60 x 60'	710 - 0.3g/l	40.4	9.58	50.02
				60 x 60'	711 - 0.6g/l	39.54	12.12	48.34
04	Dychufix Red 3BXF	2%	50/12	60 x 60'	Normal water	38.39	14.59	47.02
				60 x 60'	710 - 0.3g/l	33.17	11.46	55.37
				60 x 60'	711 - 0.6g/l	34.14	12.66	53.20
05	Dychufix Red 3BXF	2%	50/12	60 x 60'	Normal water	47.86	6.51	45.63
				60 x 60'	710 - 0.3g/l	47.96	5.77	46.27
				60 x 60'	711 - 0.6g/l	41.37	10.56	48.07

Table 11: Fixation(%) of Dychufix Yellow 3R XF

SL No.	**Dyes Name**	**Shade %**	**Salt/Soda Dosing (g/l)**	**Dyeing Step**	**Process**	**Integral Strength %**		
						B/D (a)	**wash off** (b)	**Total (F%)**
01	Dychufix Yellow 3R XF	2%	50/12	60 x 60'	Normal water	22.93	20.09	56.98
				60 x 60'	710 - 0.3g/l	22.28	17.87	59.85
				60 x 60'	711 - 0.6g/l	20.8	20.7	58.50
02	Dychufix Yellow 3R XF	2%	50/12	60 x 60'	Normal water	21.64	14.86	63.50
				60 x 60'	710 - 0.3g/l	20.3	10.08	69.62
				60 x 60'	711 - 0.6g/l	22.07	9.77	68.16
03	Dychufix Yellow 3R XF	2%	50/12	60 x 60'	Normal water	22.81	20.33	56.86
				60 x 60'	710 - 0.3g/l	24.46	18.97	56.57
				60 x 60'	711 - 0.6g/l	24.52	20.83	54.65
04	Dychufix Yellow 3R XF	2%	50/12	60 x 60'	Normal water	38.39	14.59	47.02
				60 x 60'	710 - 0.3g/l	33.17	11.46	55.37
				60 x 60'	711 - 0.6g/l	34.14	12.66	53.20
05	Dychufix Yellow 3R XF	2%	50/12	60 x 60'	Normal water	22.28	17.87	59.85
				60 x 60'	710 - 0.3g/l	21.57	14.49	63.94
				60 x 60'	711 - 0.6g/l	21.34	14.86	63.80

Table 12: Fixation (%) of Dychufix Navy Blue 2GLXF

SL No.	**Dyes Name**	**Shade %**	**Salt/Soda Dosing (g/l)**	**Dyeing Step**	**Process**	**Integral Strength %**		
						B/D (a)	**wash off** (b)	**Total (F%)**
01	Dychufix Navy Blue 2GLXF	2%	50/12	60 x 60'	Normal water	34.19	22.28	43.53
				60 x 60'	710 - 0.3g/l	33.67	21.28	45.05
				60 x 60'	711 - 0.6g/l	34.19	22.28	43.53
02	Dychufix Navy Blue 2GLXF	2%	50/12	60 x 60'	Normal water	28.71	22.92	48.37
				60 x 60'	710 - 0.3g/l	29.39	21.46	49.15
				60 x 60'	711 - 0.6g/l	34.35	17.86	47.79
03	Dychufix Navy Blue 2GLXF	2%	50/12	60 x 60'	Normal water	34.17	17.89	47.94
				60 x 60'	710 - 0.3g/l	33.89	17.77	48.34
				60 x 60'	711 - 0.6g/l	37.85	16.89	45.26
04	Dychufix Navy Blue 2GLXF	2%	50/12	60 x 60'	Normal water	37.78	17.24	44.98
				60 x 60'	710 - 0.3g/l	28.71	22.92	48.37
				60 x 60'	711 - 0.6g/l	28.78	22.97	48.25
05	Dychufix Navy Blue 2GLXF	2%	50/12	60 x 60'	Normal water	33.26	21.54	45.20
				60 x 60'	710 - 0.3g/l	34.89	17.77	47.34
				60 x 60'	711 - 0.6g/l	37.65	16.89	45.46

13.5.11 Getting RFT shade controlling 22 points

To get a shade at Right First Time (RFT) in exhaust dyeing is very difficult. Because there a lots of process parameters and process need to accurately controlled to achieve a RFT shade. Any one among them can the cause for a not RFT shade. But this process and process parameters may vary in different industries. This experiment was carried out in a medium quality exhaust dyeing unit. Form the working experience in this industry, it was summarized in 22 points, controlling these can be achieved the RFT shade. These were based on existing problems and improper utilization of 3M (Man, Materials and Methods). The summarized points are mentioned and described at below:

1. Increasing lab to bulk reproducibility
2. Dyeing Recipe should be done computerized to avoid calculation mistake, to save time
3. The dyes, chemicals measuring balance must be digital and must need to calibrate at least twice in a month to get the accurate reading
4. The dyes and chemicals quality have to check after receiving a new LC in lot to lot and several drums to drums
5. After H_2O_2 Killing it must need to check either it has removed or not by H_2O_2 killing test kit/strip
6. The fabric absorbency after scouring should check with the 0.5% Potassium Permanganate Solution to observe easily as a full full circle
7. Water Hardness in the all the dyeing process, especially in dye bath must need below 50 ppm
8. The temperature of the M/C should check often by Temperature Gun during dyeing process, because temperature sometimes vary from program monitor to M/C inside
9. Liquor ratio must be controlled in every batch
10. The fabric core pH should be measured especially for light & critical Colors to better fixation
11. Grey fabrics shades should be checked before loading into M/C, because sometimes it varies.
12. Dyes, chemicals TDS & MSDS must have to analyze accurately by the R &D department always and compare with required properties.
13. Neutralization after scouring and B/D must be accurate within a pH of 6.5-6.8
14. Cycle time of the fabric must have to maintain strictly, such as 2.30 min to 2.45 min for light & critical colors
15. Dissolve the dyes perfectly.
16. Soda & Color dosing must have to give according individual rules of different shades. Generally three steps (progressive system) soda dosing is best for light & critical color.
17. Have to avoid the dye bath addition specially in the first Batch.
18. The shade matching decision must be provided by the technical person only.
19. Wash off after B/D, Hot wash, fixing must clear as there has no any colored water.
20. Right combination selection of shade is most important.
21. The maintenance section must provide the minimum M/C breakdown during running and provide best M/C parameters.
22. Finally a good housekeeping should be controlled in all over the dye house.

13.5.12 The practical reasons & remedies against the 22 points

I have summarized the above mentioned points to achieve RFT shade because I have faced these types of problems during practical working. So the reasons and remedies are explained in brief below:

1. **Increasing the lab to bulk reproducibility**

Assuming the above factors are well controlled, actual lab practice is another factor which can seriously impact RFT and lab to bulk reproducibility. Quite often, lab dyeing is carried out on pre-bleached, dry fabric, which can lead to immediate errors, both from a liquor ratio and from a dye concentration point of view. In bulk practice, we may start with grey fabric, which can contain up to 10% impurities. After pre-treatment, a 100 kg batch can actually weight as little as 90 kg. However, everything is calculated for 100 kg –dye, salt, alkali, etc. If we start in the lab with dry pre-bleached fabric and base all calculations on this, we have immediate errors – exacerbated if impurity level is high. Ideal lab practice is to take customer's grey fabric and cut into, say, 10 g portions; then bleach and dry (check weight to confirm amount of impurities – if say 9.5 g, you know that fabric contains 5% waxes etc) and then carry out the lab dyeing on this fabric assuming the original weight of 10 g. An alternative method is to check quantity of impurities first – and then if impurities are say6%, use 9.4 g of dry pre-bleached fabric for your lab dyeing instead of 10 g, but still basing all your calculations on 9.4 g. so it is mandatory to consider the following factors before start lab dip dyeing:

- Fabric must be same of both lab and dyeing (yarn lot, yarn count, fabric G.S.M, separate Scouring).
- The fabric must be RFD before start dyeing.
- Accurate weight in calculation of fabric due to bleached fabric in lab and grey fabric in bulk.
- Dyeing process should be same (usually All in one dyeing method in lab, progressive method and isothermal method in bulk).
- Should use the same chemicals in both lab and bulk (such as sequestering agent, leveling agent, fixing agent, softener etc.).
- Fabric is 60 minutes in dye solution in lab, but in bulk after 2.30-3.0 minutes fabric touches dyes solution once. Where say for example 2.0-2.15 minutes in solution and rest seconds is without touches dye solution.
- Dyes, chemical and auxiliaries must be of same lot
- The Lab Dips must be matched under at least 2 Light Source.

❖ **The Fabrics used for lab dip dyeing should be collected from the same fabric which will be provided during bulk production**:

In the knit manufacturing industries there is a practical phenomenon that sometimes the fabric is different from Lab Dip to Bulk Production Fabric. The fact is when swatch is match first time to send for approval then it is done from available fabric in the Lab. And when the lab dip is approved as well as the order is confirmed then the swatches are to re match with the approval Shade. This time the available fabrics are used again. But the problem is the Bulk Fabric is not same as the available fabrics. Because of the following parameters:

a. Yarn lot
b. Yarn count

c. Yarn type (Card/Comb)
d. Properties of yarn (TPI, TM, Natural color, dead cotton, matured fibre, cellulose, protein, pectin etc.)
e. S.L of the fabric
f. Scouring & Bleaching quality of Fabric

So if any parameter of above is different then there is a great possibility to shade variation. Actually it is very difficult to ensure the same quality of yarn and fabric parameters before getting any orders. But this can be done easily to ensure the same yarn, fabric and scouring-bleaching quality during re-checking the lab dip before going to bulk production by collecting the scoured sample during sample dyeing for Pre production sample approval.

- **Cotton yarn quality test**

It is unfortunately true that we never test quality of yarn through which we dye a fabric. In several times we faced problems related yarn that we should check from the yarn supplier. The problems arise from poor quality of yarn are such as thick-thin , patta, dead cotton, yarn contamination, spirality or skewness problem and G.S.M problem for count variation . It was tested for several yarn counts and observed for some cones, there were 0.8-1.1 count variations between the actual and tested sample. All these problems are mostly visible after dyeing. So if any of these occurred, there is nothing to do immediately. Hench it is mandatory to test the minimum standard quality of yarn or at least the collect the test report from the supplier in every L/C to arise these problems. Otherwise again the poor yarn quality will also affect the RFT shade. The standard quality parameters of combed cotton yarn for knit dyeing is shown in table 13:

Table 13: Standard quality parameters of combed cotton yarn for Knit Dyeing

Yarn Characteristic	Required value for 30s combed	Other combed counts
Average count	30(29.6 to 30.4)	Nominal count plus or minus1.3%
Count C.V%	Less than 1.5	Less than 1.5%
Twist Multiplier (T.M)	3.5 to 3.6	3.5 to 3.6
TPI C.V%	Less than 2.5	Less than2.5%
U%	9.2 to 9.8	50 to 10% uster stat. value
-50% thin place /100m	Less than4	5to 10% uster stat. value
-30% thin place /100m	Less than650	5to 10% uster stat. value
+50% thick place /100m	Less than30	5to 10% uster stat. value
+200 Neps/100m	Less than50	5to 10% uster stat. value
Total imperfection/100m	Less than85	5to 10% uster stat. value
RKM(tenacity)gms/tex	More than16.5	More than16.5
RKM c.v%	Less than7.5	5to 10% uster stat. value
Elongation %	More than 5.5	More than 5.5
Hairiness H	4.0 to 4.5	<50% value of uster statistics
Hairiness standard deviation	Less than 1.5	25% uster stat value
Objectionable classimat faults(both short and long)	Less than 1per 100km	Less than 1 per 100km
Total classimat faults	Less than150	5 to 10% uster stat.value
H1-thin faults	Less than 5per 100km	5 to 10% uster stat.value
Shade variation on cones in UV lamp	No shade variation	No shade variation

- **The Lab Dips must be matched under at least 2 Light Source**:

Generally the lab dip is matched under one light source. Sometimes it creates a lot of problem in shade matching between Manufacturing Unit and The Buyer. Because they can match the shade in their available light source or without any light source or normally in the office room. As a result the lab dip may not be matched sometimes as their requirements. Most of the cases the buyer provide the light source to match the colors. Generally they recommend one light source. In spite of this we should match the lab under two light sources for our benefit. So the shade will be closer and the less chance to metamerism. The Lab Dip Recheck must be between the Original swatch and the Approval swatch. Then the Bulk Production Reproducibility will be efficient in bath to batch. DE value must keep within 0.5

- **The fabric must be RFD before start dyeing**

The Ready For Dyeing (RFD) fabric must have following criteria:

a. pH
b. Absorbency power
c. Residual H_2O_2
d. Degree of whiteness
e. Hairiness

The most important criteria of a RFD fabric is good absorbency power. Because if the fabric has not good absorbency power, it cannot absorb the further chemicals and specially the Dye stuffs. So better shade cannot accept from less absorbable fabric. There are several tests to check the absorbency of a scoured-bleached fabric. Among them the drop test is widely used around the industries. But 0.1% potassium permanganate solution gives preferable result instead of water. As a result the circle is clearer easily (One drop is suggested).

Another important criteria of a RFD fabric is having good degree of whiteness. Because the degree of whiteness depends specially on the removal of natural color. The fabric which natural color does not remove fully there is yellowish tone present in the fabric. This is absolutely against in case of light colors dyeing as well as the critical color also. Hence the more the degree of whiteness the better shade reproducibility is achievable. It depends on the quality of H_2O_2 purity %. In general there are both 35% and 50% purity available in the market. But it should test the quality of H_2O_2 in the laboratory.

Hairiness is an optional criterion for a RFD fabric as it depends on the Buyer requirements. But it is found practically the shade is more even, smooth and shining of a good hairiness removal fabric. But in this case the softness is less.

2. Dyeing Recipe should be done computerized to avoid calculation mistake, to save time.

Most of the industries do the dyeing recipe manually. As a result the following problems are to face:

a. Writing mistake
b. Dosing mistake
c. Calculation mistake
d. Incomplete digit
e. Time killing

First three points are vital issue to complete a dyeing recipe. If any one of these are mistaken that may be a great problem for any shade matching. Such as if the dyes, chemical name is wrong it will be rejection of fabric. Sometimes the recipe man mistakes the common dosing of chemicals, which can damage the fabric. The mistake of calculation is very dangerous for doing recipe manually. It can provide any kind of problem in the desired shade.

The calculated digits are maintained with negligence in case of both dyes and chemicals. But there are some chemicals which can effect adversely due to more/less quantity. Especially for dyes it will impact greatly due to more/less quantity.

All of this can hamper the shade matching easily. There is another fact that the recipe man think that he takes the more digits which is very little amount. But it is analyzed that there is huge amount of dyes chemicals we can save monthly as well as yearly due to taking the right digits of dyes, chemicals consumption. It is also very time consuming to do the recipe manually. Whereas computerized recipe making will save the time as well as manpower. Because one person is enough to do computerized recipe against three to four.

3. The dyes, Chemicals measuring balance must be digital and must need to calibrate at least twice in a month to get the accurate reading.

The measuring balance is an important issue in a dye house to measure the dyes, chemical to produce a RFT shade. There are several types of measuring balance. Among them the digital balance is more preferable to measure accurately. But most of the industries do not calibrate the balance timely. For which the dyes, chemical amount vary. It is analyzed in our industries sometimes it varies 50 gm – 160 gm of each 1 kg of product. As a result it can be a barrier to produce the RFT shade. Measurement variation mostly effect on dyes. If there is a little amount of variation in dyes measuring that may the cause of shade variation. So the calibration of measuring balance is hardly needed for a dye house.

4. The Dyes and Chemicals Quality have to check after receiving a new L/C in lot to lot and several drums to drums.

Dyes and chemicals quality must be tested in the laboratory of manufacturing industries. It should test the quality of each new LC product. The reference quality report or Technical Data sheet should have in hand to compare the tested result. It is analyzed that sometimes the Dyeing shade varies due to the strength difference between the running and new coming LC dyes. But this can be adjusted by doing the related tests before going through the new Dyes in production. It is also suggested to test the strength and other qualities from lot to lot for each new LC. Because sometimes it varies the strength even in lot to lot. This will be a silent reason of shade matching problems. Sometimes for this problem the batch need to addition and topping. The following tests can be done for each new LC Dye Stuff quality check:

a. Single shade matching (1%, 2%, and 4%) and compare with reference visually.
b. Measure the DE value of the single with the saved standard by Spectrophotometer.
c. Measure the strength difference% of single shade from dyed fabric sample.
d. Measure the fixation % from the dye solution after B/D by liquid measurement etc.

New Chemicals quality check:

1. pH
2. Specific Gravity
3. Hardness
4. Strength
5. Purity etc.

5. After H_2O_2 Killing it must need to check either it has removed or not by H_2O_2 killing test kit/strip.

After scouring and bleaching with Hydrogen peroxide a peroxide killer is used. Otherwise there is yellowish tone on the fabric. Whether a fabric is free from Hydrogen peroxide this can be tested by using a simple per oxide killer test strip. The value is acceptable up to 0.5 mg/l.

Figure 41: Peroxide test strip

6. The fabric absorbency after scouring should check with the 0.5% Potassium Permanganate solution to observe easily as a full circle.

The quality of scoured fabric must need to check accurately. Because without well scouring, the further process will be affected and may cause for against RFT. Scouring test can be tested by the following test methods:

1. Immersion Test
2. Drop Test Method
3. Column Test Method

Among these the Drop Test method is widely used due to its simplicity & short time. It can be test by water drop. If the drop on the fabric is a full circle, then the scouring quality is excellent. But only the water Drop is not clear to understand. In this case 0.5% solution of Potassium permanganate can be used to identify the circle clearly.

7. Water Hardness in the all the dyeing process, especially in dye bath must need below 50 ppm.

Hardness must be checked of raw water every day. Water treatment Plant should be installed before set up a dyeing unit for good dyeing performance. If the Hardness is controlled the following advantages will be added to the dyed batch:

- Prevention of pinhole formation due to catalytic oxidation caused by iron during bleaching) chelates iron / heavy metals)
- During dyeing, it prevents spots, shade change and uneven less by chelating heavy metals and dispersing impurities.
- Provides improved fixation level of dyes.
- Improved rinsing due to the scale inhibition(effective at low concentration such as in rinse bath)
- During fabric preparation sequester also provides iron chelating to prevents fabric / yarn damage and provides additional stabilizing effect on the hydrogen peroxide.

To control the hardness of water have to follow the following process:

- Raw water hardness must need to test
- Hardness of the scouring bath has to test.
- Hardness of the dye bath before dye stuffs dosing including the salts and leveling need to test.
- In the laboratory this work can be done randomly until setting the dosing of chelating agent. It can be repeated on different salt and soda dosing ratio.
- Use suitable chelating agent in all the dyeing process (Scouring, enzyme, dyeing, softener etc).

Special care of dyeing water

- We in general talk about the hardness of water in scouring, dye bath or after treatment. But there are some crucial processes where we neglect the hardness, such as during dye dissolving in the drums for long time before dosing in the machine. And this dissolving process is observed in the medium quality dye house. Here, if there are metal ions in that dissolving water they will react with the anionic reactive dyes, thus create ionic bonds. i.e. that will be the aggregation of dye stuffs. So it is very important to use chelating agent in the dissolving drums as well as in the mixture tanks on a required amount. Some leveling agent can also be used for better result.

- Another important process which we neglect generally, that is during addition we most of all forget about the hardness of water. Because when we drain some liquor from dye bath before addition, then we need to fill by fresh water at required amount. But we don't use chelating agent to control hardness of the dye bath. Again when we give dosing of addition's color, we don't think about the hardness of the mixture tank.
- Before softener dosing if we add chelating agent or other water softening process to control water hardness, it was observed there was got best softness quality also.

So in these cases the water hardness must need to control for better fixation as well as softness quality.

8. The temperature of the M/C should check often by temperature Gun during the process:

The temperature may change during process from set up in the machine. Suppose we set the process temperature 60'c in the program, but actually the temperature inside the machine may vary to 58'c or 62'c. So this variation should be checked by using a temperature gun. Which help to measure the inside temperature of the machine during any process. Some machines might take a longer period of time to reach the temperature required. These should be monitored and adjusted so that the required time to reach the right temperature is maintained. Check frequently the calibration of the thermometer or temperature gun. Maintaining the correct temperature for every process is very important. Dyes, enzymes and some inorganic chemical treatment too require specific temperature. Maintaining the correct temperature gives better repetitive results.

The above mentioned parameters are considered very important for Right First Time dyeing concept. Usually, at first, test dyeing for color matching is conducted in a laboratory, and the data thus gained is important for reproducibility in practical dyeing because it is used to decide the practical dyeing conditions. It is difficult to perfectly reproduce the dyeing conditions of the laboratory in practice, but it is important to try to get them as close as possible.


Figure 42: Digital laser temperature gun

9. Liquor ratio must be controlled in every batch.

The correct liquor ratio for the recipe must be maintained otherwise incorrect concentrations of dyes and other chemicals will be present in the dye bath and the right shade will not be achieved first time. The water gauges should be clean so that they can be easily read and should be monitored at each step during the entire dyeing process.

The liquor ratio will be altered when extra water is added to mix the dyes, the salt and the alkali. This should be factored into the liquor ratio in the recipe, i.e. if a total of 1000 L is needed but 50 L of caustic soda will be added, then the volume of water initially put in the dye bath should be 950 L. At lower liquor ratios, there is Higher exhaustion, and Higher color strength. So it is mandatory to maintain the total liquor ratio after adding dyes, salt and alkali in the process and control batch to batch.

10. The fabric core pH should be measured especially for light & critical Colors to better fixation.

For better fixation of cellulosic fabric it must have the core pH 5.5-6.0 before starting dyeing. So after scouring the fabric must be neutralized well. And it should check the pH after leveling dosing. Dyeing should be started at neutral pH. Otherwise if the pH is higher at starting point then fixation will start earlier before exhaustion. As a result uneven dyeing occurs.

❖ **Influence of pH in reactive dyeing at every stage of dyeing**

- In the beginning of dyeing, the water bath should be carefully adjusted to a neutral to slightly acidic pH, as otherwise premature hydrolysis of dyestuff will take place and cause (a) uneven dyeing and (b) lighter depths than the previous batches or in other words batch to batch variation will occur.
- If the fabric or yarn has not been neutralized properly the core alkali presence will adversely affect the dyeing, forming patchy uneven dyeing. The places were alkali residue was high have the tendency to make deeper dyeing.
- Lower alkali dosages and hence lower pH leads to partial reaction of reactive dyes; most of the dye may remain in water; the dyestuff that has got absorbed in to the fiber would also have less tendency to get fixed on to it, leading to poor washing and rubbing fastness.
- Higher dosage of alkali may cause hydrolysis of dyestuff in the water itself. Thus lower depth of shade and poor washing and rubbing fastness.
- After dyeing is over, when the alkali still fully remain on the fiber, if we do not neutralize the alkali properly with adequate quantity of acid, that also leads to higher amount of dyestuff

bleeding during subsequent soaping and hot wash operations.

- Finally after completing the dyeing, before unloading, if we do not keep the pH neutral - alkaline pH will slowly hydrolyze the dyestuff in the fiber and acid pH will tender the cotton fiber itself.
- Every dyestuff appears in different tone under different pH conditions. Bright Lemon yellow, if allowed dry under alkaline pH, it will turn to a dull redder yellow and similarly Turquoise blues and royal blues will appear yellowier and duller in alkaline pH and brighter and redder in acidic pH. So make sure that the pH is exactly neutral or slightly acidic during final drying process.
- Final cationic fixation and cationic softening treatment if not done in acidic pH, that will leave higher tonal changes and improper dye fixation and improper softening effect.

Figure 43: Digital electronic pH meter

11. Grey fabrics shades should be checked before loading into M/C.
It plays a very important role in shade variation after dyeing if the grey fabric shade is not checked properly. We observed for several times that there is a lot of variation in shades of grey fabrics in roll to roll. It can easily occur when yarn lot is mixed up or yarn count is mixed up. But this should be checked before loading into dyeing Machine. Then different shades should be separated.

12. Dyes, chemicals TDS & MSDS must have to analyze accurately by the R &D Department always and Test the Dyes, Chemicals Required Properties.
The technical data sheet (TDS) and Material safety data sheet (MSDS) must have to collect from every supplier of dyes, chemical. Then check the properties by in-house laboratory testing and compare the standard properties in the TDS. Adjust the chemicals and auxiliaries dosing keeping relation with the optimum recommended dosing by the manufacture. Store the dyes, chemical and auxiliaries maintaining the best storage condition, safe area according to MSDS. The life time of chemicals and auxiliaries should find out from the TDS and maintain to get the best quality. Such as in general the life time of enzyme is 6 months, so after exceeding its activity will reduce.

13. Neutralization after scouring and B/D must be accurate within a pH of 6.5-6.8
Scouring and bleaching was carried out in highly alkaline media at pH 10.5-11.0. If this alkaline media is neutralized then it will hardly affect the further process especially in dyeing. Such as uneven dyeing, color spots etc. and if the fabric is not neutralized after B/D, there will further possibility to fixation of unfixed des deposited on fabric surface. Hence again it will cause for uneven, running shade problems. So it is mandatory to neutralize the fabric after scouring and B/D at a pH 6.5-6.8

14. Cycle time of the fabric must have to maintain strictly, such as 2.30 min to 2.45 min for light & critical colors.

Uneven dyeing is a very common dyeing fault and a great headache for the dyers. Too much difficulty has to be faced in maintain a required degree of levelness of the dyed goods. Knitted goods are usually dyes in loop or a Continuous rope from in which or jet dyeing machine.

The time required to move the whole loop is termed as cycle time .In exhaust dyeing method cycle time is important factor. If the integer of movement of the loop can be ensured during each dosing and run time then every portion of the rope will get same time to stay in the liquor contact. No. of contracts is the number of time of which the fabric comes into contact with the dye; liquor during dyeing process. This will depend on the fabric rope speed and number of jet nozzles passages. In consequence each portion of the loop will absorb the same amount of dyestuffs. To ensure the uniform dyeing one should calculate the maximum rope length with a fabric of particular weight per square meter and rope speed has to maintain the same rope length. Cycle time was determined by the following equation.

$$\text{Cycle time, } t = \frac{k}{w \times v}$$

Where

k= Load per nozzle in kg.
w= wt of one meter fabric (open width) in kg
v= velocity (reel speed) in m/min

- **Dosing time:**

Dosing time is the term used to denote the time required in minute for transferring the dyes or chemicals from the addition tank to the interior of the machine.

- **Runtime:**

After any dyes or chemical dosing the fabric needs some time to absorb that dyes or chemical before another chemical dosing this time is usually known as run time in the textile wet processing industries.

$$\text{The linear weight per linear yard (lbs)} = \frac{N \times L \times CPI \times 36}{36 \times 840 \times Ne}$$

Where,
N= Number of needles in the machine
L=stitch length in inches
CPI= courses per inches
Ne=cotton count
For the simplification of the calculation the following formula can also be used:

$$= \frac{\text{Open width of the fabric in inch} \times \text{Grey G.S.M} \times \text{Wt of 1 meter fabric in kg}}{39.37 \times 1000}$$

$$\text{Loop length in meter} = \frac{\text{Load per nozzle in kg}}{\text{Wt of 1-meter fabric in kg}}\ \text{m}$$

- **Importance of Cycle time**

Say for example cycle time of a batch is 3.0 minutes. And the color dosing, salt dosing, run time, soda dosing are fixed without considering the cycle time. If the reel speed is 300 m/min, so the following will occur:

Color dosing =28 min=3x9+1
Color run time=23 min=3x7+2
½ salt dosing =10 min=3x3+1
Run time =5 min=3x1+2
½ salt dosing =10 min=3x3+1
Run time =10 min=3x3+1
Soda dosing =50min =3x16+2

From the above expression it is observed that during color dosing the whole loop in a nozzle will travel 9 times in 27 min and remaining 1 min only 300 m of the whole loop will travel in the nozzle. On the other hand during color run time the loop will travel 7 times in 21 min and in remaining 2 min only 600m of the whole loop will travel in the nozzle. So these 300m and 600m of the loop will get more time to absorb dyes stuff. So dye absorption will uneven throughout the whole loop. In the same way during every dosing and run time the loop will travel a fractional on of turns through the liquor which will cause uneven absorption and uneven fixation. Finally uneven dyeing will result in.

But when each dosing & run time is selected considering the cycle time which is described below:
Color dosing =27 min=3x9
Color run time=18 min=3x6
½ salt dosing =15 min=3x5
Run time =9 min=3x3
½ salt dosing =9 min=3x3
Run time =15 min=3x5
Soda dosing =45min =3x15

From the above expression it is observed that during color dosing the whole loop in a nozzle will travel 9 times in 27 min and there is no remaining fabric. On the other hand during color run time the loop will travel 6 times in 18 min and there is no remaining fabric also. So dye absorption will even throughout the whole loop. In the same way during every dosing and run time the loop will travel a full of turns through the liquor which will cause even absorption and even fixation. Finally even dyeing will result in.

It can be concluded from this research work that by selecting each dosing and run time as the multiple of the cycle time, uneven dyeing of the knitted goods can be reduced dramatically.

15. Dissolve the dyes perfectly before start dosing

Dissolving process and temperature varies in different types of dye stuffs and companies. But the target is same to dissolve the dyes before start dosing. In general the temperature is used at 80°c hot water. And the process can be highlighted that firstly make a paste of high density of dyes with less water. Then slowly add water with continuous stirring. Use some amount of chelating agent and leveling agent in the dissolving drums. Finally turn the mixture motor of tank and again use steam water. The solubility of dye stuffs can be tested as described in 4.2.5 (Solubility test of dye stuffs).

We know turquoise is hot brand dye stuff. So it needs near boiling temperature to dissolve it. Industrially we are familiar with a common term “migration’’ means transfer to another form previous. We normally use the migration process to dye a turquoise color. Actually this is nothing but the dye solubility. To dissolve the color perfectly we use this migration, generally 60°c to 80°c. from experience we observed for several times that in spite of doing migration there are some dye spots on the fabric surface, which is due to dyes coagulation.i.e there the dye stuffs have not dissolved perfectly yet. In this case we again increase the temperature form 80°c to 90°c and run for 20 to 30 minutes. Finally those dye spots remove dramatically. In fact there were dye dissolve problems. The actual dissolve process of independent dyes of different companies may be different, that should collect from the supplier or the direct manufacturer.

16. Soda & Color Dosing must have to give according individual rules of different shades. Generally progressive dosing is best for light & critical color.

Actually the color and soda dosing depends on affinity of the dye stuff to the substrate. Dyes of lower affinity, there is no need to give soda dosing at long time. But in case of higher affinity/reactivity of dyes, it should set the soda dosing for long time. Otherwise there will have possibilities of immature dye fixation. So before set the dosing time of color, salt and soda we have to know the functional groups of the used dyes as well as the affinity or reactivity of that dyes. Reactivity properties of major reactive dyes are given below:

Table 14: Properties of major reactive dyes

Sl No.	Functional Group	Commercial Name	Reactivity	Exhaust Dyeing Temp.(°c)	Dosing Time of salt, color and soda
1	Dichlorotriazine (DCT)	Procion MX (Zeneca)	high	25-40	less
2	Monochlorotriazine (MCT)	Procion H (Zeneca) Procion EXL (Zeneca) Basilen (BASF) Cibacron C (Ciba)	low	80-85	more
3	Monoflurotriazine (MFT)	Cibacron F (Ciba)	Moderate	40-60	medium
4	Diflurochloropyrimidine (DFCP)	Drimarine K (Clarient) Levafix E-A (Dystar) Levafix P-A (Dystar)	Moderate to high	30-50	medium
5	Dichloroquinoxaline (DCQ)	Levafix E (Dystar/Bayer)	moderate	50-70	medium
6	Vinyl sulphone (V.S)	Remazol (Dystar)	Moderate to low	40-60	more
7	Trichloropyrimidine (TCP)	Drimarine X (Clarient) Cibacron T (Ciba)	low	80-95	more

However industrially the following two rules of progressive dosing follow for dosing color and soda for best results:

1st Rule
1/10th part at 40’c for 15 min (set by cycle time)
Run time 5 min
3/10th part at 40’c for 15 min (set by cycle time)
Run time 5 min
6/10tth part at 40’c for 15 min (set by cycle time)
Run time 15 min
Check shade

2nd Rule
20% at 40’c for 15 min (set by cycle time)
Run time 5 min
30% at 40’c for 15 min (set by cycle time)
Run time 5 min
50% at 40’c for 15 min (set by cycle time)
Run time 15 min
Check shade

And the salt is given in portion wise dosing:
1st portion in 15 min
Run time 5 min
2nd portion in 10 min
Run time 5 min

17. Have to avoid the dye bath addition specially in the first Batch.

Dye bath addition should strictly avoid getting a good quality dyed fabric. Because we know that dyeing must start under neutral pH to prevent immature fixation. This causes uneven running shade or other dyeing faults. But in the dye bath already there are alkaline media, so addition of any color may cause uneven dyeing, color spot, running shade etc. so if the shade is lighter or tonally different, which needs to add some color, there it is better to add some. This will increase the exhaustion. If it is not enough and it must need to further addition of color, then firstly it is better to drain the dye bath solution almost half and take the warm water by heating and dosing system. So the alkali pH will reduce some. Now one can add some color, but still is risky. However without drain some or half of the dye bath solution it is hardly advisable for not add any color during dyeing. Especially in the first batch it is not allowed to give addition in dye bath. It is suggested to find out the lab to bulk co-relation and when one can know it, that will play at advantage to set the correlation between lab to bulk and also it will be easier to do recipe correction before dying.

18. The shade matching decision must be provided by the technical person only.

There are lots of technical parameters which effect the color or shade variation. So the shade matching person should minimum technical to understand the parameters and also to apply these practically. Some the parameters are given below:

- **Previous experience**

Experienced person knows the color tolerance very well. This experience may vary according to educational background also. Such as for a non technical person there should be at least 10-12 years experience in the dyeing shade matching job. Whereas 4- 5 years for B.Sc eng in textile a 6-8 years for Diploma engg,.in textile.

- **Age**

The more age, there is a possibility of observe more red in the shade. Older people see redder tone in shades. When there is an older worker in a dye house, his colleagues make fun of him saying that he has developed red eye.

- **Background effects**

During the shade difference assessment, It is extremely important that proper light box with proper grey color is used because it affect on color judgment of the person. It is normally observed that color of light cabinet is faded with the use and never repainted to bring to original color which reflects around 30% light. The appearance of a color is influenced by surrounding colors. If we place the same color against different background colors, the color will look different in each case. In addition a color appears lighter when surrounded by a dark background than when surrounded by light background. This color vision effect is called chromatic induction trust.

We can experience one color vision effect byl converging half a sheet of brightly colored paper with plain white paper. If we stare at the colored area for about 30 second s and then remove the white paper. It seems lighter because our eyes adapt to color such a visual effect is called chromatic adaption. If we look at a colored image for about 30 second and then look at a white surface we see an afterimage. The afterimage has the same shape as the original image but different colors. Where the image green the afterimage will be red. Blue areas become yellow and yellow areas become blue. Black and white also reverses.

❖ Opacity (Sample thickness)

It is important that fabric is opaque (non- transparent). So that background color doesn’t influence the object color. If a sample it too thin you can make it opaque giving many folds to the sample.

❖ G.S.M

The sample shade, one wants to match can vary, when its G.S.M is different with the required shade. So it should make sure before matching a shade that the G.S.M of both sample and target shade’s fabric is of same G.S.M

❖ Fabric type

A shade can also vary due to fabric types. Such as a shade of same color %, the single jersey fabric will be lighter than single lacost or interlock fabric about 15%. So in case of a same color in different fabric types are observed then the recipe done for single jersey should reduce all over 15% in lacost fabric, gradually reduce 15-20% in Interlock fabric and 5-10% for rib. These are only for deep colors. And in case of light color it may needs to reduce a little or not.

❖ Orientation (Sample Positioning)

Since fabric’s warp or weft direction (in woven) or Wales and courses (in knits) have a different look thus color appearance could be different when fabric direction /Orientation is change . It is important to decide one orientation for all samples which require color assessment.

❖ Shade change in long time

The standard or required shade with which the sample has to be matched should not collect for long time like 20 days – one month. Because it is observed that most of the cases the person who match the shade, he matched a shade correctly with the available standard sample. But when it goes to finishing section it does not match with their standard. The reason, in dyeing section where the color is matched, there the standard sample is most of the time is under light and it is handled frequently to match a shade. So after every 15 days at least the standard sample should be changed it will be a great advantage during shade matching, especially in the case of white. This same procedure should follow of lab swatch.

❖ Right Viewing Techniques

During the shade assessment it is important to consider several points so that accuracy of color different to consider several points so that accuracy of color different is ensured.

- Samples should be placed side by side and the center of light box
- Light Box should be placed at such a height so that the viewing angle is around 45° degree.
- Don’t use tinted eyeglass or contact lenses
- The person who is checking shade difference should not wear bright clothing and no bright nail polish

- When sample and standard are of different size, it is useful to make rectangular holes on grey card to evaluate color difference otherwise these two shades will look very different because of different sizes.

19. Wash off after B/D, Hot wash, fixing must clear as there has no any colored water.

After B/D (Bath drain of color steam) of any batch, it needs to rinse and wash for several times, especially for deep and critical color (where the color% of each dye is almost same or near). Otherwise the unfixed and hydrolyzed dyes will remain on the fabric surface, which will create problem in further process. Such as if without clear the B/D wash, it is given the fixing agent o any batch there is possibilities of running shade problem. And it also causes for poor rubbing fastness. Rubbing and wash fastness also occurs due to poor Ht wash as well as poor wash off after hot wash. Again the running shade may occur when there is not clear wash off after fixing agent.

20. Right Combination selection of shade

The selection of reactive dyestuff for a tri-chromatic or bi-chromatic combination plays a very important role in the performance and reproducibility of reactive dyeing in textile processing. The following points are to be borne in mind, while selecting the dyestuff for a combination shade.

Solubility of individual dyestuff in grams liter without salt (straight) and with salt should be checked prior to dye selection for a combination shade. In a tri-chromatic combination, all the dyes should have almost similar solubility property. The dyestuff that gets affected by the presence of salt would, a) produce tonally different shade, b) produce poor rubbing and wash fast dyeing and c) batch to batch difference in depth and tone would result.

Some important Criteria to be considered while selecting dyestuffs for a tri-chromatic matching:

- **Use of Primary colors**

One should try to use the Basic Colors such as Red, G.Yellow and Blue. The secondary colors should be avoided as far as possible. The Red's and Blue's varies with shade and requirement of fastness properties.
Such as in Ornage shade, the right combination is, orange + yellow or orange + red. But it should avoid orange + red + yellow. There should be possibility of running shade.

- **Dyes with similar exhaustion and fixation values**

  The Reactive dyeing takes place in three steps:

1. Exhaustion (primary and secondary)
2. Fixation
3. Wash off

Primary Exhaustion is the amount of dyestuff migrated on the substrate in the presence of salt. While secondary exhaustion is the total amount of dye migrated on the substrate in the presence of salt and alkali.
While selecting a combination, one has to ensure that the Percentage Exhaustion (PE) and The Percentage Fixation (PF) of dyes should be similar.
In the case of

Reactive ME Dyes	PE is 60 to 70%
Reactive HE dyes	PE is 70 to 80%
Reactive VS dyes	PE is 40 to 50%

If is always preferable to use dyes with PE about 60 to 70%, i.e., ME dyes. Patchy dyeing may occur if proper care is not taken while using dyes with higher PE, or lower PE.

- **Dyes with similar affinity**
  Generally the dyes are classified as Low, Medium, High and Very High affinity dyes. For Exhaust dyeing, High and very high affinity dyes are preferred. Whereas low affinity dyes are used in continuous dyeing.

21. The maintenance section must provide the minimum M/C breakdown during running.

The maintenance section should have good schedule maintenance and preventive maintenance program and should maintain accurately. They should provide the accurate machine parameters. Such as reel speed, pump speed, temperature grading in both monitor and machine. Machine breakdown during soda dosing, color steam will cause dyeing faults. Also the machine parameters variation also causes dyeing faults.

Machine: Winch Dyeing Machines

Table 15: Mechanical check points for a winch dyeing machine

Sl No.	Item need to be checked & Serviced
01	Crease the winch bearing.
02	Complete cleaning of machine
03	Cleaning of drain valves, replace seals if required
04	Check air supply filter, regulators, and auto drain seals
05	Clean filters element and blow out
06	Greasing of Unloading Roller Bearings.
07	Checking of oil level and bolts of Unloading Roller Gearbox.
08	Checking of unloading roller coupling and packing.
09	Checking and cleaning (if required) of Min Vessel Level Indicator
11	Check the oil level of pump bearing and refill if required.
12	Check the function of heat and cool modulating valves
13	Check all belts and belt tension
14	Check all door seals

Table 16: Electrical check points for a winch dyeing machine

SI. No.	Items need to be checked & Serviced
1	Check & clean fluff and dirt at all motor fan covers
2	Check all motors terminals
3	Check min panels (by using compressed air)
4	Check panel cooling fan & clean it filter
5	Clean main pump inverter and its cooling fan
6	Check all circuit breaker, magnetic contractors and relays
7	Check current setting of all circuit breaker & motor over loads.
8	Visual checking of all power & control cables
9	Check DC drive of reel motors
10	Check all pressure switches
11	Check calibration of main vessel & all additional tank
12	Check all pneumatic solenoids
13	Check calibration of heating/cooling. Modulating value
14	Check setting of tangle sensor.
15	Check setting & operation of lid safety switches
16	Check all emergency Switches

17	Check all indicating lamps
18	Check all on/off switches
19	Check all signal isolators
20	Check key pad & display of controller

- **Dyeing m/c maintenance Schedule:**

Daily:

- Check belt tension
- Check steam or water system & air supply
- Check chemical pump
- Machine clean

Weekly:

- Bearing & belt check
- Check leakage of air, steam &
- Water line
- Greasing bearing points
- Add gland packing at pump

Monthly:

- Greasing bearing points
- Replace bearing points (if required)
- Gasket check
- Clean steam trap
- Lubricating all chemical pump

Quarterly:

- Replace belts
- Repairing of pulley, shaft & bearing housing
- Painting m/c & pipe line
- Clean steam trap
- Replace seals (if leakage)
- Change gasket of steam of water lines

Half yearly:

- Replace belts
- Repairing pulley, shaft & bearing housing
- Painting m/c, pipe line
- Replace seals
- Machine body repairing

Yearly:

- Machine overhauling

Table 17: Yearly mechanical check points for a winch dyeing machine

SL No.	**Item needed to be checked & Serviced**
1.	Checking of Steam pipe lines
2.	Checking of pneumatic pressure valves
3.	Checking of belt conveyor system
4.	Checking of plaiting device
5.	Checking of speed regulating unit

22. Finally a good housekeeping should be controlled in all over the dye house.
Good housekeeping is a no or low cost way of improving efficiency and reducing costs. A good housekeeping can accelerate the RFT shade dyeing. To achieve a good housekeeping, the chemical store, Laboratory Batch section and Dyeing floor must follow a minimum standard. This will reduce very simple and general mistake that can effect dangerous in RFT Shade. A minimum standard is described for all the section related to RFT Shade.

❖ **Dyes, chemicals storage:**

- Provide MSDS of every Dyes and Chemicals in Local Language (Bangla) in chemical store
- Logbooks should be used to record when dyes come into the store and should be updated when dyes are used or replaced
- A sample of every new shipment of dye must be sent to the laboratory and tested before being used on the factory floor as each shipment may be slightly different.
- All the dyes, chemicals should identify with product label. Otherwise there is a possibility to use improper dyes, chemicals against one.

Figure 44: Goods without proper identification

Figure 45: Goods properly identified

Figure 46: Goods without Lot No.

- Industrially often we need repack the dyes and chemicals from original cartoon or drums for easier use. During this repackaging it should be identified properly like original. And the most important thing to cover the packet or drum properly. Otherwise the strength of chemicals and dyes may reduce a lot. Uptake of moisture makes reactive dyes and auxiliaries heavier and therefore an incorrect quantity of dye or auxiliaries can be measured out. In the case of dyes, this will reduce the effective depth of dyeing and result in the need for re-shading. Moisture can also accelerate the hydrolysis of reactive dyes, (when the dye reacts with hydrogen ions in the air) especially in warm conditions, which will also contribute to lower fixation because the dye becomes less reactive.

Figure 47: Repackaging of dyestuffs with the original labeling attached at their upper lid

Figure 48: Repackaging of dyestuffs without proper identification

- In a shade, there are generally more than one dye stuffs in the combination. During measuring these dyes we often measure all the dyes together. It should be separately measured.

Figure 49: Correct measure of dye stuffs

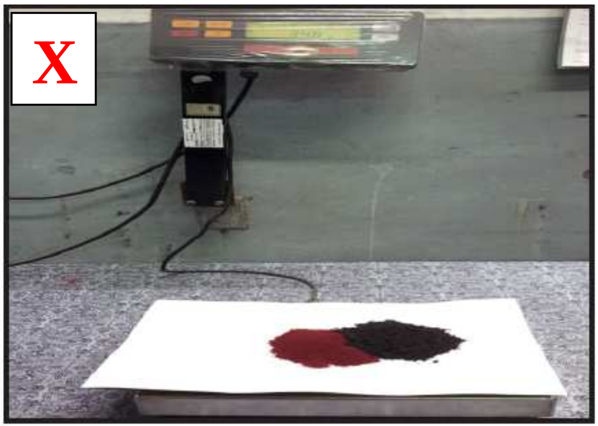

Figure 50: Incorrect measure of dyestuffs

- To measure the dyes, chemicals and auxiliaries we use mug and spoon. To achieve RFT shade there must be separate spoon and mug for individual dyes and chemicals. Because a little change in measure can change a shade. And these spoons or mugs should be also identified for specific goods.

Figure 51: Dyestuffs with separate spoon

Figure 52: Auxiliaries without their own spoon

- The measuring balance is very important factors for RFT shade. It should calibrate timely (at least twice in a year). It should be very neat and clean after every use for better measuring result. And it should be placed at a flat space.

Figure 53: Balance in a clean, dry and flat surface

Figure 54: Balance under inappropriate condition

- The dyestuffs should be stored in a conditioned room, according to MSDS storage.

Figure 55: Proper dyestuff storage

Figure 56: Improper dyestuff storage

- The liquid chemicals and solid chemicals must be segregated.

Figure 57: Liquid and solid chemicals stored segregated

Figure 58: Liquid and solid chemicals improperly stored

- Store the Dyes, Chemicals and auxiliaries at specific condition mentioned in MSDS/TDS. Enzyme and Dyes should be stored at room temperature.
- Check and use the dyes, chemicals according to its lifetime/validity mention in MSDS/TDS. In general the lifetime of Enzyme is only 6 months. If it is expired the validity then informs and discuss with Management as well as Supplier.

❖ Handling of Chemicals

The dyes and chemicals must be accurately weighed using appropriate scales to ensure the correct quantities for the recipe used. This must always be done, the bag weight must not be assumed. Instruments ideally should be calibrated every six months.

❖ No fabric on direct floor

No fabric should keep directly on the floor of both grey fabric store and dyeing. Plastic palate can be used to keep fabric. Because there are a lots impurities in the floor. They can attach with fabric, and among these any substance can color spot on fabric that can not remove. Most of these impurities come from dyes, chemicals handling.

❖ Use clean trolley to unload fabric

In this study we faced sometimes a problem of color spot deposited on fabric surface from the trolley. In case of light color, this can hamper dangerous. We had to stripping and re-dyeing some batches of light color for this problem. So it should carry the dyes on the dyeing floor very carefully, better to cover the drums during carrying. It should also ensure that no chemicals and auxiliaries left on dyeing floor by continuous cleaning the dyeing floor.

CHAPTER – 04
RESULTS AND DISCUSSION

14. Results and disscussion:

There are lots of findings we got from this experiment. All the experimented data are discussed below:

14.1 Calculation of dye Fixation: Dye fixation is carried-out as per 13.5.9

14.2 Fixation curves

This fixation value is plotted in curve to understand the comparison of fixation of with Sequestering agent and without sequestering agent. The individual dyes fixation curves are shown below:

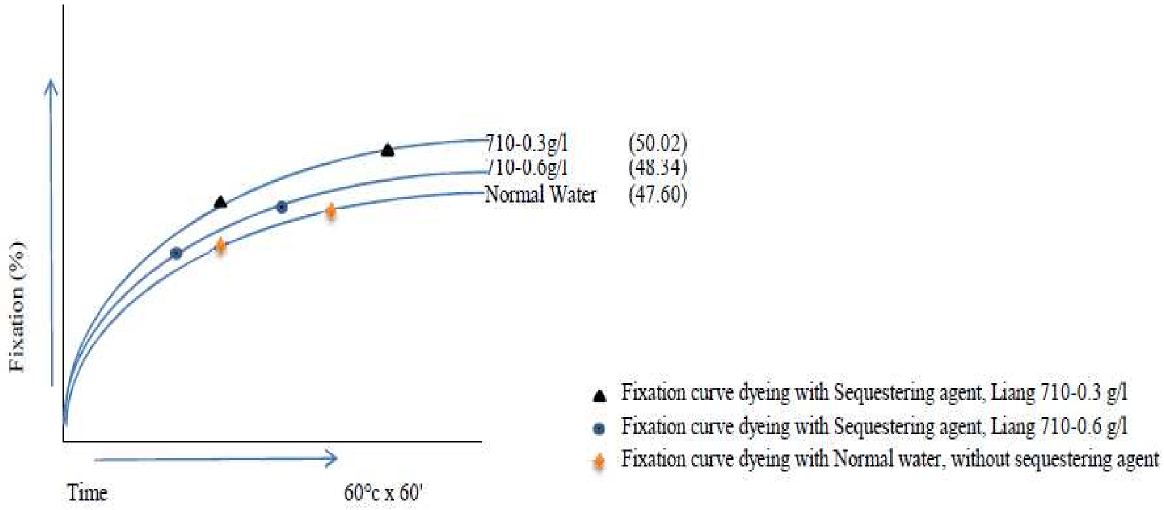

Figure 33: Fixation curve of Dychufix Red 3BXF [Ref-Table 10, Sl. No.-03]

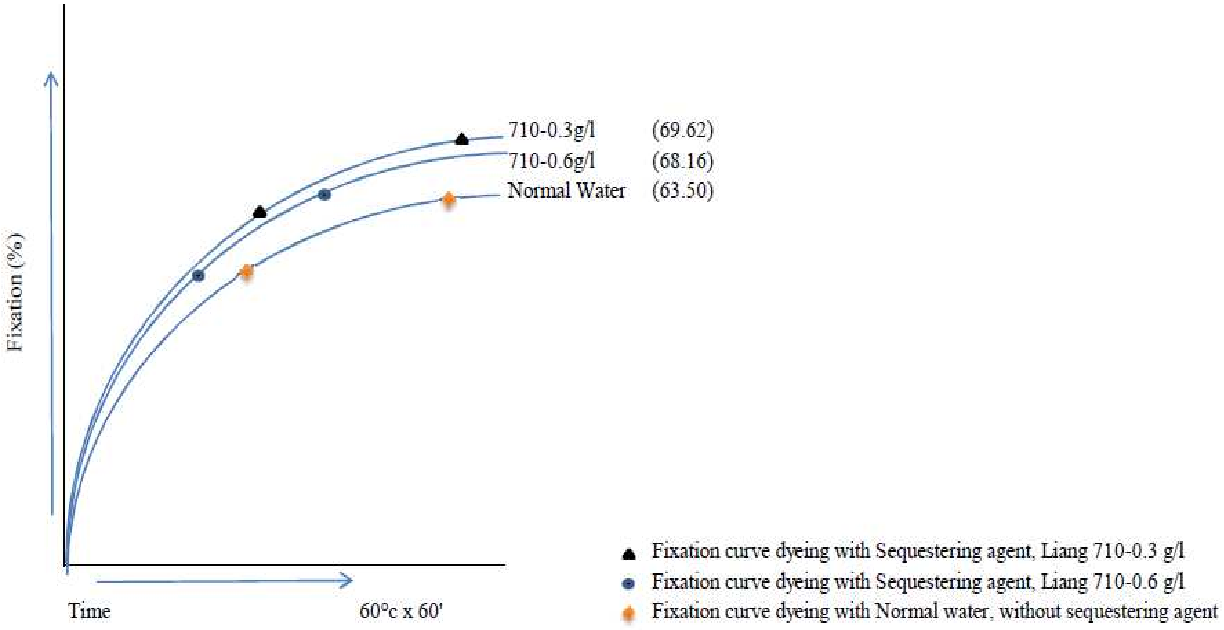

Figure 34: Fixation curve of Dychufix Yellow 3R XF [Ref-Table 11, Sl. No.-02]

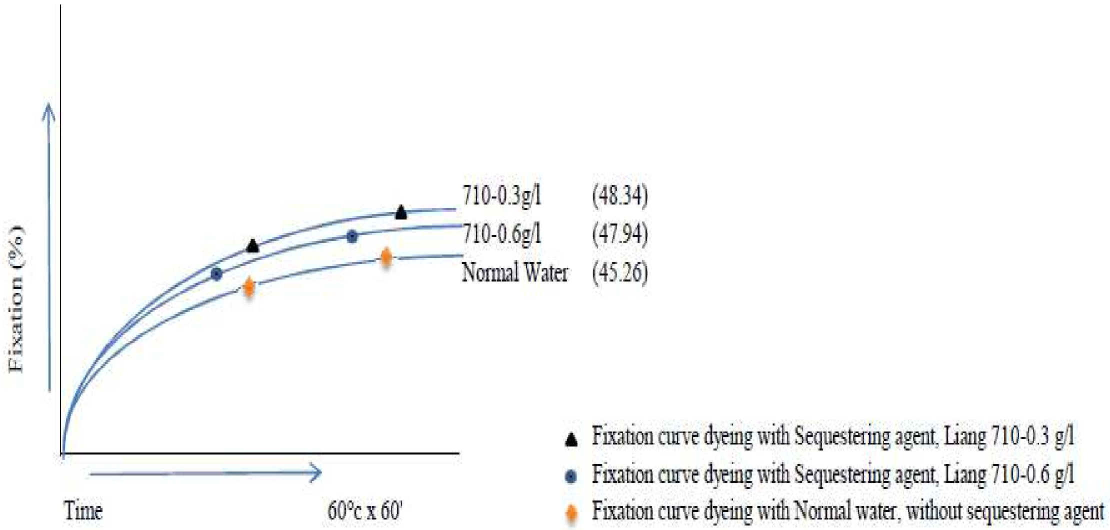

Figure 35: Fixation curve of Dychufix Navy Blue 2GL XF [Ref-Table 12, Sl. No.-03]

After showing the individual effect of water hardness on reactive dyes fixation, then it was established the combined effect al in graphically. Where it was shown that, the Dychfix Yellow 3RXF has the highest fixation level than others two dyes. It is shown below:

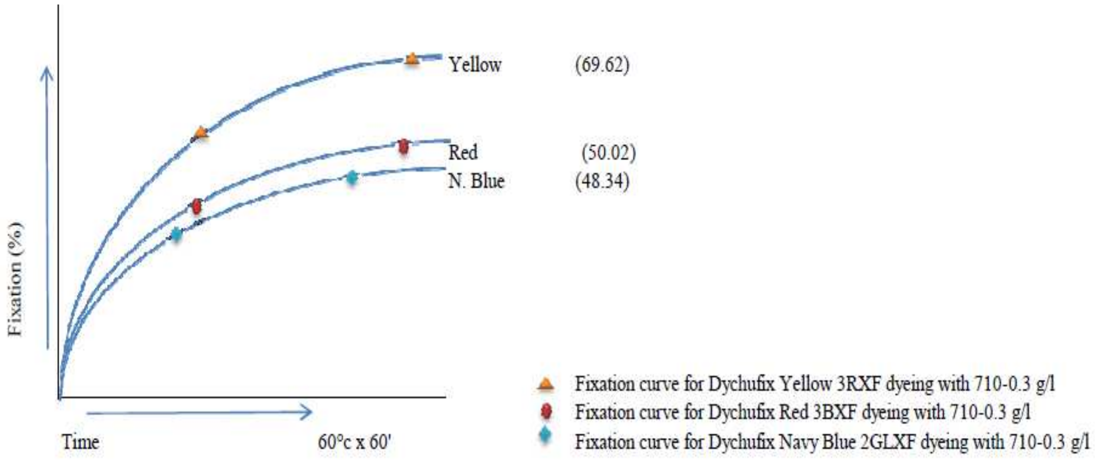

Figure 36 : Combined Fixation curve of Red, Yellow, N. Blue (710-0.3 g/l) [Ref-Table 10, 11, 12 Sl. No.-03, 02, 03]

14.3 Fixation graphs

All the three dyes fixation average value is plotted in graph at different process. Where it is easier to find out the difference in fixation level at different process (adding chelating agent, without chelating agent) of individual dyes and their combined effect also. The fixation% of three dyes are presented graphically in figure 37-40:

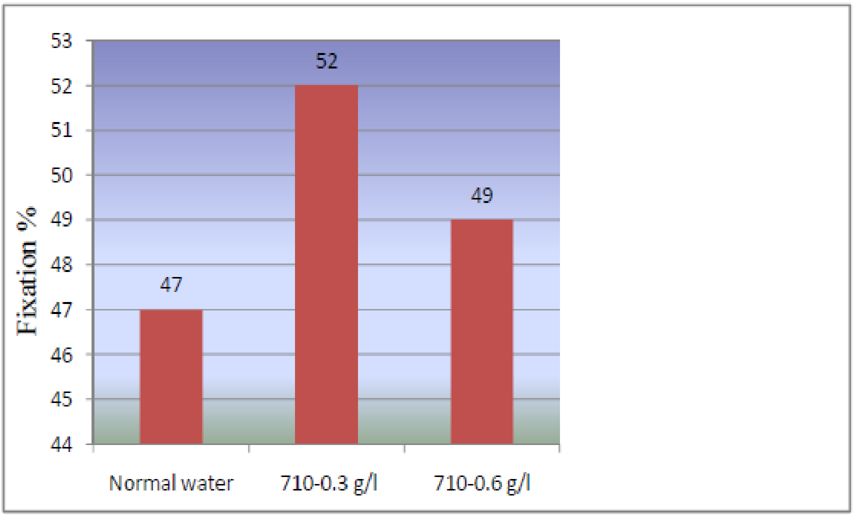

Figure 37 : Fixation Graph of Dychufix Red 3B XF (Average value from Table 10-apprx)

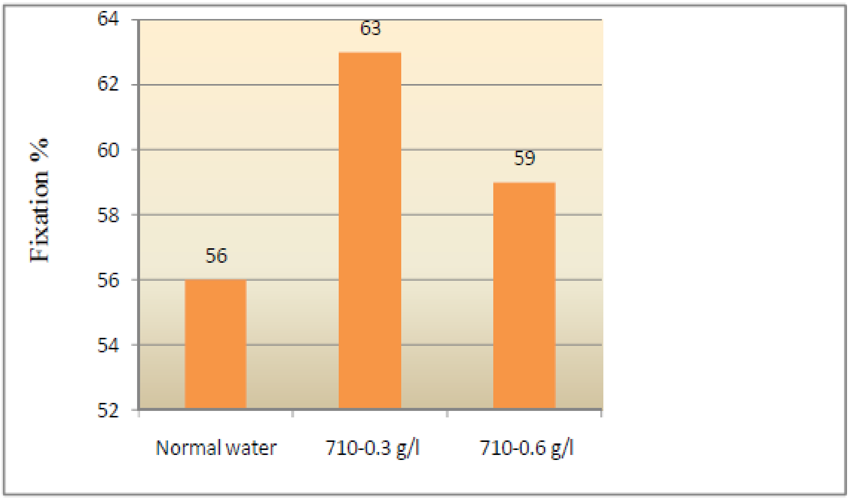

Figure 38 : Fixation Graph of Dychufix Yellow 3B XF (Average value from Table 11-apprx)

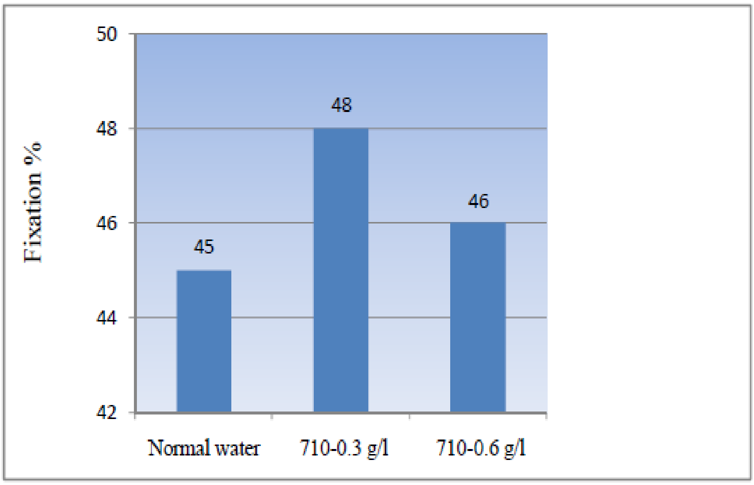

Figure 39 : Fixation Graph of Dychufix Navy Blue 2GL XF (Average value from Table 12-appr

From the above values the fixation (%) of Dychufix Red, Yellow and N. Blue are plotted in graph combined. It was shown the difference in fixation level of three different dyes for a process adding chelating agent Liang 710-0.3 g/l. where it was observed the highest fixation level in average is also for Yellow.

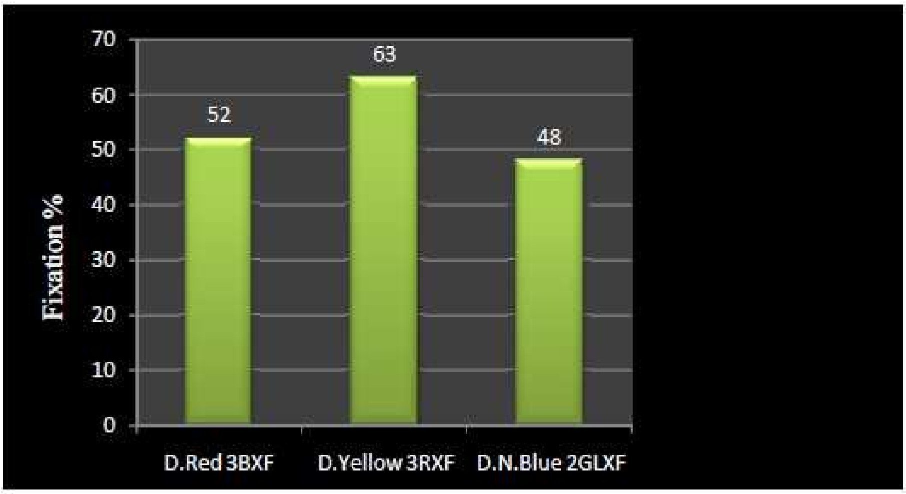

Figure 40 : Combined Fixation Graph of Dychufix Red, Yellow, Blue (710-0.3 g/l, Average value from Table 10, 11 and 12).

14.4 CMC reports:

The CMC report of every dye at different stage was measured and recorded using the spectrophotometer, Datacolr 600^{TM}. The stages were, 1) before starting dyeing without adding alkali the solution is measured, 2) after adding alkali, with run time 60 min at 60'c (B/D) the solution is measured, 3) after wash off again the solution is measured. Also three processes, a) using normal water, b) sequestering agent, Liang 710-0.3 g/l, c) using sequestering agent, liang710-0.6g/l. Their CMC report, K/S value, integral strength%, T% were collected and summarized in the following tables18-20:

Table 18: Data Color Reports of Dychufix Red 3BXF [Table 10 - 03]

Name of Process	DL*	Da*	Db*	Dc*	DH*	DE*	CMC DE	K/S Strength %	Integral Strength %
Normal Water (60 x 60) B/D	15.96	9.39	-44.26	-8.72	-44.39	47.97	30.80	43.14	38.19
Liang 710 – 0.3 g/l (60 x 60) B/D	15.92	8.76	-45.13	-9.44	-44.99	48.65	31.19	41.82	36.95
Liang 710 – 0.6 g/l (60 x 60) B/D	16.18	9.27	-44.74	-8.90	-44.82	48.47	31.19	41.82	37.01
Normal Water 1st Wash Off	43.34	-19.03	-67.14	-35.82	-59.89	82.15	48.59	7.42	6.53
Liang 710 – 0.3 g/l 1st Wash Off	38.73	-9.11	-68.50	-25.88	-64.08	79.22	48.83	9.48	8.37
Liang 710 – 0.6 g/l 1st Wash Off	473.21	-18.22	-67.53	-34.94	-60.59	82.21	48.86	7.45	6.56

Table 19 : Data Color Reports of Dychufix Yellow 3RXF [Table 11- 02]

Name of Process	DL*	Da*	Db*	Dc*	DH*	DE*	CMC DE	K/S Strength %	Integral Strength %
Normal Water (60 x 60) B/D	25.09	-54.30	-13.76	-31.31	46.45	61.38	36.32	20.07	20.93
Liang 710 – 0.3 g/l (60 x 60) B/D	24.86	-53.35	-9.81	-27.29	46.88	59.67	36.33	21.31	22.28
Liang 710 – 0.6 g/l (60 x 60) B/D	25.15	-54.31	-14.02	-31.58	46.35	61.47	36.28	19.95	20.80
Normal Water 1st Wash Off	27.76	-61.26	-12.83	-30.82	54.48	68.47	42.04	19.12	20.09
Liang 710 – 0.3 g/l 1st Wash Off	28.62	-62.88	-18.80	-36.80	54.34	71.60	42.40	17.04	17.87
Liang 710 – 0.6 g/l 1st Wash Off	27.86	-60.98	-10.65	-28.63	54.88	67.88	42.21	19.67	20.70

Table 20: Data Color Reports of Dychufix Navy Blue 2GLXF [Table 12 - 03]

Name of Process	DL*	Da*	Db*	Dc*	DH*	DE*	CMC DE	K/S Strength %	Integral Strength %
Normal Water (60 x 60) B/D	15.41	29.32	-40.61	49.99	-3.07	52.40	78.76	30.28	34.77
Liang 710 – 0.3 g/l (60 x 60) B/D	15.86	29.00	-40.34	49.59	-3.06	52.15	78.23	29.61	33.89
Liang 710 – 0.6 g/l (60 x 60) B/D	14.00	29.25	-40.50	49.87	-3.06	51.88	78.32	32.69	37.85
Normal Water 1st Wash Off	43.21	-4.01	-42.26	42.25	-4.15	60.58	77.98	15.62	17.89
Liang 710 – 0.3 g/l 1st Wash Off	43.59	-4.70	-42.22	42.27	-4.18	60.86	78.22	15.52	17.77
Liang 710 – 0.6 g/l 1st Wash Off	45.67	-5.87	-41.11	41.31	-4.17	61.73	78.13	14.578	16.63

Where,

D L* being the lightness difference (lighter or Darker)
D a * being the red/green difference (redder or green)
D b* being the yellow/blue difference (yellow and blue)
DC* being the chroma difference
DH * being the hue angle difference

14.5 Color fastness measurement:

The effect of different colorfastness properties for various processes with and without using sequestering agent. After tested all the samples, the comparison of fastness properties is made among three dyes at three dyeing processes. The following tests were done:

Table 21: Color fastness test methods

SL No.	Test Name	Test Method
1	Color Fastness to Rubbing (Dry, Wet)	ISO-105-X12:1993(E)
2	Color Fastness to wash	ISO - 105-C06: 1994(E)
3	Color Fastness to Water	ISO -105-E01: 1994(E)
4	Color Fastness to perspiration (Acid & Alkali)	ISO 105 E04:1994(E)
5	Color Fastness to light	ISO-105-B02:1994(E)

Table 22: Color fastness test report of Normal water process

Process : 60x60 (Normal water)		**Dychufix Red 3BXF 2%**		**Dychufix Yellow 3RXF 2%**		**Dychufix Navy Blue 2GLXF 2%**	
Test name	**Test method**	**Test result**		**Test result**		**Test result**	
01. Color fastness to rubbing	**ISO-105-X12**						
	Dry rub	4		4—5		4	
	Wet rub	3—4		4		3	
02. Color fastness to wash	**ISO - 105-C06**						
	Color staining	4—5		4—5		4	
	Aceted	4—5		4—5		4—5	
	Cotton	4—5		4—5		4	
	Nylon	4—5		4—5		4—5	
	Polyester	4—5		4—5		4—5	
	Acrylic	4—5		4—5		4—5	
	Wool	4—5		4—5		4—5	
03. Color fastness to perspiration	**ISO 105 E04**						
	Reagent	acid	alkali	acid	alkali	acid	alkali
	Color staining	4	4	4—5	4--5	3--4	3—4
	Aceted	4—5	4--5	4—5	4--5	4--5	4—5
	Cotton	4	4	4—5	4--5	3--4	3—4
	Nylon	4	4--5	4—5	4--5	4	4—5
	Polyester	4—5	4--5	4—5	4--5	4--5	4—5
	Acrylic	4—5	4--5	4—5	4--5	4--5	4—5
	Wool	4—5	4--5	4—5	4--5	4--5	4—5
04. Color fastness to water	**ISO -105-E01**						
	Color staining	4		4		3—4	
	Aceted	4--5		4—5		4—5	
	Cotton	4		4		3—4	
	Nylon	4--5		4—5		3—4	
	Polyester	4--5		4—5		4—5	
	Arylic	4--5		4—5		4—5	
	Wool	4--5		4—5		4—5	
05.Color fastness to light	**ISO-105-B02**						
		4--5		4—5		4	

Table 23: Color fastness test report of Liang 710-0.3 g/l process

Process : 60X60 (710-0.3 g/l)		**Dychufix Red 3BXF 2%**		**Dychufix Yellow 3RXF 2%**		**Dychufix Navy Blue 2GLXF 2%**	
Test name	**Test method**	**Test result**		**Test result**		**Test result**	
01. Color fastness to rubbing	**ISO 105-X12**						
	Dry rub	4		5		3	
	Wet rub	3--4		4—5		3	
02. Color fastness to wash	**ISO 105-C06**						
	Color staining	4--5		4		4—5	
	Aceted	4--5		4—5		4—5	
	Cotton	4--5		4		4—5	
	Nylon	4--5		4—5		4—5	
	Polyester	4--5		4—5		4—5	
	Acrylic	4--5		4—5		4—5	
	Wool	4--5		4—5		4—5	
03. Color fastness to perspiration	**ISO 105-E04**						
	Reagent	acid	alkali	acid	alkali	acid	alkali
	Color staining	4	4	4--5	4--5	3—4	3—4
	Aceted	4—5	4--5	4--5	4--5	4—5	4—5
	Cotton	4	4	4--5	4--5	3—4	3—4
	Nylon	4	4--5	4--5	4--5	4—5	4—5
	Polyester	4—5	4--5	4--5	4--5	4—5	4—5
	Acrylic	4—5	4--5	4--5	4--5	4—5	4—5
	Wool	4—5	4--5	4--5	4--5	4—5	4—5
04. Color fastness to water	**ISO 105-E01**						
	Color staining	4		4—5		3—4	
	Aceted	4--5		4—5		4—5	
	Cotton	4		4—5		3—4	
	Nylon	4		4—5		3—4	
	Polyester	4--5		4—5		4—5	
	Arylic	4--5		4—5		4—5	
	Wool	4--5		4—5		4—5	
05.Color fastness to light	**ISO 105-B02**						
		4--5		4—5		3—4	

Table 24: Color fastness test report of Liang 710-0.6 g/l process

Process : 60X60 (710-0.6 g/l)		**Dychufix Red 3BXF 2%**		**Dychufix Yellow 3RXF 2%**		**Dychufix Navy Blue 2GLXF 2%**	
Test name	**Test method**	**Test result**		**Test result**		**Test result**	
01. Color fastness to rubbing	**ISO 105-X12**						
	Dry rub	4		4		3—4	
	Wet rub	3		4		3	
02. Color fastness to wash	**ISO 105-C06**						
	Color staining	5		5		4—5	
	Aceted	5		5		4—5	
	Cotton	5		5		4	
	Nylon	5		5		4—5	
	Polyester	5		5		4—5	
	Acrylic	5		5		4—5	
	Wool	5		5		4—5	
03. Color fastness to perspiration	**ISO 105-E04**						
	Reagent	acid	alkali	acid	alkali	acid	alkali
	Color staining	4	4	4--5	4--5	3--4	3—4
	Aceted	4—5	4--5	4--5	4--5	4--5	4—5
	Cotton	4	4	4--5	4--5	3--4	3—4
	Nylon	4—5	4--5	4--5	4--5	4--5	4—5
	Polyester	4—5	4--5	4--5	4--5	4--5	4—5
	Acrylic	4—5	4--5	4--5	4--5	4--5	4—5
	Wool	4—5	4--5	4--5	4--5	4--5	4—5
04. Color fastness to water	**ISO 105-E01**						
	Color staining	4		4—5		2—3	
	Aceted	4--5		4—5		4	
	Cotton	4		4		2—3	
	Nylon	3--4		4		4—5	
	Polyester	4--5		4—5		4—5	
	Arylic	4--5		4—5		4—5	
	Wool	4--5		4—5		4—5	
05.Color fastness to light	**ISO 105-B02**						
	Test method	4--5		4—5		4	

The above results show that the fixation (%) of the most individual dyes is higher at using sequestering agent Liang -710 at 0.3 g/l, and gradually lower fixation is shown at using 710-0.6 g/l and where has no use of sequestering agent. It was also found that there were the higher fixation level of Dychufix yellow 3RXF compared to other two dyes, Dychufix Red 3 BXF and Dychufix Navy Blue 2 GLXF. It proves that using sequestering agent eliminate the ionic bond between dye and substrate, thus increase the fixation (%), but after optimum use it will have a reverse effect due to more hydrolysis of dyes. We also tested color fastness and compared among the dyes. The results show that almost all the fastness properties are better in the process using sequestering agent, Liang 710 at 0.3 g/l than the process using only normal water and using sequestering agent, Liang 710 at 0.6 g/l accordingly. The colorfastness to wash for the two dyes was excellent(GS rating 5.0) for Yellow and Red where as Navy blue was in 4-5 rating in the process using sequestering agent, Liang 710 at 0.6 g/l. It was also observed that the fixation (%) is mostly higher of Dychufix Yellow 3RXF rather than Dychufix Red 3 BXF and Dychufix Navy Blue 2 GLXF accordingly.

14.6 Economical loss due to poor fixation of dyes

Fixation levels for reactive dyes, when doing deep dyeing, can be as high as 70%. Tests in several factories in Bangladesh have shown that currently fixation ranges from 40-65%. In this experiment it was studied the fixation level of used dyes in Hotapara Garments Ltd. It was found at Table10, 11 and 12 that average fixation% of Red, Yellow and N.Blue are 52, 63 and 48 accordingly. So their combined fixation% is about 55. If, on average, the fixation is 55% then about 15% of the dye is essentially being wasted. If 20 kg of dye is used to dye a batch of 200 kg of fabric then 4 kg is being wasted per batch. If, on average, dye costs Tk. 460 per kg then this is a loss of Tk. 1,840 per batch. If a factory dyes 1,000 tones of fabric each year, using 100,000 kg of dye and wastes 15% because of poor fixation, this is the equivalent of a loss of Tk. 55,68,750.00 per year (approximately US$ 71,394.231) (Table 25).

Table 25: Explanation of the calculations of the cost of wasted dyes per year

Explanation	Amount	Unit
a. Fabric dyed per year (8,000 kg/day x 26 days/month)	24,96,000.00	kg
b. Quantity of dye used per year (aproximate)	82,500.00	kg
c. Average fixation achieved* (range of 40%-70%)	55	%
d. Avoidable percentage of dye lost (70% - c)	15	%
e. Quantity of dye lost per year (kg) (b x d)	12,375.00	kg
f. Average price of dye (per kg) bought by factory (Tk)	450	tk
g. Annual cost of buying dyes (Tk) (b x f)	3,71,25,000.00	tk
h. Cost of 'avoidable' dye lost per year (Tk) (e x f)	55,68,750.00	tk
i. Cost per year (US$)	**71,394.23**	**$**

14.7 Cost analysis of chelating agent, Liang 710 for improved fixation level

Chelating agent is needed for rreducing the hardness present in the supplied water. We know that the water hardness is required 50-60 PPM for good quality dyeing in the dye bath. Where we had 72 -84 ppm in supplied water which increases adding salt, leveling agent, fabric alkali, at 110-120 ppm which can influence on the overall dyeing causes a great loss per Day for the Company. So we sholud analyse of the existing water hhardness in details before use. It was analysed in bulk dyeing with sequestering agent controlling hardness in dye bath 45-50 ppm and compared with dyeing using sequestering agent not controlling the harness 90-110 ppm.

Form the table 10, 11 and 12 it is clear that using chelating agent, Liang 710 has higher fixation level than without using any chelating agent. And this improved fixation level at optimum dosing usage of chelating gent is about 4-6%. We assume that our improved fixation% is on average 5%. Now let us review the cost saving for this 5% improved fixation level of dyes.

Table 26: Explanation of the Calculations of the cost saved for improved fixation% of dyes

Explanation	Amount	Unit
a. Fabric dyed per year (8,000 kg/day x 26 days/month)	24,96,000.00	kg
b. Quantity of dye used per year (approximate)	82,500.00	kg
c. Improved fixation% using chelating agent, Liang 710	5	%
d. Quantity of dyes saved per year (b * c)	4,125.00	kg
e. Cost of dyes per kg	460	tk
f. Total cost save per year for improved fixation level of dyes (d * e)	18,97,500.00	tk
g. Total cost saved per yyear in US$ ($1.0 = tk.78)	**24,326.92**	**$**

14.8 Cost analysis through Right First Time (RFT) shade

Further savings can be made by ensuring that the least RFT points are maintained carefully and accurately. Strict following RFT points will reduce the re-shaded and re-dyeing a lot. Also it will reduce the dyeing faults, such as Running shade, Uneven dyeing, color spot, Softness not ok etc.

Table 27: Explanation of the calculations of cost saved reducing re-shade and re-dyeing by RFT

Explanation	Amount	Unit
a. Fabric dyed per year	24,96,000.00	kg
b. Cost of dye per kg of fabric dyed	30	tk
c. Cost of other chemicals per kg of fabric dyed	20	tk
d. Cost of labour per kg of fabric dyed	15	tk
e. Cost of energy per kg of fabric dyed	10	tk
f. Total cost per kg of fabric dyed (b+c+d+e)	75	tk
g. Estimated quantity of production re-dyed per year (2% of total production)	49,920.00	kg
h. Estimated cost of re-dyeing assuming it is 100% of the total production cost (f * g)	37,44,000.00	tk
i. Estimated quantity of production re-shaded per year (15% of total production)	3,74,400.00	kg
j. Cost of re-shaded per kg (30% of total dyeing cost)	22.5	
k. Estimated cost of re-shading (i* j)	84,24,000.00	tk
l. Total cost (i+j)	1,21,68,000.00	tk
m. Total cost (US$) ($1.0 = tk.78)	**1,56,000.00**	**$**
n. Assume Half of this cost are saved for RFT (if 1% re-dyeing + 7.5% re-shaded can improved)	60,84,000.00	tk
o. Half of the Total cost (US$) ($1.0 = tk.78)	**78,000.00**	**$**

14.9 Cost analysis of reduced dyeing faults by RFT

There are various types of dyeing faults in a dye house. Running shade is one of the most important problems occurred almost regularly in cotton knit dyeing. Out of this, color spot, uneven dyeing, crease mark and softness quality not ok etc. It was observed about 10-15% 0f total production have running shade. Most of the batches of running shade are corrected by re-process, but there are some major running shade problems that need to re-dye often. Sometimes we have to re-soft a few batches (2%) due to poor softness quality. All of these problems can be reduced a lot, when it can achieve RFT shades. If we can reduce half of the total problems, so we can save a huge amount of US$ per year. Our estimated calculation is shown in table 28:

Table 28: Explanation of the calculations of cost saved for reducing dyeing faults by RFT

Explanation	**Amount**	**Unit**
a. Fabric dyed per year (8,000 kg/day x 26 days/month)	24,96,000.00	kg
b. Quantity of Running shade , (10% of total production)	2,49,600.99	kg
c. Re-process cost per kg for running shade (cost of re-process + 1/3rd over head cost)	13	tk
d. Total cost for Running shade per year (b *c)	32,44,800.00	tk
e. Quantity of softness quality not ok (2% of total production)	49920	kg
f. Re-softness cost per kg (cost of softness process + 1/3rd of over head cost)	11	tk
g. Total cost for re-softness process (e * f)	5,49,120.00	tk
h. Quantity of re-dyeing from major running shade (2% of running shade quantity)	4,992.00	kg
i. Re-dyeing cost per kg (almost total dyeing cost + over head cost)	75	tk
j. Total cost for major running shade per year (h * i)	3,74,400.00	tk
k. Total cost (d + g + j)	41,68,320.00	tk
g. Total cost saved per yyear in US$ ($1.0 = tk.78)	**53,440.00**	**$**

So this huge amount ($53,440.00) wasted money can easily save per year using suitable chelating agent to control the water hardness in every process of dyeing.

14.10 Total cost saved through this experiment

If we add all the costs saved above together, it will be a huge amount of US$1, 55,766.90 per year. These cost savings can be achieved only getting RFT shade without investing a lot of money. Because of the RFT points can be controlled by creating awareness about RFT in all classes of man power working in the dyeing industry (Lab, R&D, knitting, batch, chemical store, yarn store, dyeing).

Table 29: Total cost saved by this experiment per year

Explanation	**Amount**	**unit**
a. Total cost saved for improved fixation level of dyes using chelating agent, Liang 710 (per year)	18,97,500.00	tk
b. Total cost saved for reducing dyeing faults using chelating agent, Liang 710 (per year)	41,68,320.00	tk
c. Half of the cost saved for re-shaded and re-dyeing controlling RFT points (per year)	60,84,000.00	tk
d.Total cost saved in this experiment per yaer	1,21,49,820.00	tk
e. Total cost saved in US$ ($1.0 = tk.78)	**1,55,766.90**	**$**

15. Conclusion:

In Bangladesh we do not have the dyes, chemicals manufacturing unit yet. We are to import the huge amount of dyes, chemicals per year for the whole country. So most of the profit from dyeing is still going to them. On the other hand these dyes, chemicals price is increasing day by day a lot. Where the buyers are not giving this higher dyeing price. In the year of 2013 the dyes price is dramatically increased to almost double. In this situation there are nothing to do rather than utilizing the 3 M (man, machine and materials). In this experiment we studied on RFT shade concept, which is in fact very mandatory for a dyeing unit. At the present competitive market, there has no alternative way to reduce the overall dyeing cost. It is proved from this experiment achieving the RFT shade we can save a big amount of money ($1, 55,766.90) per year assuming the controlled RFT on half of total, which will directly add on our profit margin. From this study it is also proved that in reactive dyeing for cotton, the chelating agent played a very important rule on fixation effect. It improves the fixation level. It is also clear that water treatment plant is not sufficient to reduce the hardness of dye bath. Because there are used not only raw water but also various chemicals like, salt, leveling agent which increase the dye bath hardness a lot. There is also scope of increasing hardness from grey fabric. So it is mandatory to use chelating agent in the dye bath for improved fixation. And controlling the RFT points that will improve the fabric quality (minimize the uneven, patchy dyeing , running shade, re-shade, re-dyeing, color spot, poor softness quality) and improve colorfastness properties also. But it was proved from this study that the use of chelating agent should be at an optimum dosing, otherwise exceeding the level it will reversely affect on fixation level. If the optimum dosing of chelating agent can be selected and used in all process of dyeing, there will be increased fixation on an average 4-6%. So achieving RFT will not only save money by reducing the very common dyeing faults but also it will reduce the effluent to environment.

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