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**BIO - DISCHARGE PRINTING ON COTTON  
FABRIC USING HORSERADHISH PEROXIDASE**

**PROJECT REPORT**

*Submitted by*

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**Register No: 0920201007**

*in partial fulfillment for the award of the degree*

*of*

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IN  
TEXTILE TECHNOLOGY**

**KUMARAGURU COLLEGE OF TECHNOLOGY**

**COIMBATORE – 641 049**

**(An Autonomous Institution Affiliated to Anna University of Technology Coimbatore)**

**APRIL 2011**

## BONAFIDE CERTIFICATE

Certified that this project report “**BIO- DISCHARGE PRINTING ON COTTON FABRIC USING HORSERADHISH PEROXIDASE**” is the bonafide work of **KARTHIKEYAN.K** (Reg. No. 0920201007) who carried out this project work under my supervision during the year 2010-2011.

  
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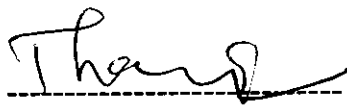
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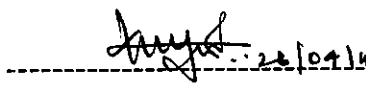
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## LIST OF ABBREVIATIONS

AATCC	-	American Association of Textile Chemists and Colorists
ASTM	-	American Standard Testing Materials
COS	-	Cotton Original sample
CDS	-	Cotton Dyed sample
CEPS	-	Cotton Enzymatic printed sample
CCPS	-	Cotton conventional printed sample
HRP	-	Horseradish Peroxidase
H <sub>2</sub> O <sub>2</sub>	-	Hydrogen Peroxide
L*	-	Lightness value (CIE 1976)
c*	-	Chorma value (CIE 1976)
H°	-	Hue value (CIE 1976)
ΔL*	-	Difference in Lightness
Δc*	-	Difference in chroma
ΔH°	-	Difference in Hue
ΔE*	-	Difference in Colour
N	-	Newton
Sec	-	Seconds
GSM	-	Grams per Square meter
Ne	-	British English count
cm	-	Centimeter
kPa	-	Kilopascal
ppm	-	Parts per million
ISO	-	International Organization for Standardization

## ABSTRACT

Textile discharging printing is the most versatile and important of the methods used for introducing design to textile fabrics. Discharge styles the pattern is produced by the chemical destruction of the original dye in the printed areas. The discharging agents used can be oxidizing or reducing agents, acids, alkalis and various salts. But, most important methods of discharging are based formaldehyde sulphonylates & Thiourea dioxide.

Recently, the environmental and industrial safety conditions increased the potential for use of enzymes in textile processing to ensure eco-friendly production. Sulphonylate Formaldehyde ( $\text{NaHSO}_2 \cdot \text{CH}_2\text{O} \cdot 2\text{H}_2\text{O}$ ) is a powerful discharging agent, however, it is considerably toxic, and evolve formaldehyde known as a human carcinogenic associated with nasal sinus cancer and nasopharyngeal cancer.

This work features an enzymatic method of discharging printing using Horse radish peroxidase which oxidizes compounds in the presence of hydrogen peroxide. The effects of enzymes concentration, pH of the printing paste, treatment time and temperature of enzymatic treatment have studied. The Optimum conditions for enzymatic discharge printing are found to be 8.5 pH, 70° C Temperature, 80g concentration and 60 min time of treatment.

The main objective of the present work is to replace the hazard chemicals which are used in discharge printing with an eco-friendly Horseradish peroxidase enzyme.

## CHAPTER 1

### INTRODUCTION

Biotechnology has dramatically increased the scope for application of enzyme systems in all areas of textile processing. Enzymes can be tailored to implement specific reactions, such as decomposition, oxidation and synthesis, for a variety of purposes. There is a growing recognition that enzymes can be used in many remediation processes to target specific purpose in textile industry (Doshi, R. and Shelke, V, 2001). In this direction, recent biotechnological advances have allowed the production of cheaper and more readily available enzymes through better isolation and purification procedures (Mishra, A. and Rani, A., 2007).

Discharging of the ground colour (dyed colour) can be carried out by oxidation (or) reduction, says Jaiprakash R.D, 1997. Oxidation discharge produces sharper prints and pure white than reduction discharge due to the bleaching effect in the discharged parts of the design. Oxidizing discharge agents are not widely used as they degrade the fibres. Some of the limitations of conventional discharge printing using reducing agents are described by Parmar (2003).

- Discharging of the colour takes place only at high temperature, which demands steaming (or) curing.

Conventional Discharging printing have been carried out by using reducing type discharging agent especially sulphoxylates & Thiourea dioxide chemical. In which, Suphoxylate formaldehyde based chemical is mostly used as discharging agent for this kind of printing which pose as a carcinogenic to humans (Suresh et al., 1996).

Enzymes have been used in textile industry because it operates under mild conditions of temperature and pH, it replaces non-selective harsh chemicals. Due to its high catalytic power they are needed in small quantity. Their action is easy to control, biodegradable point, It reduces the used of water and traditional chemicals. It also reduces the use of energy and thus lowers levels of carbon dioxide emissions (Rai, I, 2004).

“A phenol oxidizing enzyme system” is meant a system in which an enzyme by using hydrogen peroxide or molecular oxygen is capable of oxidizing organic compounds containing phenolic groups. In this present work, Horseradish peroxidase enzyme has been used as discharging agent which oxidizes dye compounds in the presence of hydrogen peroxide. The effects of enzymes concentration, pH of the printing paste, treatment time and temperature of enzymatic treatment have been studied.

The Optimum conditions for enzymatic discharge printing are found to be pH 8.5, 70° C temp, 80g concentration and 60 min time of treatment.

## **1. OBJECTIVE OF THE PROJECT**

- (i) Dye the cotton fabrics with Vinyl Sulphone Reactive dye.
- (ii) Preparation of enzymatic printing paste.
- (iii) Carry out enzymatic discharge printing on dyed cotton fabrics.
- (iv) Evaluate the Bio- discharge printed fabric properties against conventional discharge printed fabric.

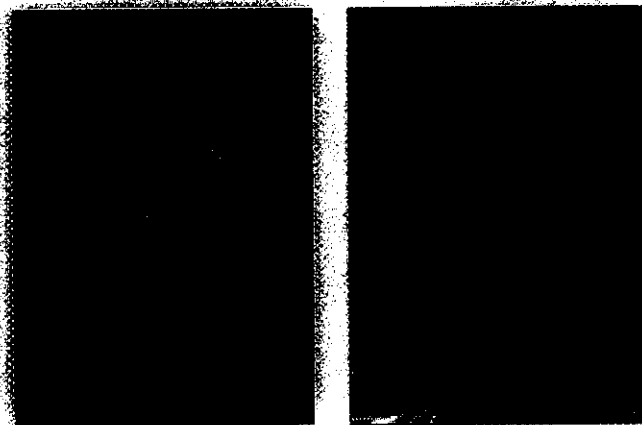
In the present work an attempt had made to replace the hazard chemicals which are used in discharge printing with an eco-friendly Horseradish peroxidase enzyme

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 COTTON

Cotton remains the most miraculous fiber under the sun no other fibre comes close duplicating all the desirable characteristics combined in cotton ([www.cotton.org](http://www.cotton.org)). Cotton fibre boast for its properties, like good absorption of fluid, biodegradability, breath ability, drape ability, sterilisability, heat resistant, high wet strength, insulation, non-allergic, non-irritation, renewable resource and water retention (Narayanan, S.S, 2005). Cotton is comfortable, strong, durable, has good colour retention and it withstands high temperature, stand up to abrasion and wears well ([www.handlooms.com](http://www.handlooms.com)).



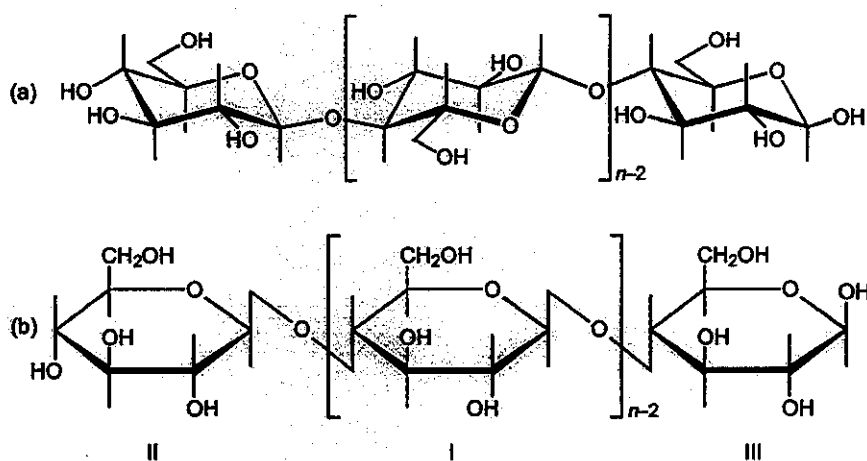
**Fig: 2.1 Optical micrographs of raw cotton fibers x 100**

**(Source: Cellulosic Dyeing Handbook, 1995)**

The mature cotton fiber forms a flat ribbon varying in width between 12 and 20 micrometer. It is highly convoluted, probably on account of the twisting that takes place when the tubular shape formed during growth collapses on drying. The number of convolutions varies between four and six per millimeter, reversing in direction every millimeter or so along the fibre. These characteristics make cotton easy to recognize under both optical and electron microscopes (John Shore, 1995).

### 2.1.1 CHEMICAL STRUCTURE

The main features of the chemical structure of cellulose are well known. It may be most conveniently described as a 1, 4- $\beta$ -D-glucan, i.e. a condensation polymer of  $\beta$ -D-glucopyranose with 1, 4-glycosidic bonds. For the sake of clarity and in accordance with convention the ring carbon atoms and the hydrogen atoms attached to them are omitted. Some authors also omit the C—H bonds. Hydroxyl groups are always, and methylol groups are sometimes, printed in full.

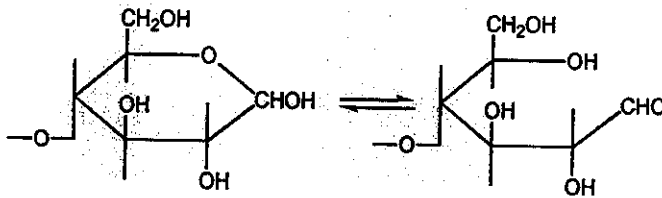


**Fig: 2.2 Cellulose: Fully extended conformational formula**

That all the substituent's, including the glycosidic bonds, are in the mean plane of the ring (equatorial) and not perpendicular to it (axial) as might be supposed from the Haworth formula. Only the C—H bonds are axial. The essential features of the polymer chain are the main sequence of intermediate units (I), the non-reducing end group (II), the reducing end group (III) and glycosidic linkages. The intermediate units possess one primary and two secondary alcohol groups each. The non-reducing end group possesses one extra secondary alcohol group at C4, and the reducing end group (so-called because it reduces Fehling's solution and ammoniacal silver nitrate) is a cyclic hemiacetal (Mishra, S.P., 2000).

Cook, J.G, (2000), indicates that the degree of polymerization (DP) of cellulose varies with its source and is usually expressed as an average, since a wide distribution is found in most samples. In native cellulose it may be as high as 14, 000 but purification

involving treatment with alkali usually reduces this to about 1000—2000 thus purified native cellulose is normally devoid of reducing power. All fibres regenerated from viscose solution contain a very small number of aldehyde, ketone and carboxylic acid groups introduced during manufacture. Thus chemically, regenerated cellulose differs from native cellulose only slightly. Differences in properties arise mainly from differences in supramolecular structure.



**Fig: 2.3 Cellulose cleavages**

An industrially important feature of cellulosic fibers is chemical stability, enabling them to withstand degradation with its consequential loss of tensile strength under normal conditions of use. Even slight degradation during processing, however may be accompanied by unacceptable loss of strength and other undesirable effects. Six different degradative agencies have been identified: acids, alkalis, oxidizing agents, enzymes, heat and radiation.

### 2.1.2 PROPERTIES

#### i) Moisture absorption:

The rate of absorption and desorption of water with change of humidity is very fast for an isolated fibre. For fibre assemblies, the changes are much slower and involve interaction between the rate of diffusion of water molecules and the evolution and transmission of heat of sorption.. A standard half-change period of 12 hours applies to a slab of cotton fibres 2.5 cm thick, with a density of 0.5 g/cm<sup>3</sup> when dry, at a regain of 7% and a temperature of 18 °C.

Mishra, S.P., (2000) showed that up to about 85% RH, the regain of cotton at a given humidity decreases with rise of temperature from 50 to 110 °C. The reduction increases from 0.9% at 20% RH to 1.8% at 70% RH. At 85% RH, the curves cross over and

there is a higher regain at higher temperatures. In a standard atmosphere of 65% RH and 20 °C, the absorption regain of cotton is 7-8%.

ii) Heat of sorption:

Cotton decreases rapidly from a high value for dry cotton as the starting humidity increases. The upper rows are measured values for absorption of liquid water; the lower row is corrected by adding the latent heat of vaporization of water, 2.45 kJ/g. Values of heat of sorption from the dry state ranging from 1.19 to 1.33 kJ/g have been reported for three different types of cotton (Mishra, S.P., 2000). The corresponding heats of wetting from the dry state ranged from 46.1 to 47.3 kJ/g; other data for various types and methods ranged from 41 to 54 kJ/g.

iii) Swelling:

Change of density of cotton with change of regain; this is converted into change in specific volume. Initially from the dry state, there is an increase of density due to water molecules occupying 'empty space' within the fibre. The density is a maximum at about 2% regain, and then decreases since the density of water is less than that of fibre.

Above 20% regain, the volume increase equals the equivalent volume of liquid water. The swelling of cotton fibers is predominantly in the transverse direction, (Cook, J.G., 2000) states that, in going from the dry to the wet state, the increase in length is 1.2% but the increase in diameter is 14%.

## 2.2 REACTIVE DYES

Cotton fabrics as the substrate, the most suitable class of dyes for coloring it are the class known as 'reactive' dyes. As the first part of the project work, the relevant information of this class of dyes has been collected and reviewed.

It is well known that cellulosic textiles can be dyed with reactive dyes. Reactive dyes have groups that form covalent bonds with the cellulose molecules (John Shore, 1995). A significant difficulty in using reactive dyes on cellulosic textiles is that reactive



dyes are not naturally strongly substantive to cellulose so that large amounts of salts example NaCl are used to encourage deposition of the dye onto the textile. Even with the use of salt, complete exhaustion of the dye bath is not obtained so that substantial amounts of dye are left in the dye bath. Residual reactive dye and hydrolysed dye (which is often formed because for many reactive dyes on cellulosic substrates, the dyeing is carried out under alkaline conditions) needs to be removed from the fabric after dyeing by often prolonged and complex wash off procedures. Failure to carry out this post-dyeing washing thoroughly generally leads to poor wash fastness.

Reactive dyes are dyes which include a reactive centre will react with a nucleophilic group (conventionally on the material of the textile being dyed) to form a covalent bond which strongly bonds the dye to the fibre.

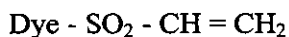
### **Vinyl sulphone (Remazol)**

Introduced by Hoechst (Dystar) in 1958, these are alkali controllable reactive dyes. These dyes have optimal temperatures of fixation between 50°C to 60°C. They are characterized by relatively low exhaustion in neutral salt solution, before alkali is added. They have high reactivity and it is necessary to be careful when adding alkali to achieve level dyeing, preferably at a controlled dosage rate ( Venkidusamy, P, 2000).

### **Reactive Dye Molecular Structure**

The vinyl sulphone dyes react via a nucleophilic addition. In the presence of alkali, the parent sulphatoethyl sulphone precursors form vinyl sulphone. The hydroxyl group of cellulose can react with the vinyl group to form an ether bond.

Typical Components of a Vinyl sulphone Dye



Example:

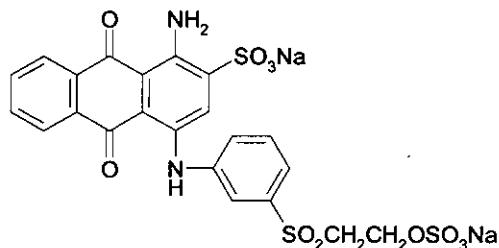


Fig: 2.4 Sulphatoethyl sulphone dyes

### Reactive Dye (vinyl sulphone) Vs Cellulose

A vinyl sulphone group, the dyeing conditions will typically be strongly alkaline (pH typically 10.8 to 11.2) and the dyeing temperature typically 60°C. After dyeing the cellulosic textile material with reactive dyes, it is necessary to remove any unbound, for example unreacted or hydrolyzed reactive dyes (Kanetkar, V.R., 2001).

### Nucleophilic addition reaction

The most important dye class is the Remazol reactive dye. This dye type reacts in the presence of a base such as  $\text{OH}^-$ . The mechanism for the reaction of one of these dyes is shown below (John Shore, 1995).

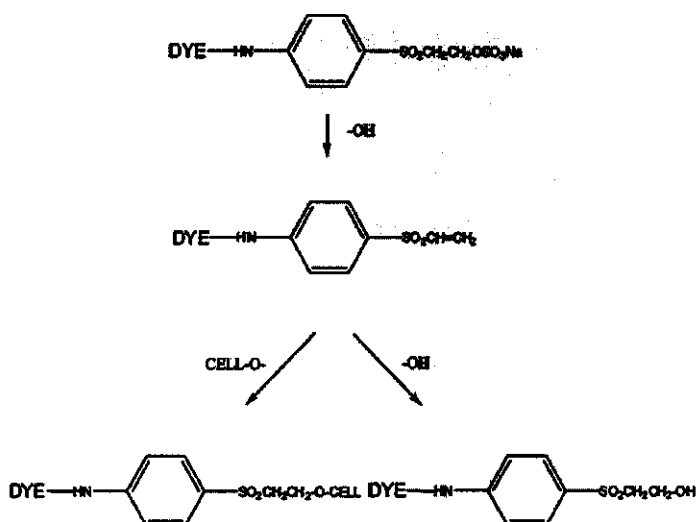


Fig: 2.5 Nucleophilic Addition Reactions

An important issue to consider when dealing with reactive dyes is the fact that two competing reactions are always involved in the coloring process:

Alcoholysis : dye + fibre  $\longrightarrow$  dye fixed on the fibre.

Hydrolysis : dye + water  $\longrightarrow$  hydrolyzed dye washed away after dyeing  
(undesired reaction).

### 2.3 TEXTILE PRINTING

Textile printing is a process of bringing together a design, idea, some colorants and textile substrate, the fabric and working out a technique for applying colorants with precision, says Leslie W C Miles, (2003). According Jai Prakash, R.D., (1997), printing is a new method of coloration to obtain novel design. Printing gives colour to the particular area of fabric in accordance with a predetermined design.

Patnaik and Chakraborty (1995) say that textile printing is called “localized dyeing” and the dye penetrates into the selective areas of the substrate. Leslie W C Miles, (2003) describes that textile printing is a localized or restricted form of dyeing and used to signify the production, by various means of coloured patterns or designs on textile materials. The term “printing” is used to signify the production by various means of coloured patterns or designs on textile materials, other than woven, embroidered, or painted designs.

The technology of printing enables us to produce sharp outlines that can be obtained by new techniques like screen, roller, photographic models, airbrushing, jet printing, remarks Parmar, M.S., (2003). Printing has been classified into different methods like diazo style, sublimate, spray, direct, discharge and pigment printing, that methods of printing used for producing the printing effect depends upon the method employed (Patnaik, M. and Chakraborty, M., 1995).

### 2.3.1 METHODS AND STYLES OF PRINTING

Abrahat (1982) classify the styles of printing as direct, resist and discharge. Storey (1992) says that it is possible to divide printed fabrics into four different classes or styles, the resist styles, the dyed style, the discharge style and the direct style. In direct style of printing, the dyes are printed directly at the required places and the multicolored print on a white ground can be produced. Now-a-days most of the designs are printed in direct style.

The direct style may be produced by the direct application of colour to the fabric. The resist style as the name implies comes from printing the material with the substance which will resist dyeing and hence produce a pattern on a coloured background, state Menezes, E. and Rossari, D., (2007). According to Abraham (1982), styles of printing differ from method of printing. Method of printing deals with the mechanical means employed to apply colour in a design to a textile material while styles of printing deals with different process utilized for fixing various classes of dyes on textile materials.

Screen printing, is a relatively simple method of printing which can be carried out without the use of complicated and expensive equipment. Leslie W C Miles, (2003) remarks that screen printing is a manual method of applying colour locally, fundamentally it is stenciling. The more intense and brighter prints can be produced in screen printing than in roller printing, the printer is able to print very short runs economically is screen printing.

According to Patnaik, M. and Chakraborty, M., (1995) originally this technique was referred to as silk screen printing because the screens were made of fine, strong silk threads, the screen printing principle is almost the same as that of stenciling. The rotary screen printing machine can print upto 24 colours on any kind of fabrics and in widths ranging from 180-320 cms has a speed of 0-80 mts. per minute.

### 2.3.2 DISCHARGE PRINTING

Discharge printing a wide scope of ornamentation with appeal as it can produce contrasting designs. Parmar (2003) says that the technology to carry out discharge printing of fabrics is well established. There is a need to develop a commercially acceptable simple method to carry out discharge printing of textiles.

Discharging of the ground colour (dyed colour) can be carried out by oxidation (or) reduction, says Jaiprakash (1997). Oxidation discharge produces sharper prints and pure white than reduction discharge due to the bleaching effect in the discharged parts of the design. Oxidizing discharge agents are not widely used as they degrade the fibres. Some of the limitations of conventional discharge printing using reducing agents are as follows described by Parmar (2003).

- The range of dyes available for printing is limited, all dyes cannot be easily discharged, and all dyes are not compatible with discharging agents.
- Discharging of the colour takes place only at high temperature, which demands steaming (or) curing.
- After printing the material has to be washed thoroughly to remove discharging agent and other printing ingredients, such as thickener.

Recently, the environmental and industrial safety conditions increased the potential use of enzymes for textile processing to ensure eco-friendly production.

In discharge style of printing the ground colour is applied by dyeing or padding with dischargeable dyes. The motifs are printed with discharging agent (reducing type) which destroys the ground dye chromophore during steaming. Thus a white discharge is formed. By incorporating a dye unspoiled by the discharging agent in the printing paste, a colour discharge is formed. In colour discharge the ground colour is discharged and replaced by a new colour in the printed area.

It is the production of a printed pattern on a pre-dyed cloth, with a paste containing a suitable reducing agent, which destroys (strips) the ground colour dye during subsequent steaming at the printed portions. Thus discharge style is nothing but localized stripping, remarks Parmar (2003).

### **White Discharge**

If the ground colour on the printed area is destroyed by the reducing agent, leaving a white pattern on the printed area it is called as “White Discharge Printing”.



### 2.3.3 SCREEN PRINTING TECHNIQUES

John Foulds, (1990) says that printing is carried out on a flat, solid table covered with a layer of resilient felt and washable blanket and small batch quantities can also be manufactured without incurring any additional costs. Two people position the screen on the fabric, apply the colour, move the screen to new position and repeat the process until all the fabrics is printed.

According to Jai Prakash, R.D., (1997) for direct style the cloth to be printed is pinned or pasted to a padded long table. The colour in the paste form is poured on the screen and forced through the screen by moving a squeeze.

Printing is carried out on a flat, solid table covered with a layer of resilient felt and washable blanket and small batch quantities can also be manufactured without incurring any additional costs. Two people position the screen on the fabric, apply the colour, move the screen to new position and repeat the process until all the fabrics is printed (John Foulds, 1990).

According to Venkidusamy, P. and Ramasundaran, S., (2000) for direct style the cloth to be printed is pinned or pasted to a padded long table. The colour in the paste form is poured on the screen and forced through the screen by moving a squeeze.

### 2.4 PRINTING PASTE

The viscosity of the printing paste is very important as it influences the clarity and appearance of the printed pattern. According to John Foulds, (1990), printing involves the deposition of a viscous paste containing the dye stuffs, a thickening agent, and a small amount of water on the surface of the fabric and immediately dried to prevent any spreading of the colour beyond the boundaries of the design.

The printing paste consists of essential components like dyes and pigments, wetting agents, solvents and solution aids, thickeners, de-farmers, oxidizing and reducing agents,

acids and alkalies. Each compound may suit one particular class of dye describe the action of dye molecules within the printing paste as follows:

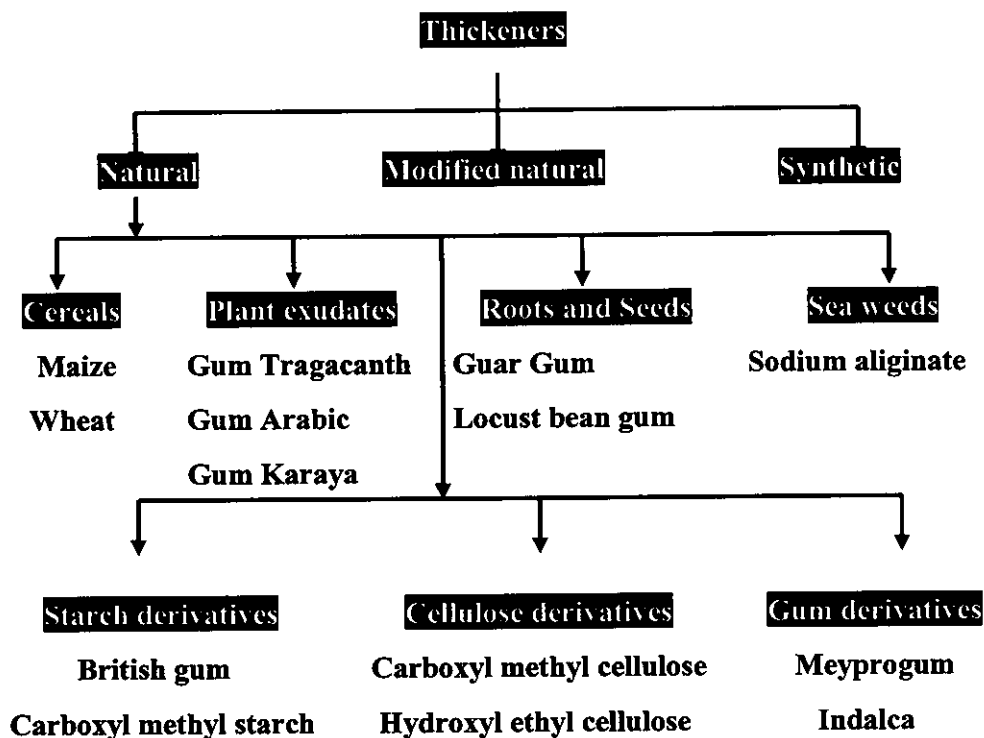
- Forces of repulsion are developed between the dye molecules and the constituents of the printing paste.
- Forces of attraction are developed between the dye molecules and the fibres of the textile material to be printed.

Leslie W C Miles, (2003) explains that while preparing the printing paste, the required dyes and chemicals are dissolved in minimum quantity of water; thickener paste is added and stirred vigorously to produce a uniform paste. Stability of printing paste has to be considered while preparing the paste.

Thickeners are mainly employed in giving consistency to colouring matters; they are often of service as dilatants, view Clarke, W., (1980). The clarity of the printed pattern depends very much on the particular thickener used. The success of printing textile materials depends very much on the type and quality of the thickeners. They also state that the purpose of the thickener is to produce a medium for the dye paste and the resultant product is called printing paste.

Clarke, W., (1980) explain that thickeners ensure that the particular shape to be printed can be reproduced without being distorted by bleeding. Venkidusamy, P. and Ramasundaran, S., (2000) review that the thickeners used in textile printing is high molecular weight compounds, giving viscous solution, when dissolved in water. According to Prayag (1989) the thickener used in printing is the form of a paste or emulsion in order to prevent spreading of the dye beyond the boundaries of the design and hold the dye particles in the printed portions until they are fixed into the fabric.

- . Clarke. W (1980) states that prime function of a thickening agent in textile printing is to enable the dye stuff or pigment to be transferred to the fabric at the printing stage. the thickeners are classified as follows:



All the richly varied products brought back from the orient and South America, were natural gums to add to the starch paste. He also states that the traditional thickeners are starches and gums. They were used for about 200 years without any development. In recent years, thickeners such as starch, ethers, locus bean flours, aliginates, cellulose derivatives and emulsion thickeners are used (Clarke.W 1980).

Patnaik, M. and Chakraborty, M., (1995) opine that there are number of thickeners available but the easiest to mix, use and store are those based on sodium aliginates, manufactured from sea weeds. It is available in powder form.

## 2.5 ENVIRONMENTAL IMPACT OF DYEING AND PRINTING

Dyeing and printing textiles can have a significant impact on the environment from discharge of dyes, pigments and other chemicals into water systems, components that contribute to problems include colour, salt, acids and heavy metals, state Suresh (1996).



Some materials create problems because of high Biological Oxygen Demand (BOD), others have high Chemical Oxygen Demand (COD). High BOD and COD materials create an environment that are hostile to aquatic plants and animals and may create problems with future use of the water, refer: Rai, I., (2004).

According to Nishkam, A. and Verma, N., (2003) synthetic dyes involve many violent chemical reactions and the by-products formed; have to be discharged in water or in the atmosphere. Harmful effects of synthetic dyes have promoted the researcher to look for eco-friendly products and technologies. The reaction conditions are drastic. In the eyes of many, these products embody incalculable risks for human beings and the environment.

The effect of pollution has attained global dimensions examples include the formation of the "hole" in the ozone layer by halocarbons and the potential effects of green house gases on the world's climate, elaborate Prasad, M.C., and Manikam, M.M., (2006). Many synthetic dyes, particularly those azo dyes, obtained from alphaarylamines have been found to be potentially carcinogenic.

Most textiles are colored in one manner or another because consumers demand colour, one option to decrease environmental impacts is to use fewer dyed (or) printed textiles.. Owing to the global consciousness about the use of eco-friendly dyes due to the hazardous and carcinogenic effect of many synthetic dyes, awareness has been created on selection of dyes that may be used for textiles. According Suresh et al., (1996) dyes and pigments with low environmental impact will continue to be a major thrust in preparing goods with consumer appeal.

### **2.5.1 FORMALDEHYDE AND ITS PROBLEM**

Formaldehyde is a colorless, strong-smelling gas. When present in the air at levels above 0.1 ppm (parts in a million parts of air), it cause watery eyes, burning sensations in the eyes, nose and throat, nausea, coughing, chest tightness, wheezing, skin rashes, and allergic reactions.

It also has been observed to cause cancer in scientific studies using laboratory animals and may cause cancer in humans. Typical exposures to humans are much lower;

thus any risk of causing cancer is believed to be small at the level at which humans are exposed. Formaldehyde can affect people differently. Some people are very sensitive to formaldehyde while others may not have any noticeable reaction to the same level. Persons have developed allergic reactions (allergic skin disease and hives) to formaldehyde through skin contact with solutions of formaldehyde or durable-press clothing containing formaldehyde.

Others have developed asthmatic reactions and skin rashes from exposure to formaldehyde. Formaldehyde is just one of several gases present indoors that may cause illnesses. Many of these gases, as well as colds and flu, cause similar symptoms (US, CPSC., 1997).

## 2.6 ENZYMES

Enzymes are large protein molecules made up of a long chain of amino acids which are produced by living cells in plants, animals and micro organisms such as bacteria and fungi, view Doshi and Shelke (2001). Enzymes are complicated chemical substances found in all living things. They act as catalyst – that is they cause chemical reactions (changes) without being changed themselves. Enzymes are specific that is, they control only one particular chemical change or type of change, quotes Gokilavani, R. and Gopalakrishnan, D., (2007)



**Fig: 2.6 Enzyme- Substrate binding**

These principles can be applied to enzyme catalysis where an intermediate transition state is formed between a substrate and an enzyme accelerating the conversion of a substrate into a product. In this reaction, the substrate must fit precisely into the active site of the enzyme. Since enzymes are highly specific catalysts, it can be expected that the formation of the enzyme—substrate complex or the binding of the substrate in the active site will require only little energy. Consequently, enzymes are very effective catalysts., review Churi, R., Khadilkar, S. and Sules, S (2004).



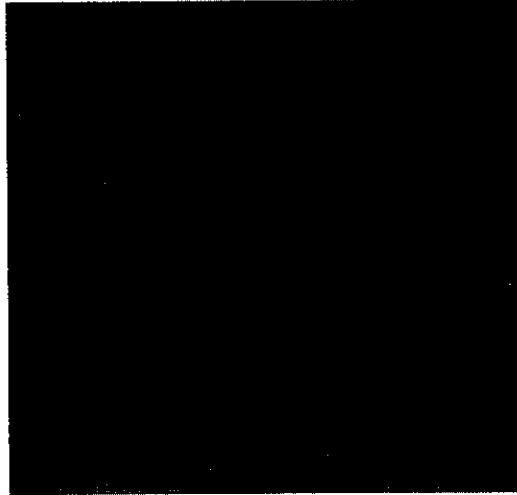
**Table 1: Major Enzyme Classes**

<b>Class</b>	<b>Function</b>
Oxidoreductases	Catalyze oxidation-reduction reactions
Transferases	Catalyze group transfer reactions
Hydrolases	Catalyze hydrolytic reactions
Lyases	Catalyze reactions involving a double bond
Isomerases	Catalyze reactions involving isomerization
Ligases/Synthetases	Catalyze reactions involving joining two Molecules coupled with the breakdown of a peptide bond .
Peroxidase	Catalyse of oxidation of variety substrate by H <sub>2</sub> O <sub>2</sub>

### 2.6.1 STRUCTURE FEATURE OF HORSERADISH PEROXIDASE

Horseradish peroxidase is a protein with a molecular weight of about 40,000 which contains a single protoporphyrin IX hemegroup. This enzyme catalyzes the oxidation of a variety of substrates by hydrogen peroxide. Most scientists demonstrated of heme and carbohydrate as components of horseradish peroxidase, the first observation of the catalytic intermediates known as compounds I and II and the first kinetic analysis of the reaction with hydrogen peroxide (Nigel C. Veitch, 2004).

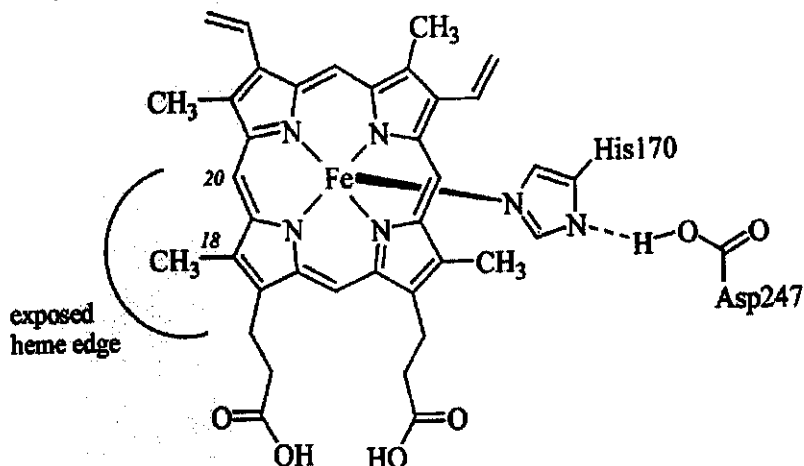
The enzyme horseradish peroxidase (HRP), found in horseradish, is used extensively in biochemistry applications primarily for its ability to amplify a weak signal and increase detect ability of a target molecule.



**Fig: 2.7 Horseradish plant (Source: General history of planets)**

Horseradish peroxidase enzymes belong to class III ('classical' secretory plant peroxidases) of the plant peroxidase super family, which includes peroxidases of bacterial, fungal and plant origin. The remaining two classes comprise yeast cytochrome c peroxidase, gene-duplicated bacterial peroxidases and ascorbate peroxidases (class I), and fungal peroxidases (class II).

The overall integrity of the structure in this region is maintained by the disulphide linkage. What is particularly interesting in the case of HRP is the location of residues in helix F0 that are involved in substrate access and binding. Some authors have speculated that this structural region is important for stabilization or retention of radical species produced in reactions catalyzed by plant peroxidases (Mark A. Ator, Shantha K. David, and Paul R 1987).



**Fig: 2.8 Structural features of Horseradish peroxidase enzyme**

HRP contains two different types of metal centre, iron (III) protoporphyrin IX (usually referred to as the 'heme group') and two calcium atoms. Both are essential for the structural and functional integrity of the enzyme. The heme group is attached to the enzyme at the proximal histidine residue by a coordinate bond between the histidine side-chain atom and the heme iron atom. The second axial coordination site is unoccupied in the resting state of the enzyme but available to hydrogen peroxide during enzyme turnover.

### 2.6.2 MECHANISM OF HORSERADISH PEROXIDASE WITH HYDROGEN PEROXIDE

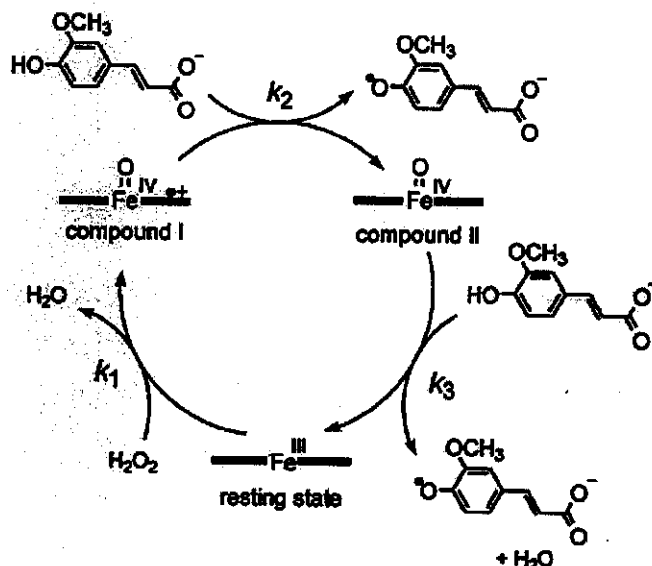
Hydrogen peroxide reacts with ferrous horseradish peroxidase and converts it to oxypoxidase in a sequence of two reactions. The first is the reaction of ferrous peroxidase with H<sub>2</sub>O<sub>2</sub> to form Compound II; the second is the reaction of Compound II with H<sub>2</sub>O<sub>2</sub> to form oxypoxidase.

Most reactions catalyzed by HRP and other horseradish peroxidase enzymes can be expressed by the following equation, in which AH<sub>2</sub> and AH\* represent a reducing substrate and its radical product, respectively. Typical reducing substrates include aromatic phenols, phenolic acids, indoles, amines and sulfonates.



### 2.6.3 Enzymatic Catalytic Mechanism

Important features of catalytic cycle can illustrate in below figure with ferulic acid as reducing substrate. The generation of radical species in the two one – electron reduction steps can result in a complex profile of a reaction products, including dimmers, trimers and higher oligomers that may themselves act as reducing substrate in subsequent turnovers.



**Fig: 2.9 Catalytic cycle of horseradish peroxidase**

The first step in the catalytic cycle is the reaction between H<sub>2</sub>O<sub>2</sub> and the Fe (III) resting state of the enzyme to generate compound I, a high oxidation state intermediate comprising an Fe (IV) oxoferryl center and porphyrin based cat ion radical. In formal terms, compound I is two oxidizing equivalents above resting state (Nigel C. Veitch, 2004).

The first one – electron reduction step requires participation of a reducing substrate and leads to the generation of compound II, an Fe (IV) oxoferryl species that is one oxidizing equivalent above resting state. Both compound I and compound II are powerful oxidants, with redox potentials estimated to be a close to +1V. The second one - electron reduction step returns compound II to the resting state of the Enzyme. Bio discharge printing concept derived from this enzymatic catalytic mechanism (Oxidation of dyes).

## CHAPTER 3

### MATERIALS AND METHODS

#### 3.1 MATERIALS

##### 3.1.1 FABRIC PARTICULARS

Woven cotton fabric (full bleached) having plain weave was used as the substrate for dyeing and enzymatic discharge printing. The geometrical properties of the fabric are given in Table-1

**Table 2: Geometrical parameters of 100 % Cotton Fabric**

100% Cotton	34	33	140	40	40
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##### 3.1.2 CHEMICALS USED

The following chemicals were used for dyeing and enzymatic discharge printing on the cotton fabric. The details of the dye and the chemicals used are given in Table-3.

**Table 3: Dyes and Chemical used**

1	Reactive Black CLS (Commercial name)	Dyeing
2	Glauber Salt	Exhaustion agent
3	Sodium Carbonate ( $\text{Na}_2\text{CO}_3$ )	Fixing agent
4	Horseradish Peroxidase (Hi Media)	Discharging agent
5	Sodium Alginate	Thickener
6	Hydrogen Peroxide	Oxidizing agent
7	Sodium Perborate	$\text{H}_2\text{O}_2$ precursor

### 3.2. METHODS

The practical work of our project was divided into six stages as described below:

- Stage 1:** Dyeing the cotton fabrics with Vinyl sulphone Reactive dyes.
- Stage 2:** Preparation of enzymatic printing paste
- Stage 3:** Optimize the Horseradish peroxidase enzyme activity.
- Stage 4:** Carry out enzymatic discharge printing on dyed cotton and silk fabrics.
- Stage 5:** Washing printed fabric with water.
- Stage 6:** Evaluate the enzymatic discharge printed fabric properties against Conventional discharge printed fabric.

#### 3.2.1 REACTIVE DYEING

The fabric dyed with reactive dye using Exhaust dyeing method which was carried out at liquor ratio 1:30. Dyeing of fabric was carried out at 60° C for 60 min. Fixation was conducted for 20 min. using 6 to 8 gpl of Na<sub>2</sub>CO<sub>3</sub> and 0.01 to 0.5 gpl of caustic lye. Process conditions for dyeing are given in Table-4.

**Table 4: Process conditions for dyeing**

Dyeing Temperature	60 °C
Glauber's salt	60 gpl
Na <sub>2</sub> CO <sub>3</sub>	20 gpl
pH	10-11
Time of Dyeing	60 min
Fixation time	20 min.



After dyeing, the fabric was rinsed thoroughly in three changes of soft water and dried in shade.

### 3.2.2 ENZYMATIC DISCHARGE PRINTING

Screen printing method was used in this work wherein print paste is forced through the unblocked areas of the screen. Pressure is applied to the paste by squeeze which is moved when the screen is stationary. Screen printing facilitates the production of delicate or bold designs.

First, the table was set by lying of fabric to get a padded surface and the fabric to be printed was spread over it without creases or wrinkles. It was pinned on four corners to keep it in position. Enzymatic discharge printing (White Discharge printing) was carried out as per below recipe, this was mixed well and using the screens, printing was done on the cotton and silk fabric samples to discharge the ground colour.

The printing paste was poured on the screen and two strokes were given with the squeeze with equal pressure. Then the samples were allowed to dry flat on the table. After giving the enzymatic printing, samples were washed and dried.

#### Printing Recipe

Horseradish Peroxidase	:	30, 50, 70, 80, 90 g / Kg
Sodium Alginate	:	20 g
Hydrogen peroxide	:	20 ml
Water	:	Yg
<hr/>		
Total	:	<hr/> 1000g

The optimization of standard conditions for Horseradish peroxide enzyme treatment was also done. Optimization for enzyme treatment was carried out for various parameters such as enzyme concentration, pH, time, temperature and viscosity.

### 3.2.3 WASHING

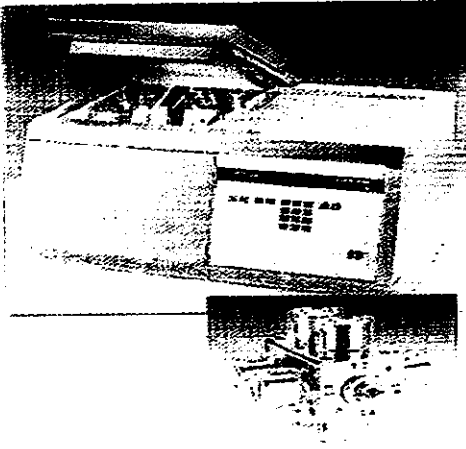
The printed fabrics were rinsed with cold water followed by washing in presence of sodium perborate at 60° temperature for 30 min. After the washing, the incubated fabrics were again washed with ECE detergent (4g/L) at 60° temperature for 30 minutes. Finally samples kept in air drying room.

### 3.3 TESTING METHODOLOGY

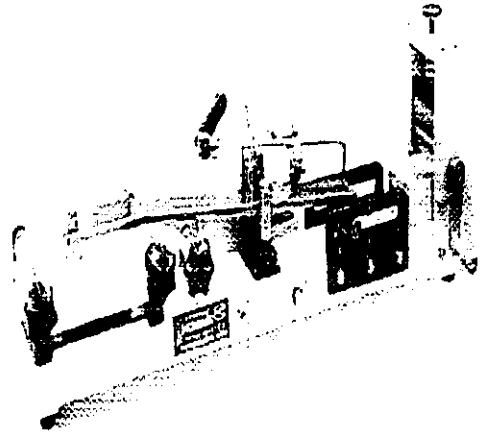
The following tests have been carried out to analyze various parameters of printed fabric was given in Table – 5.

**Table 5: Testing Methods and Instruments Used**

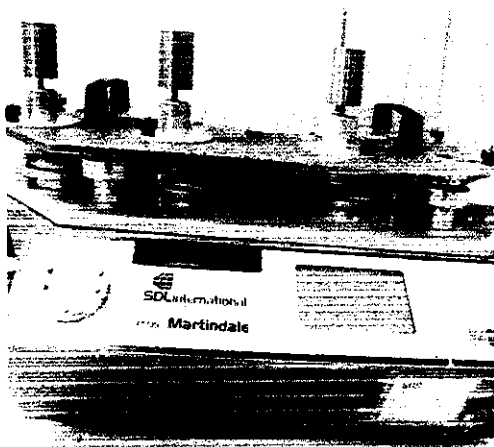
1.	Colour Change Evaluation	ISO 105 JO3:2009	X- Rite Spectrophotometer
2.	Formaldehyde Content	ISO 14184-1:1998	UV- Vis Spectrophotometer
3.	Absorbency Tests	AATCC 79:2007	Absorbency tester
4.	Crocking fastness to Washing	ISO 105 C06- B2S(50°C)	Laundr-O- Meter
5.	Color fastness to Rubbing	AATCC 08:2005	Crock meter
6.	Bursting Strength	ISO 13938-2	Pneumatic Bursting strength Tester
7.	Tensile strength	ASTM D5034-2009	Instron tensile strength tester
8.	Colour fastness to Water	ISO 105 E0:2010	Perspirometer
9.	Abrasion Resistance	ISO 12947-2 ;1999	Martindale Abrasion tester



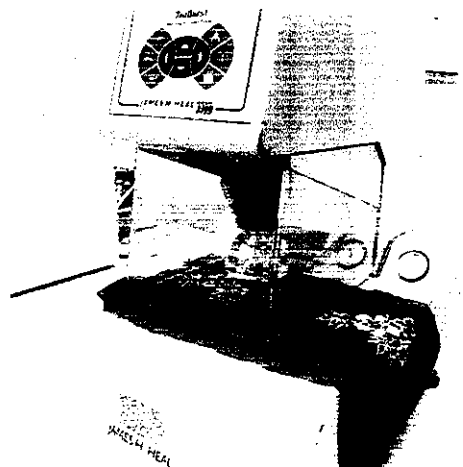
**LAUNDR-O-METER**



**CROCKMETER**



**ABRASION TESTER**

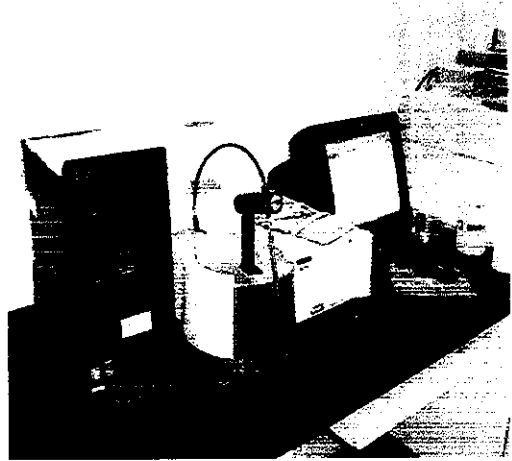


**PNEUMATIC BURSTING  
STRENGTH TESTER**

**TESTING INSTRUMENTS**



**X- RITE SPECTROPHOTOMETER**



**UV- VIS SPECTROPHOTOMETER**



**TENSILE STRENGTH TESTER**



**ABSORBENCY TESTER**

### 3.3.1 COLOUR CHANGE EVALUATION: (ISO J03:2009)

Colour change difference had determined by using X-rite Spectrophotometer in base & printed area where  $L^*$ ,  $C^*$   $h^\circ$  values were analyzed in D65  $10^\circ$  observer condition (1976 CIE LAB). The colour difference is composed of three components that comprise the differences between the reference and the specimen. These are as follows.

- a) A **lightness** component that is weighted by a lightness difference ( $\Delta L^*$ ).

If the  $\Delta L$  is positive, the specimen is lighter than the reference. If the  $\Delta L$  is negative, the specimen is darker than the reference;

- b) A **chroma** component that is weighted by the chroma tolerance ( $\Delta C$ ).

If the  $\Delta C$  is positive, the specimen is more chromatic than the reference. If the  $\Delta C_{cmc}$  is negative, the specimen is less chromatic than the reference;

- c) A **hue** component that is weighted by the hue tolerance ( $\Delta H^*$ )

If the  $\Delta H$  is positive, the hue difference of the specimen is anti-clockwise from the reference in the CIELAB  $a^*$ ,  $b^*$  diagram. If the  $\Delta H$  is negative, the hue difference of the specimen is clockwise from the reference in the CIELAB  $a^*$ ,  $b^*$  diagram.

### 3.3.2 DETERMINATION OF FORMALDEHYDE CONTENT: (ISO 14184-1:1998)

The Printed samples were tested according to ISO 14184-1:1998 standard test method: Determination of formaldehyde (Free and hydrolyzed formaldehyde – water extraction method). From the sample, two test specimens taken into small pieces, and weigh approximately 1 g of the pieces to an accuracy of 10 mg.

For each test specimen, put the weighed pieces into a 250 ml flask with stopper) and add 100 ml of distilled water . Stopper tightly and place in a water bath at  $(40 \pm 2)^\circ\text{C}$  for  $(60 \pm 5)$  min. Shake the flask at least every 5 min. Then filter the solution into another flask through a filter.

5 ml of the filtered test specimen solution putted into a tube and 5 ml of the standard formaldehyde solutions into further tubes. Add 5 ml of acetyl acetone reagent into each tube and shake them. Keep the test tubes first in a water bath at  $(40 \pm 2) ^\circ\text{C}$  for  $(30 \pm 5)$  min and then at ambient temperature for  $(30 \pm 5)$  min. Taking the solution of 5 ml of acetyl acetone reagent solution in 5 ml of water having been treated in the same way as the blank reagent and using X-rite spectrometer, measure the absorbance in a 10mm absorption cell at a wavelength of 412 nm against water.

### **3.3.3 ABSORBENCY TESTING: (AATCC 79: 2007)**

Absorbency is one of several factors that influence textile processing such as fabric preparation, dyeing, and the application of finishes. Often interchanged with the term wettability, the absorbency characteristics of a fabric can influence the uniformity and completeness of bleaching and dyeing by the ability to take in water into the fiber, yarn, or fabric construction. The suitability of a fabric for a particular use, as in the case of gauze or toweling, is also dependent upon a fabric's ability and propensity to take up water.

A drop of water is allowed to fall from a fixed height onto the surface of a test specimen. The time required for the specular reflection of the water drop to disappear is measured and recorded as wetting time. Specimen was mounted in an embroidery hoop so that the surface is taut, and free of wrinkles but without distorting the structure of the specimen.

Place the hoop 9.5mm below the tip of the burette and allow one drop of distilled water to fall on the cloth. Start the stopwatch immediately Measure the time required for the drop of water to lose its specular reflectance. If the water drop does not immediately disappear, observe the water drop from other positions until it finally vanishes.

### **3.3.4 TENSILE STRENGTH: (ASTM D5094:2009)**

The breaking strength test of printed cotton samples were carried out in both warp and weft direction using Instron tensile strength tester (CRE type). A 100-mm (4.0-in.) wide specimen was mounted centrally in clamps of a tensile testing machine and a force applied until the specimen breaks. Values for the breaking force and the elongation of the test specimen were obtained from machine autographic recording charts interfaced with the

testing machine. Specimen mounted in the clamp jaws with the previously drawn parallel line adjacent to the side of the upper and lower front, or top, jaws which was nearest this edge, and with approximately the same length of fabric extending beyond the jaw at each end. This test method carried out fabric grab tensile testing as per below condition.

#### Testing parameters

Machine Type	:	CRE
Gage length	:	75 mm
Rate of Extension	:	300 mm/ min
Specimen Size	:	100mm x 200 mm

#### 3.3.5 ABRASION RESISTANCE (ISO 12947-2:1999)

Printed fabric were mounted in Martindale specimen holder and subjected to a defined load, was rubbed against an abrasive medium (standard fabric) in a translational movement tracing a Lissajous figure, the specimen holder being additionally freely rotatable around its own axis perpendicular to the plane of the specimen. The evaluation of the abrasion resistance of the textile fabric is determined from the inspection interval to breakdown of the specimens. Abrasion load was applied as 9kPa.

End point determination depends on fabric type and our fabric is woven so when two separate threads were completely broken, test stopped and determined number of rubs for each testing fabric. Testing interval given in below table.

**Table 6: Test Intervals for Abrasion Testing**

Test Series	Number of rubs at which specimen breakdown occurs	Test intervals (rubs)
a	$\leq 5000$	Every 1000
b	$> 5000 \leq 20000$	Every 2000
c	$> 20000 \leq 40000$	Every 5000
d	$> 40000$	Every 10000

## CHAPTER 4

### RESULTS AND DISCUSSIONS

#### 4.1 COLOUR CHANGE EVALUATION

Colour change difference testing (ISO 105 J03) has been used in which  $\Delta L^*$  value was considered to evaluate the efficiency discharging effect of Horseradish peroxide enzyme in various conditions. The various parameters have studied in this project for optimizations of enzyme activity were:

- 4.1.1 Effect of pH
- 4.1.2 Effect of enzymes concentration
- 4.1.3 Effect of Temperature
- 4.1.4 Effect of Treatment time.

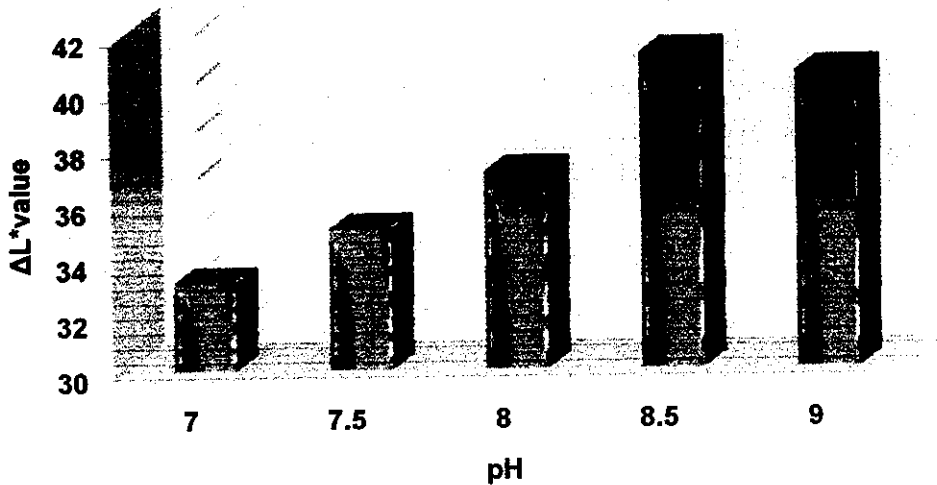
##### 4.1.1 EFFECT OF PH

It has been reported that most enzymatic activities are extremely sensitive to the pH so different pH has been maintained to get optimum condition in enzymatic discharging printing. Different printing paste containing enzyme with highest concentration was prepared and pH values was adjusted at 7, 7.5, 8, 8.5, and 9. Difference in Lightness value between the printed image and the surrounding fabric (base) indicates effectiveness of discharge of dyes by Peroxidase enzyme. Results of value are presented in Table-7

**Table 7: pH vs  $\Delta L^*$ value of Printed samples**

7.0	33.12
7.5	35.00
8	37.02
8.5	41.20
9	39.00





**Fig: 3.0 Effect of pH**

The current data reveals that the peroxidase enzyme and H<sub>2</sub>O<sub>2</sub> has its optimum oxidising activity at pH 8.5, i.e. the highest  $\Delta L^*$ . Enzymes, being proteins, exhibit Zwitter ion properties. The proton donating or proton accepting groups in enzymatic catalytic sites are at their required state of ionization at selected pH, showing the enzyme its optimal activity. A variation of pH during the course of reaction may bring about an alteration of the protein structure with denaturing effect on the enzyme or the ionization of the active site.

#### **4.1.2 EFFECT OF ENZYMES CONCENTRATION**

Different concentration of enzymes have been taken for Bio- discharge printing to estimate optimum quantity required to get maximum discharge effect in dyed fabric. A Series of white print paste containing different enzyme concentration (30, 50, 70, 80, 90 g/kg) was prepared. The cotton fabrics were then printed with these pastes using screen printing technique. Difference in Lightness value between the printed image and the surrounding fabric indicates effectiveness of discharge of dyes by Peroxidase enzyme. Results of CIE  $\Delta L^*$  value are presented in Table- 8 for different enzyme concentration.

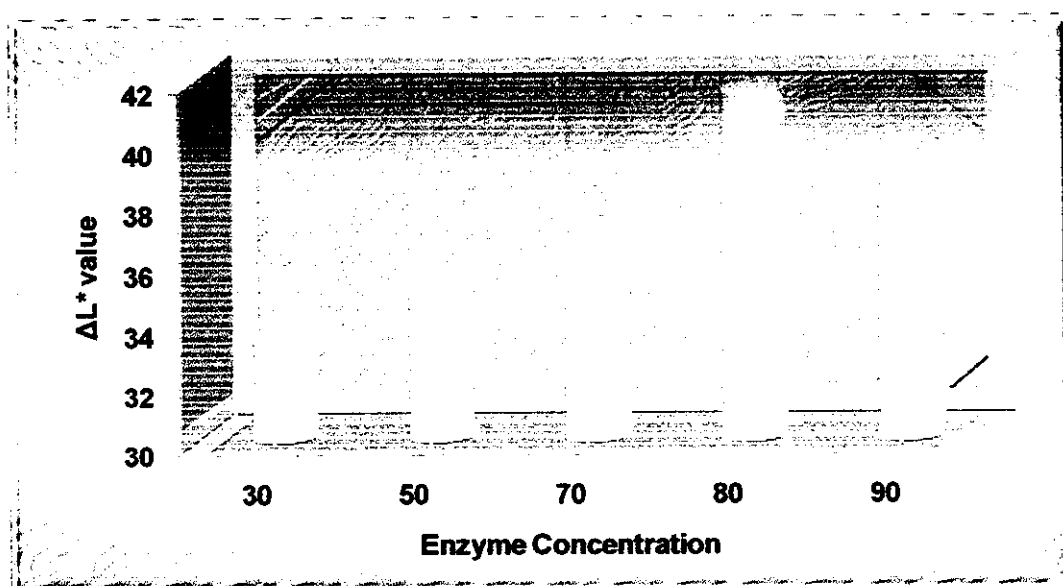
**Table 8: Concentration vs.  $\Delta L^*$  value of printed samples**

Enzyme concentration (g/Kg)	$\Delta L^*$ Value
30	33.29
50	35.18
70	36.99
80	41.53
90	39.16

From the table following observations are made.

- $\Delta L^*$  value is increased while concentration of enzyme increase up to 80g but it seems as irregular since in 100 g usage  $\Delta L^*$  value get reduced.

Above observations indicate that the optimum condition for white discharge, i.e. the highest  $\Delta L^*$ , was found to be dependent on the nature of the reactive dye used. The maximum increase in  $\Delta L^*$  of discharged printed fabric is 80 and 90 g/kg of peroxidase enzyme. The variation in amount of enzyme to obtain the high difference in lightness value depends on chemical structure, reactivity, structural configuration, bonding energy of reactive dyes with cotton fabric.

**Fig:3.1 Effect of Enzymes Concentration**

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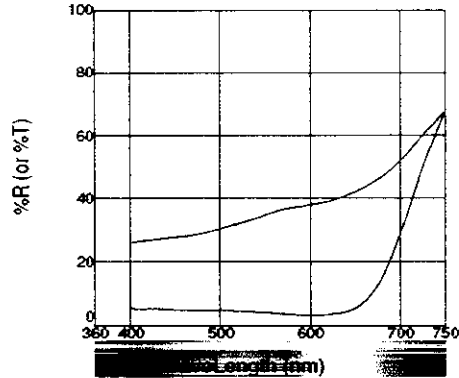
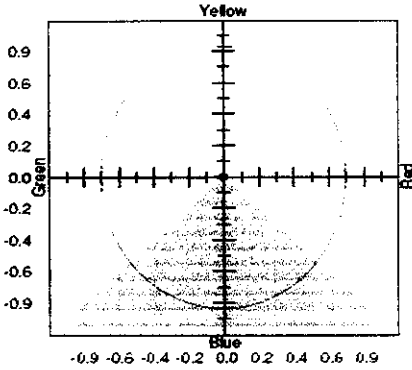
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**Bio-80g**

dCIELab: D65-10

- Base - Bio Printed- 80 g/kg



Tolerances:	DL* tol	Da* tol	Db* tol	DC* tol	DH* tol	P/F tol	Margin
D65-10	1.20	0.65	0.80	0.80	0.65	1.00	0.10

Standard Name:	L*	a*	b*	C*	H*	CV-SUM
Base	23.85	-0.02	-4.38	4.38	269.72	9.551

Trial Name	DL*	DC*	DH*	DE*	DL*cmc
Bio Printed- 80 g/kg	41.53 Lighter	5.80 Brighter	13.15 Redder	43.94	30.19

**Fig: 3.2 Colour Difference Testing Graph (Enzyme concentration – 80g)**

QC

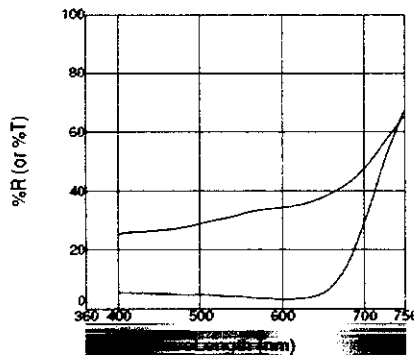
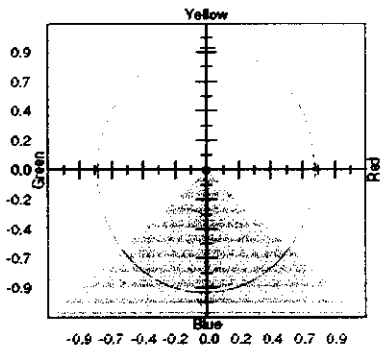
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**Bio-90g**

dCIELab: D65-10

- Base Bio Printed- 90 g/kg



Tolerances:	DL* tol	Da* tol	Db* tol	DC* tol	DH* tol	P/F tol	Margin
D65-10	1.25	0.65	0.80	0.80	0.65	1.00	0.10

Standard Name:	L*	a*	b*	C*	H*	CV-SUM
Base	24.20	-0.18	-4.77	4.78	267.79	9.284

Trial Name	DL*	DC*	DH*	DE*	DL*cmc
Bio Printed- 90 g/kg	39.16 Lighter	3.45 Brighter	12.40 Redder	41.22	28.18

**Fig: 3.3 Colour Difference Testing Graph (Enzyme concentration – 90g)**

### 4.1.3 EFFECT OF TEMPERATURE

It has been reported that the enzymes exhibit maximum activity at a specific range of temperature. Hence, it is of great interest to investigate the effect of drying temperature on the reactive dye colour discharge by Horseradish peroxidase enzyme. To achieve this goal, cotton fabric samples were printed with enzymatic white paste. After printing, the samples were subjected to drying at different temperatures, such as 40, 50, 60, 70, 80°C. Finally the fabrics were washed according to the procedure mentioned earlier. Results of CIE  $\Delta L^*$  value are presented in Table-9 for different temperature.

**Table 9: Temperature vs.  $\Delta L^*$  value of printed samples**

Temperature °C	$\Delta L^*$ Value
40	33.45
50	35.20
60	37.86
70	41.20
80	40.45

It is observed from table that as the drying temperature increase from 70°C to 80°C the  $\Delta L^*$  value decreases. The enzyme exhibit maximum activity at a specific temperature and above observation indicates 70 °C is optimum temperature for reaction of peroxidase with H<sub>2</sub>O<sub>2</sub> to produce maximum discharge effect on textile material.



#### 4.1.4 EFFECT OF ENZYMATIC TREATMENT TIME

It has been reported that the initial period of time the amount of substrate which has been transformed is directly proportional to the length of treatment time. After this initial period, the rate of reaction starts decreasing and the amount of reaction is no longer directly proportional to the treatment time. Provided the substrate is present in excess, the explanation of this phenomenon is the progressive loss of enzyme activity after a period of time. This may be due to the effect of heat on the tertiary structure of the enzyme or due to the formation of some product or side product of the reaction which inhibit the enzyme.

Therefore, the printed cotton samples were subjected to a drying process for various intervals of time in order to determine the optimum time available for attaining maximum dyes removal. The treatment was carried out at 70° C for 15, 30, 45, 60, 75 min followed by washing and drying. Finally, the printed samples were assessed for colour difference evaluation.

**Table 10: Treatment Time vs.  $\Delta L^*$  value of printed samples**

15	27.45
30	31.45
45	34.26
60	39.55
75	39.60

Table 10 shows that the colour removal increases regularly by increasing the treatment time until it reaches its maximum at 60min. Increasing the drying time beyond 60min causes a slight increase in the  $\Delta L^*$  value . This may be due to the progressive loss of enzyme activity.

## 4.2 FORMALDEHYDE CONTENT DETERMINATION

The printed samples were evaluated using UV- Vis Spectrophotometer according to ISO 14184-1:1998 standard test method: Determination of formaldehyde (Free and hydrolyzed formaldehyde – water extraction method).

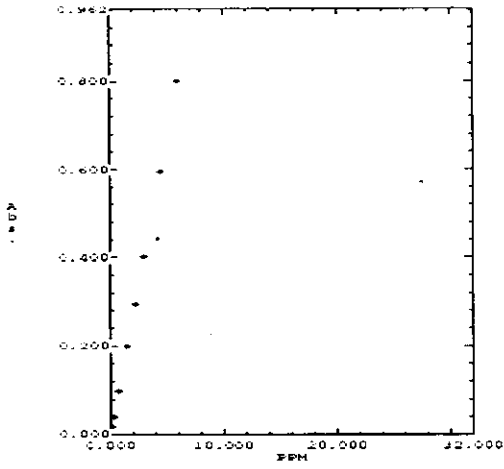
Results of formaldehyde content of samples are given in Table 11:

S. No	Sample Code	Description	Formaldehyde Content in ppm
1	COS	Cotton Original Sample	4
2	CDS	Cotton Dyed Sample	10.2
3	CEPS	Cotton Enzymatic printed sample	10.3
4	CCVS	Cotton conventional printed sample	90

It is obvious from the table that the CEPS and CDS samples had shown same formaldehyde content result whereas COS sample indicated that 4 ppm which is machine detection limit, hence there was no formaldehyde present. But, in case of CCVS fabric revealed that the formaldehyde present in the range of 90ppm. From that, we observed that Formaldehyde content in conventional discharged printed fabric was beyond acceptable limit of OKO- Tex 100 norms. (Skin contact: 75 ppm).

OEKO-TEX® Standard 100		Seite / Page / Page 26		
<b>Anhang / Appendix / Annexe 4</b>				
<b>Grenzwerte und Echtheiten, Teil 1 / Limit values and fastness, part 1 / Valeurs limites et solidités, partie 1</b>				
<small>(Die Prüfverfahren sind in einem separaten Dokument beschrieben / The testing methods are described in a separate document / Les procédures des tests sont décrites dans un document distinct)</small>				
Produktklasse / Product Class / Classe de produits	I Baby / Baby / Bébé	II mit Hautkontakt / In direct contact with skin / en contact direct avec la peau	III ohne Hautkontakt / with no direct contact with skin / sans contact avec la peau	IV Ausstattungsmerkmalen / decoration materials / matériel de décoration
pH-Wert / pH value / valeur pH <sup>1</sup>	4,0 - 7,5	4,0 - 7,5	4,0 - 8,0	4,0 - 8,0
Formaldehyd / formaldehyde / formaldéhyde [mg/kg]		75	300	300
Law 112 / Law 112 / Law 112	n.d. / n.d. / n.d. <sup>2</sup>			

Fig: 3.5 OKO-TEX standard 100



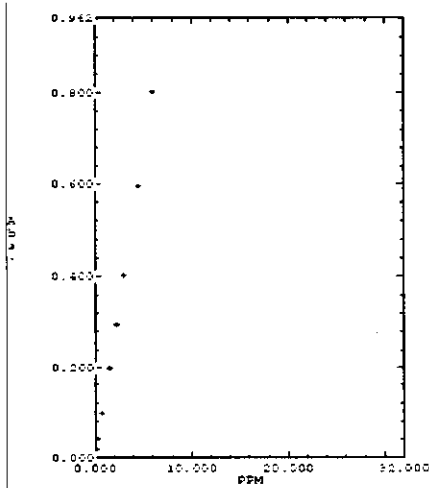
Std #	Conc.	Abs.
1	0.1500	0.012
2	0.3000	0.024
3	0.4500	0.036
4	0.7500	0.060
5	1.5000	0.120
6	3.0000	0.240
7	4.5000	0.360
8	6.0000	0.480

File Name: 15FEB11

ID	Conc.	Abs.
1	0.2010	0.120

Created: 15:53 15/02/11  
 Data: Modified  
 Wavelength: 415.0  
 Slit Width: 2.0  
 Multi-Point Working Curve  
 Conc = 7.500 Abs  
 Chi-Square: 0.00020  
 Number of Points: 8

**Fig: 3.6 Formaldehyde Testing Graph (Conventional Discharge printed sample)**

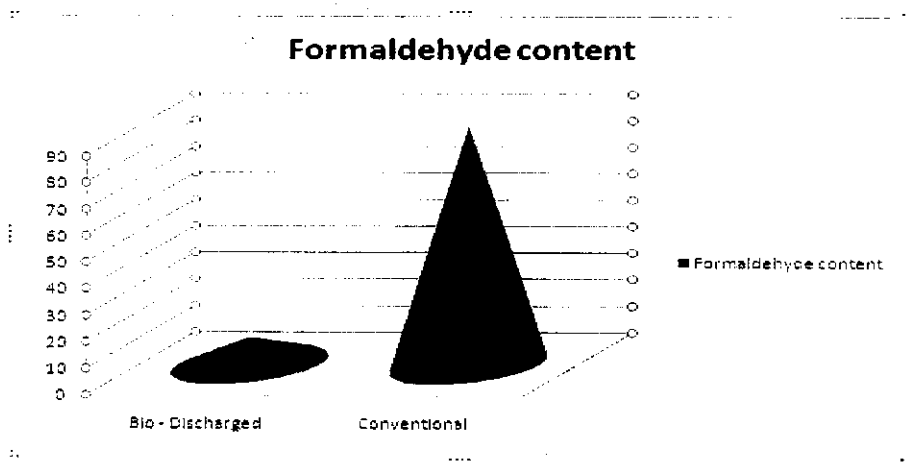


Std #	Conc.	Abs.
1	0.1500	0.012
2	0.3000	0.024
3	0.4500	0.036
4	0.7500	0.060
5	1.5000	0.120
6	3.0000	0.240
7	4.5000	0.360
8	6.0000	0.480

File Name: 15FEB11

ID	Conc.	Abs.
1	0.1010	0.014

Created: 15:53 15/02/11  
 Data: Modified  
 Wavelength: 415.0  
 Slit Width: 2.0  
 Multi-Point Working Curve  
 Conc = 7.500 Abs  
 Chi-Square: 0.00020  
 Number of Points: 8



**Fig: 3.8 Bio- Discharged Vs Conventional discharged Printed sample**

### 4.3 TENSILE STRENGTH

The printed samples were tested by using Instron tensile strength tester and results of fabric tensile strength (warp) of the samples are given in Table 12.

**Table 12: Tensile Strength Result - Warp**

S. No	Sample Code	Mean Tensile Strength in N (Warp)	Loss or gain over original	Percentage of loss or gain
1	COS	351.2	0.0	0.0
2	CDS	349.0	-2.2	- 0.62
3	CEPS	348.0	-3.2	- 0.91
4	CCVS	328.3	-22.9	-6.52

The breaking strength test of printed cotton samples were carried out in warp direction using tensile strength tester. The breaking strength of the conventional discharged printed fabric reveals slighter in strength loss compare with Bio- discharge printed fabric in both warp direction.



The results of laboratory test were analyzed statistically using test for one way analysis of variance.

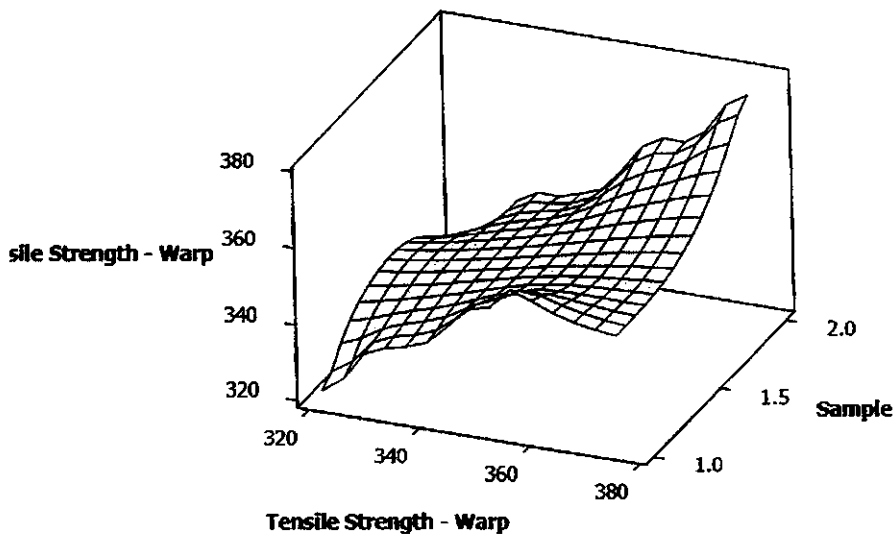
**Table 13: ANOVA – Tensile strength- Warp**

SV	Degrees of Freedom	Sum of Square	Mean Square	'F' value
Colour of Samples	1	170	170	0.59 (NS)
Error	8	2308	289	
<b>Total</b>	<b>9</b>	<b>2478</b>		

Table F Value: 5.32, NS – Not significant

Statistical analysis of the data relating to tensile strength in warp direction of conventional discharged printed fabric with that of the bio discharged printed fabric revealed statistically no significant difference in tensile strength loss.

### Surface Plot of Tensile Strength vs Sample, Tensile Strength



**Fig: 3.9 Tensile Strength Analysis - Warp**

The printed samples were tested by using Instron tensile strength tester and results of fabric tensile strength (weft) of the samples are given in Tables 14.

**Table 14: Tensile Strength Result –Weft**

S. No	Sample Code	Mean Tensile Strength in N (Weft)	Loss or gain over original	Percentage of loss or gain
1	COS	289.6	0.0	0.0
2	CDS	287.2	-2.4	- 0.83
3	CEPS	286.10	- 3.5	- 1.2
4	CCVS	266.4	-23.2	- 8.0

The breaking strength test of printed cotton samples were carried out in weft direction using tensile strength tester. The breaking strength of the conventional discharged printed fabric reveals slighter in strength loss compare with Bio- discharge printed fabric in weft direction.

The results of laboratory test were analyzed statistically using test for one way analysis of variance.

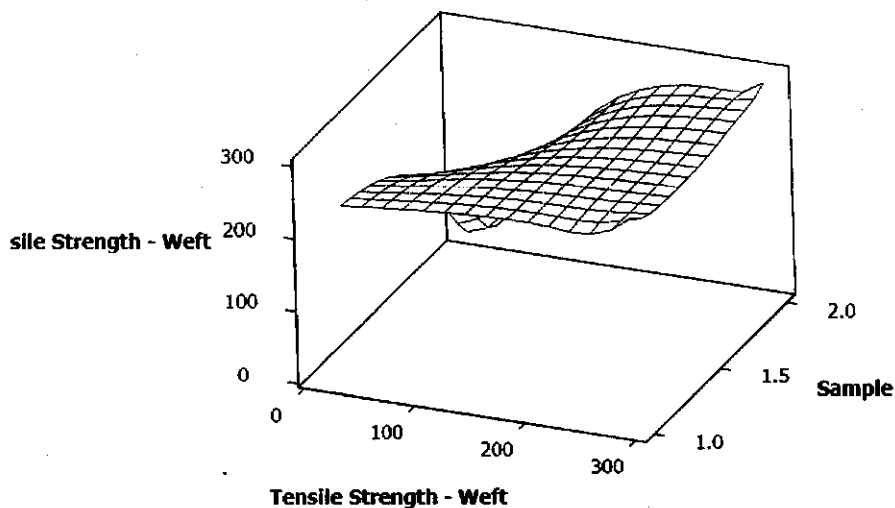
**Table 15: ANOVA- Tensile strength - Weft**

SV	Degrees of Freedom	Sum of Square	Mean Square	'F' value
Colour of Samples	1	2926	2926	0.45 (NS)
Error	8	52101	6513	
<b>Total</b>	<b>9</b>	<b>55027</b>		

Table F Value: 5.32, NS – Not significant

Statistical analysis of the data relating to tensile strength in weft direction of conventional discharged printed fabric with that of the bio discharged printed fabric revealed statistically no significant difference in tensile strength loss.

## Surface Plot of Tensile Strength vs Sample, Tensile Strength



**Fig: 4.0 Tensile Strength Analysis- Weft**

## 4.4 ABRASION RESISTANCE

The printed samples were tested for abrasion resistance by using Martindale abrasion tester and results of fabric abrasion resistance value of the samples are given in Table 16.

**Table 16: Abrasion Resistance Value**

S. No	Sample Code	Mean Abrasion Resistance in Rubs	Loss or gain over original	Percentage of loss or gain
1	COS	19100	0.0	0.0
2	CDS	18600	- 500	- 2.6
3	CEPS	18500	-600	- 3.14
4	CCVS	17000	- 2100	- 11.0

The abrasion resistance value of conventional discharged printed fabric was lesser than

The results of laboratory test were analyzed statistically using test for one way analysis of variance.

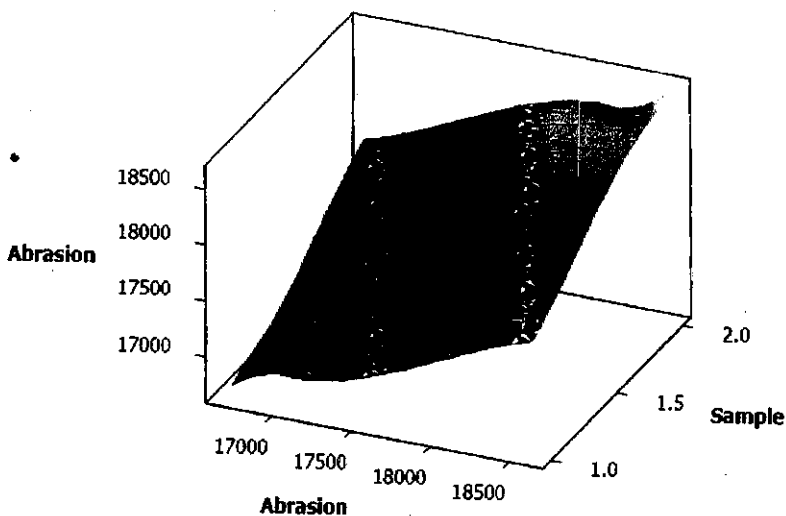
**Table 17: ANOVA- Abrasion Resistance Result**

SV	Degrees of Freedom	Sum of Square	Mean Square	'F' value
Colour of Samples	1	7396000	7396000	870.12 (SD)
Error	8	68000	8500	
<b>Total</b>	<b>9</b>	<b>7464000</b>		

Table F Value: 5.32, SD- Significant difference

Statistical analysis of the data relating to abrasion resistance value of conventional discharged printed fabric with that of the bio discharged printed fabric revealed that, there was statistically significant difference in abrasion resistance value.

### Surface Plot of Abrasion vs Sample, Abrasion



## 4.5 BURSTING STRENGTH

Printed specimens were clamped over an expansive diaphragm by means of a circular clamping ring. Increasing compressed air pressure was applied to the underside of the diaphragm, causing distension of the diaphragm and the fabric. The pressure was increased smoothly until the test specimen bursts. The bursting strength and bursting distension were determined.

**Table 18: Bursting Strength Result**

S. No	Sample Code	Mean Bursting strength in kPa	Loss or gain over original	Percentage of loss or gain
1	COS	347.0	0.0	0.0
2	CDS	342.4	- 4.6	- 1.32
3	CEPS	341.2	- 5.8	- 1.67
4	CCVS	305.0	- 42.0	- 12.1

The bursting strength of conventional discharged printed fabric was lesser than compare with Bio- discharge printed fabric. The results of laboratory test were analyzed statistically using test for one way analysis of variance.

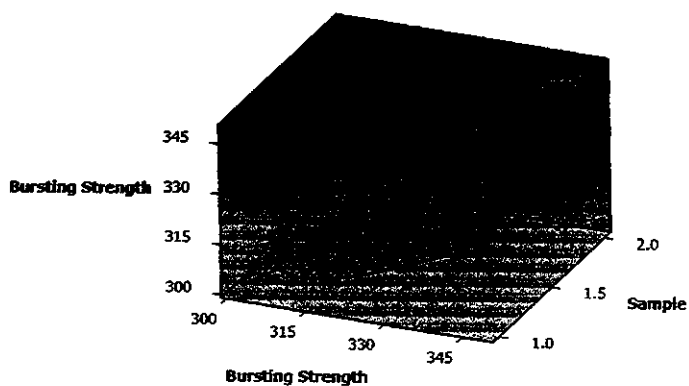
**Table 19: ANOVA- Bursting Streghth**

SV	Degrees of Freedom	Sum of Square	Mean Square	'F' value
Colour of Samples	1	4376.46	4376.46	7921.2 (SD)
Error	8	4.42	0.553	
<b>Total</b>	<b>9</b>	<b>4380.54</b>		

Table F Value: 5.32, SD- Significant difference

Statistical analysis of the data relating to bursting strength of conventional discharged printed fabric with that of the bio discharged printed fabric revealed that, there is statistically significant difference in strength parameters.

### Surface Plot of Bursting Strength vs Sample, Bursting Strength



**Fig: 4.2 Bursting Strength Analysis**

#### 4.6 COLOUR FASTNESS & ABSORBENCY PROPERTIES

Colour fastness to laundering test has been carried out in Laundr-o-meter equipment as per ISO 105 C06- B2S testing method in 50°C temperature. Colour fastness to water testing carried out in perspirometer as per ISO 105 E01 test method

**Table 20: Colour fastness & Absorbency properties**

Samples	Absorbency	Washing		Water		Croaking	
		Colour change	Staining	Colour change	Staining	Dry	Wet
	Sec					Staining	Staining
CDS	2	4-5	4-5	4-5	4-5	4	3
CEPS	2	4-5	4-5	4-5	4-5	4	3
CCPS	2	4-5	4-5	4-5	4-5	4	3

All samples had excellent colour fastness to washing & water. In case of Color fastness to wet rubbing result was slightly higher due to it is black colour sample. Absorbency properties of all samples were same which reveals that printing process have no effect in this property.

## CHAPTER 5

### CONCLUSION

Bio- Engineering is inevitable tool in modern industry where environmental aspect plays critical role to sustain in the competitive market. Innovative method of using Horseradish Peroxidase &  $H_2O_2$  formulation in discharge printing of textiles carried out successfully. Formaldehyde content & other important properties have verified by comparing conventional discharging printed fabric with Bio- discharged fabric. From that, the following conclusions are derived.

- ▶ Bio- discharge printed fabric had a formaldehyde content in least value (10.5 ppm) whereas conventional discharged printed fabric exhibited formaldehyde in the range of 90 ppm which is beyond OKO- Tex acceptable limit (Skin contact: 75 ppm)
  
- ▶ Formaldehyde liberation can be fully avoided in Bio- discharge printing using Horseradish peroxides enzyme with  $H_2O_2$ .
  
- ▶ The Statistical analysis of abrasion resistance and bursting strength results revealed that conventional discharging printing process liable to cause strength loss of fabric.

- ▶ Slight tensile strength loss was observed in conventional discharge printed fabric when compared with Bio- discharged printed fabric.
- ▶ The optimum conditions for using Horseradish Peroxidase formulation are found to be pH 8.5, 70° C temperature, 80g concentration and 60min time of treatment.

## **5.1 SCOPE FOR FUTURE WORK**

The following suggestions are made as a scope for future work in this work.

- ▶ Discharge printing using Horseradish peroxides enzyme could be tried through other printing techniques.
- ▶ The present work can be extended to other textile fibers like silk, viscose, polyester and synthetic fibers.
- ▶ Further study can be done to produce Horseradish peroxides enzyme from natural source for other application in textile industry.



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#### WEBSITES

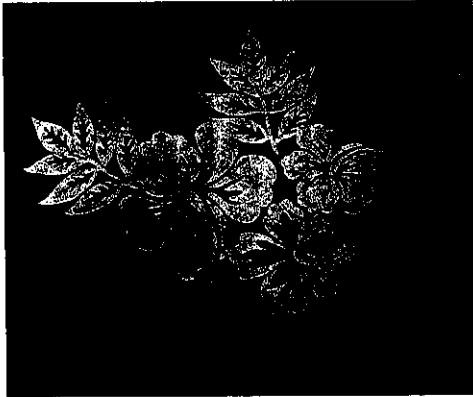
- [www.handlooms.com/textile/hloom\\_printing.asp](http://www.handlooms.com/textile/hloom_printing.asp).
- [www.dyesanddyeing.com](http://www.dyesanddyeing.com)
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- <http://pollutioncontrol.net/abstract/?enzyme.com>
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# APPENDIX I

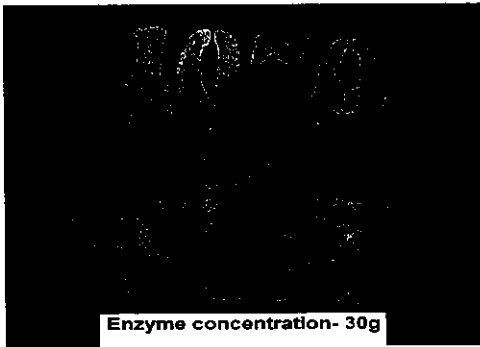
## COTTON PRINTED FABRIC



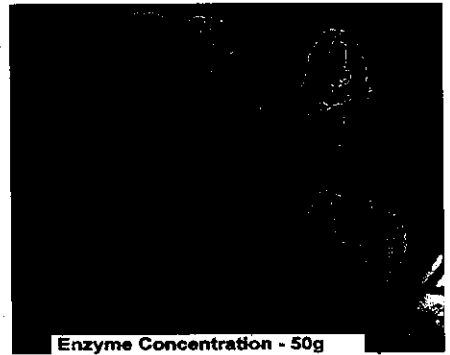
Bio- Discharged printed fabric



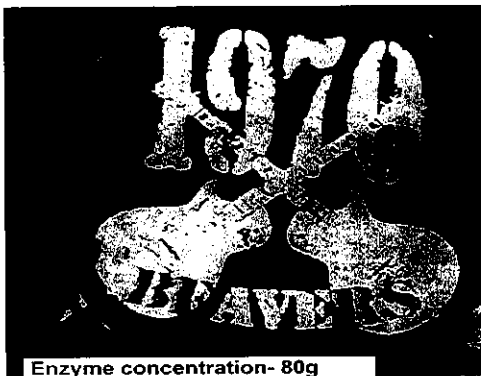
Conventional Printed fabric



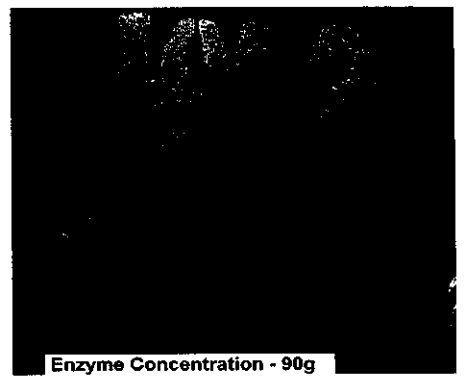
Bio Discharge printed fabric (30g)



Bio Discharge printed fabric (50g)



Bio Discharge printed fabric (80g)



Bio Discharge printed fabric (90g)

## LIST OF PUBLICATIONS

The following technical paper related to this project work has been accepted by the following Textile Journals. The details of the paper are given below.

1. Karthikeyan. K, Dr (Mrs) Bharathi Dhurai, - “New method of discharge printing on cotton fabrics using enzymes”- Textile Review- Accepted for publication on 26 Feb 2011.
2. Karthikeyan. K , Dr (Mrs) Bharathi Dhurai., - “Innovative discharge printing on cotton fabrics using Horseradish peroxidase enzyme” – Textile Trends- Accepted for publication on 09 Mar 2011.

A review paper related to this work has been selected in “RADIANT 2011”, a National Conference which will be conducted by Kumaraguru College of Technology on 21.04.2011 under the title “New method of discharge printing on cotton fabrics using Horseradish peroxidase enzyme”.