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Effect of Using Natural and Synthetic Anti Migrants in Continuous Dyeing of Cotton with Reactive Dyes

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Abstract In this project both natural and synthetic migration inhibitors were applied using different concentrations i-e 10g/L, 20g/L and 30g/L. After dyeing of fabric the dyed samples were test for: 1. Migration test; 2. Color depth; 3. Tensile/ Tear strength; 4. Bending length; 5. Wash fastness. The results showed that synthetic migration inhibitors efficiently restrict dye particles movement as compared to natural migration inhibitors. The result also shows that natural migration inhibitors make fabric stiff as compared to synthetic migration inhibitors. But on the other hand natural migration inhibitors as compared to synthetic show good color depth and do not affect tensile and tear strength of fabric.

Keywords Fiber structure and formation, Diffusion of dye, Synthetic migration inhibitors

1. Literature Review

F.Somm and R.Buser, Sandoz AG worked on migration problems during intermediate drying of pad dyeing and concluded that many continuous dyeing faults are definitely traceable to migration problem [17].

Nick j. Christle works on different natural and synthetic thickeners for the thermosol and space dyeing processes in general. Essential properties of the gums used in thermosol and space dyeing and some typical procedures of the gum preparation and techniques of application are given [18].

Allan H. Lambert and Robert J. Harper, worked on a novel approach to restrict migration of reagents during drying of cotton textiles is to add thermal gels such as cellulose ethers. Methyl cellulose was applied along with a cross linker, but methyl cellulose does not interfere with cross linker, nor does it completely restrict migration [19]. Stanely P. Rowland, Noelie R. Bertoniere and Walter D. king worked on reagent migration in fabric thickness in pad-dry-cure finishing. Migration of DMDHEU in the thickness direction of fabric was examined under conditions of forced draft drying from 40°C to 160°C. The subsequent cured fabrics were subjected to de Boer migration measure to clarify extents of migration of reagent residues to fabric surface. Unbalanced and variable migrations observed for forced draft drying in laboratory oven [20].

P. Bajaj, R. B. Chavan and Manjeet Bhatia worked on cross-linked acid based thickeners their preparation and performance in reactive dyeing and printing. For economic and technical reasons, low solid content thickeners are desirable for textile application with reactive dyes on cotton. Crosslinking of an acrylic acid based thickener (saponified acrylonitrile) was attempted with multi valent metal salts and a bifunctional cross linking agent. As the concentration of the aluminiunsulphaaate is increased, a tremendous increase in the viscosity occurred [21].

J. N. Etters worked on inducing and measuring particulate migration and reviewed a recommended method for inducing and measuring particulate migration and refinements to the method were suggested. Statistical analysis of experimental data shows that the use of a watch glass migration chamber that is saturated with water vapor can lead to slightly higher values of particulate migration than can the use of an unsaturated chamber [22].

2. Introduction to Reactive Dyes

Reactive dyes consist of a chromosphere attached to a reactive group through a -NH- group. The chromosphere is responsible for the color of the molecule. The reactive group provides capability for the dye to react with the fiber and has little or no influence on the color.

Since the dye is fixed to fiber by covalent bonds, the chromosphere can be a small, simple structure with limited reaction to the fiber. Small molecular structures in reactive dyes provide advantages such as high solubility in water, easy removal of hydrolyzed and bright colors. Therefore the chromosphere is usually a relatively small structure containing sulfonate groups to make the dye soluble in water. Typically chromospheres in reactive dye structures are mono azo, anthraquinone, pthalocyanine (for bright turquoise hue),

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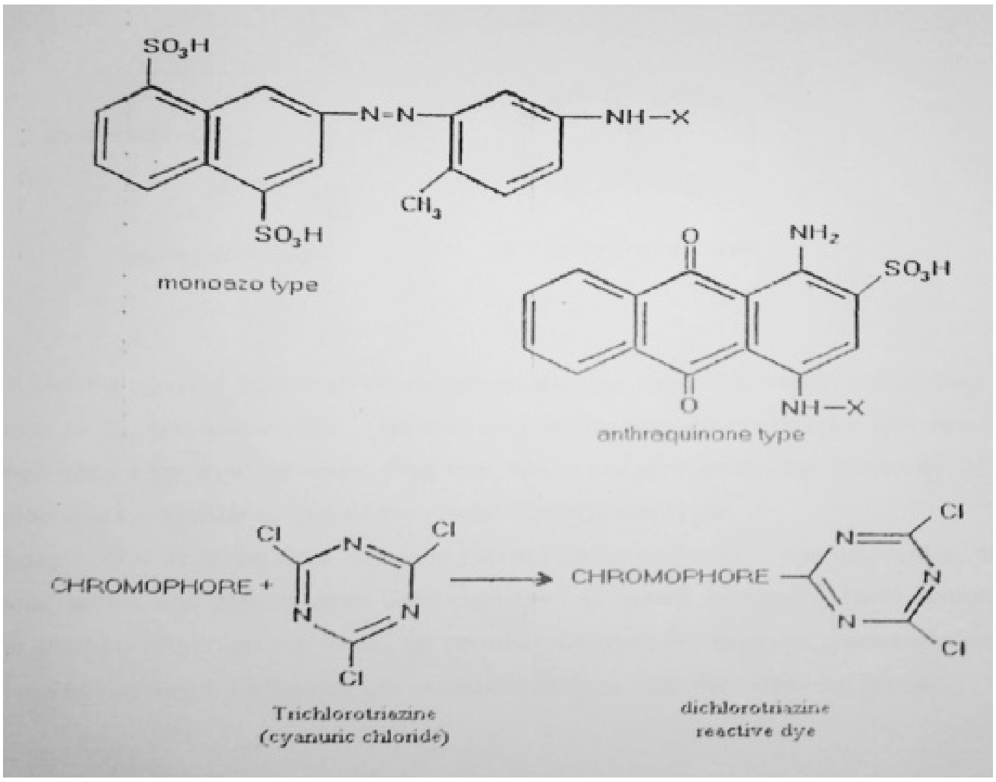
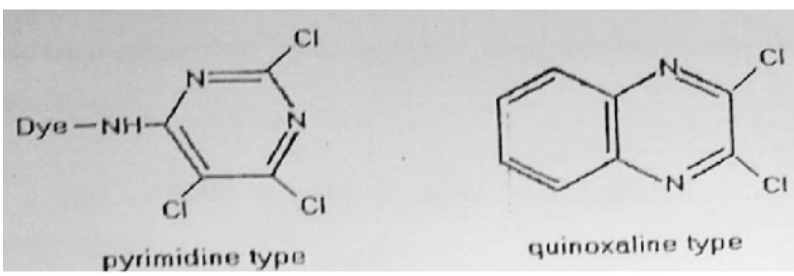
triphenodioxazine and formazan. The azo group is sometimes metallised with copper, cobalt, or chromium to produce a bathochromic shift.

Several types of reactive groups are found in reactive dyes. The first reactive dyes contained triazine reactive groups. This type of reactive group is important in reactive dyes today. The dyes are made by attaching a chromophore to trichlorotriazine (cyanuricchloride).



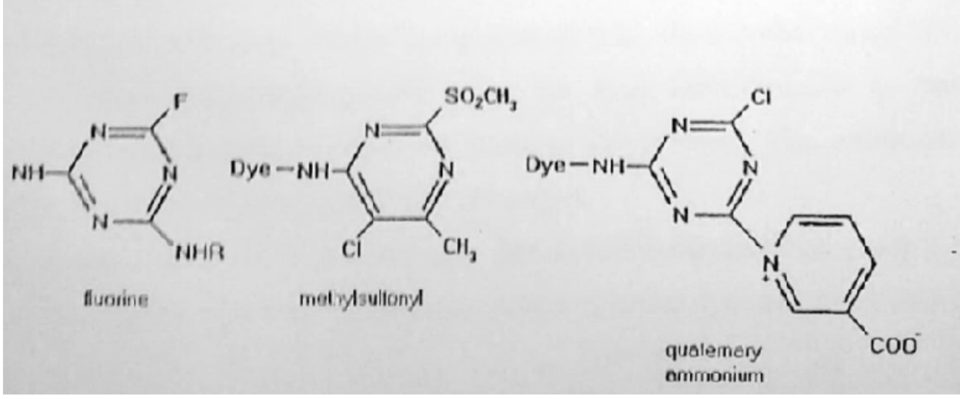
Dichlorotriazine type reactive dyes contain two displaceable (reactive) chlorine groups. Monochlorotriazine type reactive dyes are made by substituting one of the remaining chlorine atoms with an unreactive group leaving only one reactive group on the dye molecule. Dichlorotriazine reactive dyes are more reactive and are usually applied at lower temperatures then monochlorotriazine reactive dyes. Both types are widely used. Cyanuric chloride is a chromophoric blocking group. Attachment of two chromophores through the triazine ring structure produce a dye with the color that would be produced by physically mixing two chromophores. Thus attachment of a blue and a yellow chromophore through a triazine ring produces a green dye. Although the structure produced by this method are too large to be reactive dyes, the technique used in making direct dyes, CI direct green 26 is an example of a dye produced by this method.

Diazine reactive groups are also used in reactive dye molecules. Pyrimidine and quinoxaline are the most important of the diazines in commercial reactive dyes.



The leaving groups (chlorine of other) on diazine rings are less reactive then those on triazinerings. The quinoxaline dyes are less reactive then dichlorotriazine reactive dyes. Even though they may contain more than one halogen atom, the reactivity of the other diazine types is similar to that of the monochlorotriazine types.

Although chlorine is the most common leaving group on reactive dye molecules, many other leaving atoms and groups have been described in patent literature. Three leaving groups other then chlorine that are found on commercial dyes are fluorine, quartinary ammonium, and methyl sulfonyl. Following are the examples of dyes with these leaving groups.



All three of these groups are effective leaving group which makes the dye more reactive then dyes with reactive molecules containing chlorine leaving groups. The nicotinic acid leaving group shown in the quartnery ammonium example above produces dyes which react with cellulose under neutral conditions. This allows them to be applied simultaneously in the same dye bath with disperse dyes on polyester cotton blend fabrics [7].

2.1. Diffusion of Dye in the Application of Reactive Dyes

a) Diffusion of dye into the cellulose fiber. Varying the dyeing time, the dye bath temperature and the salt concentration controls it.

b) Reaction between the dye and cellulose. It is achieved by the selection of an appropriate alkalinity (pH).

The above mentioned stages very briefly describe the reactive dyeing procedure, following is given all the phases and factors that play a vital role in reactive dyeing [7].

2.2. Adsorption

Factors affecting are:

- Nature of dye (dye affinity)
- Liquor ratio
- Electrolyte concentration
- Temperature
- Nature of fiber

2.3. Absorption

Factors affecting are

- Nature of dye (diffusion co-efficient of dye)
- Liquor ratio
- Temperature
- Nature of fiber
- Particle size of fiber

2.4. Fixation

Factors affecting are:

- Reactivity of dye
- pH
- temperature

2.5. Removal of Hydrolyzed Dye

Factors affecting are

- Affinity
- Electrolyte concentration
- Temperature

2.6. Migration Inhibitors

A substance added to a dye to slow down its ability to spread or bleed into a fabric as it is applied. Natural and synthetic migration inhibitors are used in the industry.

Anti-migration agents used particularly for dyeing and printing include polyvinyl methyl ethers of a mean molecular weight of about 100,000, alginates, low molecular weight cellulose ethers, polyethylene glycols of mean molecular weights of from 8,000 to 10,000 and special polymers of poly vinyl caprolactam. Migration-inhibiting agents which are to give useful results in dyeing and printing followed by intermediate drying should neither disturb the dye neither finish nor cause loss in brilliance. In addition, the agent should have adequate liquor stability, should not cause any hardening of the handle and should have good solubility at room temperature. Finally, small amounts should give good effects.

The turbidity point of these compounds is also of special importance and should lie within a range from about 35° to 55°C. *Migration inhibitor* for continuous *dyeing*, improves surface levelness of dyeing's. Migration inhibitors are necessary to control dye particle movement during the pre-drying phase.

2.7. Synthetic Migration Inhibitors

Synthetic migration inhibitors have mostly chemical constitution of acrylic copolymer. Their ionic character is anionic. They wash off easily hence no harshening of handle. They are present in both colored and colorless forms but mostly yellowish in color. Stable in hard water and to acids, alkalis and electrolytes in the usual amounts. They are stable at 20°C and can be kept for a year or more than year but they should be tightly reclosed after each withdrawal.

Synthetic migration inhibitors to be used in the experiment are:

a) Thermaco MIN:

Ionic character:-Anionic

Physical form:-Colorless liquid

Specific gravity:-approx. 0.9

General stability:- stable to hard water and pH values between 4 and 10.

Storage stability: - stable for more than one year at 20°closed containers. Should not be stored at temperatures above 40 °C

Compatibility: - compatible with anionic and non-ionic Auxiliaries.

Ecology/Toxicology:-The usual hygiene and safety rules for handling chemicals should be observed in storage, handling and use. The product must not be swallowed.

b) Thermacol MP:

Chemical constitution:- Aqueous solution of an acrylic polymer

Ionic character:- Anionic

Specific gravity:- approx. 1

pH:- about 6

Compatibility:- compatible with anionic and nonionic auxiliaries.

General stability: - stable in hard water and to acids, alkalis and electrolytes in the usual amounts.

Storage stability: - stable for more than one year at 20°C in closed containers. Solidifies at temperatures below freezing but after reverting to room temperature it is fully effective again.

Ecology/Toxicology: - The usual hygiene and safety rules for handling chemicals should be observed in storage, handling and use. The product must not be swallowed.

c) Primasol FFAM:

No surfactant; no foaming; freely miscible with water.

Nature:-Acrylic Copolymer.

Physical form:-Yellowish viscous liquid.

Density:- 1.09 g/cm^3 at 20 °C

pH:- 6.5 - 7.5.

Storage:- Primasol FF-AM can be kept for at least 12 months in the original sealed containers at temperatures between 5°C and 25°C. Once the containers have been opened, their contents should be used up as rapidly as possible, and they should be tightly reclosed after each withdrawal.

Safety:- When using this product, the information and advice given in our Safety Date sheet should be observed. Due attention should also be given to the precautions necessary for handling chemicals

Action:- Primasol FF-AM prevents the migration of pigment articles during Intermediate drying of fabrics produced from cellulosic fibers and their blends with manmade fibers [10].

2.8. Natural Migration Inhibitor

Natural migration inhibitor used in the industry:

a) Sodium Alginate:

Sodium Alginate is the purified carbohydrate product extracted from brown seaweeds by the use of dilute alkali. It consists chiefly of the sodium salt of Alginic Acid, a polyuronic acid composed of b-D-mannuronic acid residues linked so that the carboxyl group of each unit is free while the aldehyde group is shielded by a glycosidic linkage. Molecular Formula: $C_5H_7O_4COON_a$

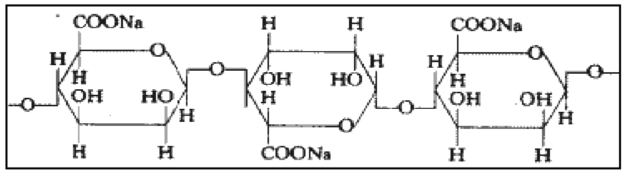


Figure 1. Sodium alginate structure

In textile dyeing and printing, alginates are used as migration inhibitors and thickeners. Alginates became important with the advent of reactive dyes. These combine chemically with cellulose in the fabric. Many of the usual thickeners, such as starch, react with the reactive dyes, and this leads to lower color yields and sometimes by-products that are not easily washed out. Alginates do not react with the dyes, they easily wash out of the finished textile and are the best migration inhibitors and thickeners for reactive dyes [11].

b) Guar gum:

Guar gum is a natural hydrocolloid that is obtained from the ground endosperm of the guar plant. Guar Gum mainly consists of hydro colloidal polysaccharide with a high molecular weight, which consists of galactopyranose- and mannopyranose- units in glycoside linkage which can be chemically described as galactomannan.

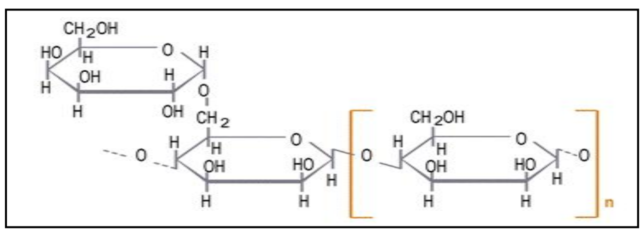


Figure 2. Structure of guar gum

The most important property of guar gum is its ability to hydrate rapidly in cold water to attain uniform and very high viscosity at relatively low concentrations.

Guar Gum gives excellent film forming and thickening properties when used for textile sizing, finishing and dyeing and printing. It reduces warp breakage, reduces dusting while sizing and gives better efficiency in production.

The viscosity of the guar gum and stock migration inhibitors shows good stability over a long period [12].

c) Carboxyl methyl cellulose:

Carboxyl Methyl cellulose (CMC) is a cellulose derivative with carboxymethyl groups (-CH_2-COOH) bound to some of the hydroxyl groups of the glucopyranose monomers that make up the cellulose backbone. It is often used as its sodium salt, sodium carboxymethyl cellulose.

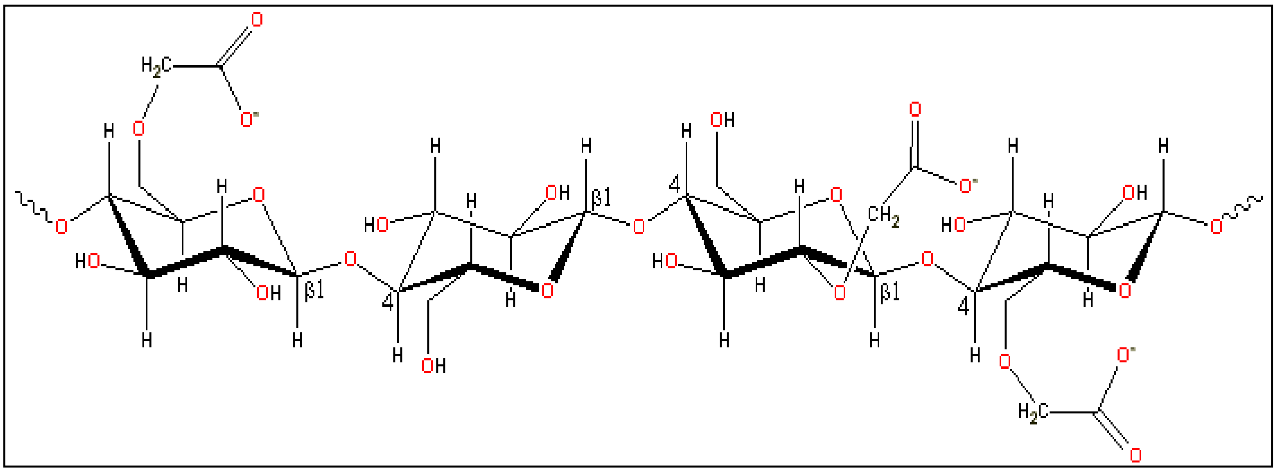


Figure 3. Structure of Carboxyl Methyl cellulose

Most CMCs dissolve rapidly in cold water and are mainly used for controlling viscosity without gelling (CMC, at typical concentrations, does not gel even in the presence of calcium ions). Its control of viscosity allows use as thickener, phase and emulsion stabilizer and suspending agent. CMC can be also used for its water-holding capacity as this is high even at low viscosity; particularly when used as the Ca^{2+} salt. CMC is non-toxic, and is non-allergenic.

3. Experimental Work

3.1. Material and Equipment

To proceed with the proposed project material and methods are selected. Methods were performed in National Textile University, Faisalabad with the exception of migration inhibitors which were acquired from CIBA and BASF chemicals.

The material and equipment used for the completion of the project are described below in detail.

- Fabric
- Chemicals
- Equipment's

3.1.1. Fabric Specifications

100% bleached cotton fabric was used in this work and its warp and weft count were 31s and its end per inch were 90 and picks per inch were 59

3.1.2. Chemicals

The chemicals were used, are given below:

Table 1. 3.1.2. Chemicals

Serial #	Chemicals	Commercial name	Manufacturer
1	Migration inhibitor	Thermacol MP	Huntsman
2	Migration inhibitor	Primasol FFAM	BASF
3	Migration inhibitor	Thermacol MIN	Huntsman
4	Migration inhibitor	Sodium alginate	
5	Migration inhibitor	Guar gum	
6	Migration inhibitor	Caroboxymethyl cellulose	
7	Reactive dye	Sandalfix red 150%	Sandal dyestuff

3.1.3. Equipments

3.1.3.1. Application Equipments

The following machines described below were used for the completion of the project:

- Padder (Manufacturer: Daiei kagakuaeikiseisakushu.Ltd)
- Thermosol (Manufacturer: Daiei kagakuaeikiseisakushu.Ltd)

Table 2. 3.1.3.1. Application Equipments

Type of Test	Instrument used	Manufacturer	Test Standard
Migration test	Simple transparent glass, watch glass and grey scale		AATCC Test Method 140-2001
Washing fastness	Launder- Meter	DAIEI KAGAKV SEIKI MFG.CO.LTD	ISO 105 CO_3
Colorfastness to crocking	Crock meter	Shirley development Manchester, UK	ISO105*12
Color strength	Spectrophotometer	Color-Eye Gretamacbeth	
Tensile strength	Tensile tester	Daiei kagakuaeikiseisakushu.Ltd	ASTM 14-32
Tear strength	Elmendrof tear tester	Daiei kagakuaeikiseisakushu.Ltd	ASTM 14-22

3.2. Application Method

First of all 100% bleached cotton was taken. The bleached cotton was then dyed with Sandalfix red 150% reactive dye for 10% shade using different migration inhibitors, both synthetic and natural. The laboratory dyeing pad padthermosol machine was used and method of dyeing was pad-dry-cure. Padding was done in padder after padding, drying and curing was done in thermosol. The drying temperature was 120°C for two minutes and curing temperature was 180°C for two minutes.

3.2.1. Recipies

Table 3. 3.2.1 Recipies

Sandalfix red 150%	10 g/L
Na_2CO_3	20g/ L
Urea	10g/ L
Migration inhibitor	10g/ L, 20g/ L and 30g/L

The same procedure was repeated by taking 10g/ L, 20g/ L and 30g/L of migration inhibitors used-e sodium alginate, Carboxymethyl cellulose, Guar gum, Thermacol MP, Primasol FFAM and Thermacol MIN. All other chemicals were remain same in the whole experiment except the concentration of migration inhibitors. Migration test was performed on each sample after padding then fabric was dried and cured.

- drying temperature 120 °C
- curing temperature 180°C

After dyeing hot washing and cold washing was done of each sample.

3.2.2. Migration Test

Fabric was impregnated with colorant and auxiliaries then fabric was padded and dried partially covering with a watch glass and partial drying was done, and therefore migration to occur. The degree of migration was evaluated by visual examination. AATCC Test Method 140-2001 was followed [23].

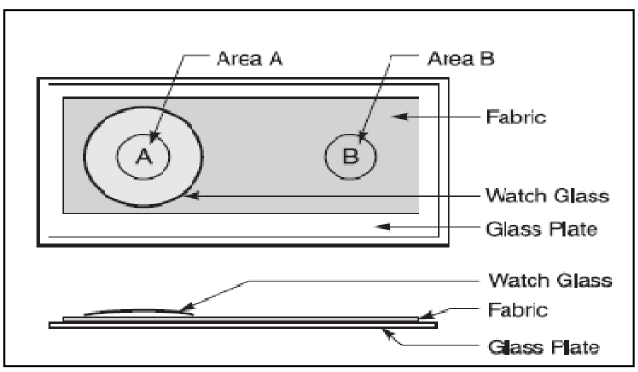


Figure 4. Layout of Migration test apparatus

Visual examination was observed on a gray scale of 1-5 by reference to the Gray Scale for Color Change:

3.3. Results and Discussion

3.3.1. Effects of Migration Inhibitors

Natural migration inhibitors when use darting obtained was:

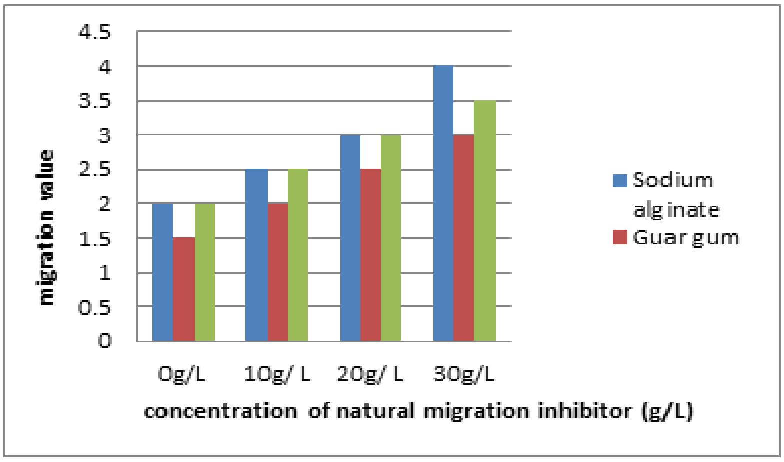


Figure 5. Natural migration inhibitors when used

Synthetic migration inhibitors when used rating obtained was:

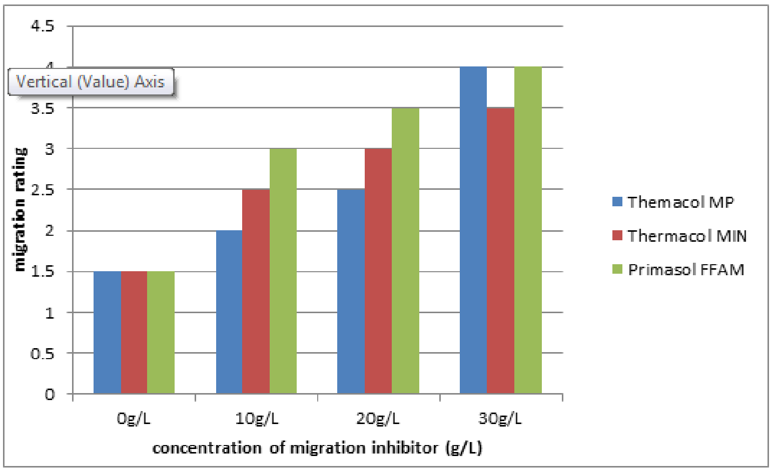


Figure 6. Synthetic migration inhibitors when used

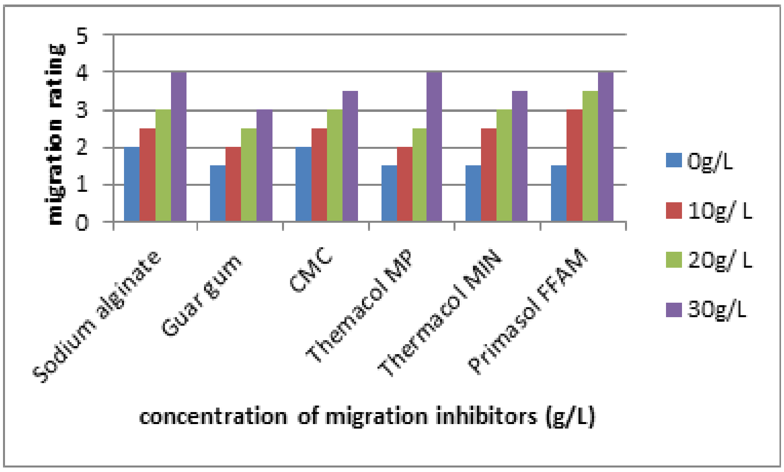


Figure 7. Migration inhibitors

From the above results we observed as the concentration of migration inhibitor is increased the migration is less, and it was also observed that synthetic migration inhibitors do their job well then natural migration inhibitors. Synthetic migration inhibitors also reduce cleaning time hence increased productivity. In natural migration inhibitor, sodium alginate prevents dye migration better than other natural migration inhibitors, while in synthetic migration inhibitors Primasol FFAM and Thermacol MP prevents better dye migration.

3.3.2. Effect of Migration Inhibitors on Tensile and Tear Strength [24]

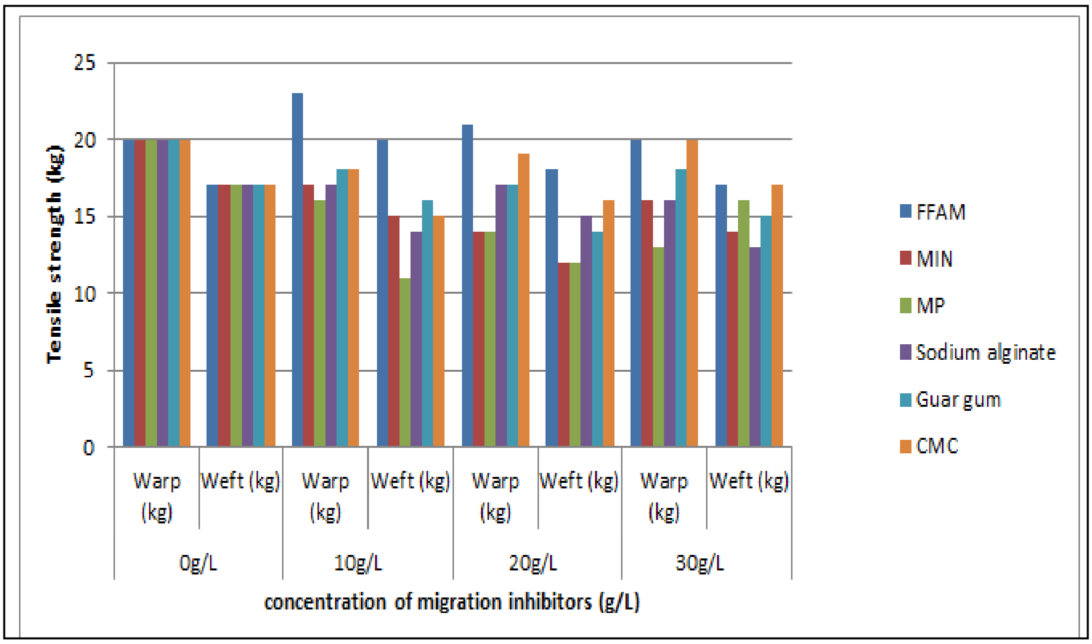


Figure 8. Effect of migration inhibitors on Tensile strength

The results shows that synthetic migration inhibitors effect on tensile strength is negative as the tensile strength is decreasing with the increasing concentration of migration inhibitor, due to acrylic acid component present in the polymer structure of migration inhibitors causing degradation to some extent while natural migration inhibitors do not affect the tensile strength of fabric too much.

3.3.2.1. Tear Strength

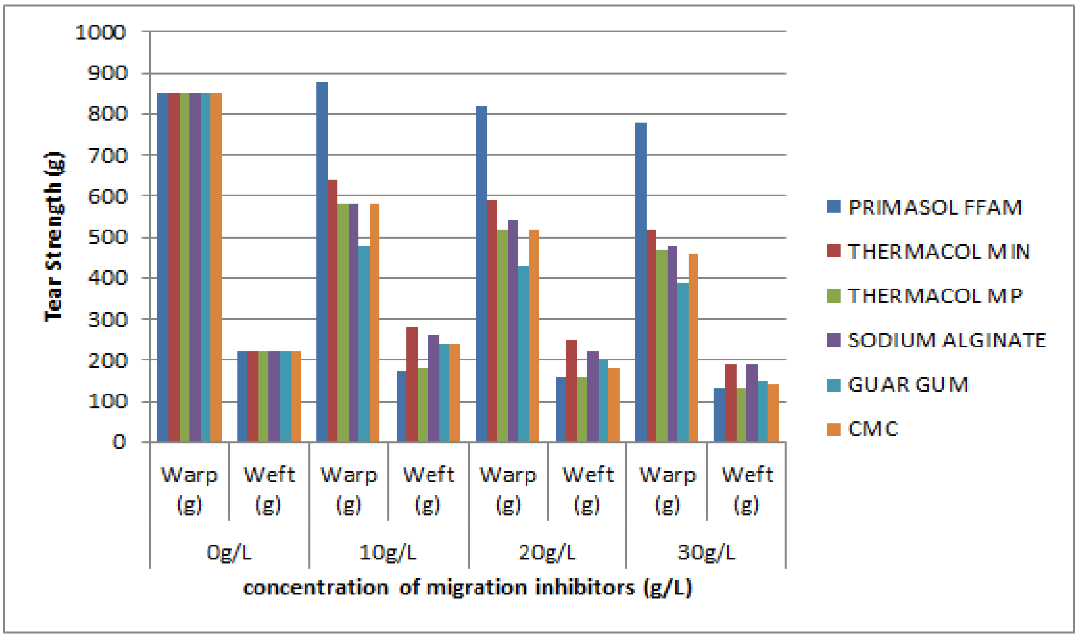


Figure 9. Effect of migration inhibitors on Tear strength

The results in table and figure show that as the concentration of migration inhibitor increases the tear strength decreases. However, in case of synthetic migration inhibitors more tear strength is lost as compare to migration inhibitors as the concentration of migration inhibitor increases as migration inhibitors are thickeners so they increases stiffness of fabric which becomes cause of decreasing tear strength.

3.3.2.2. Effect of Migration Inhibitors on Crock Fastness [25]

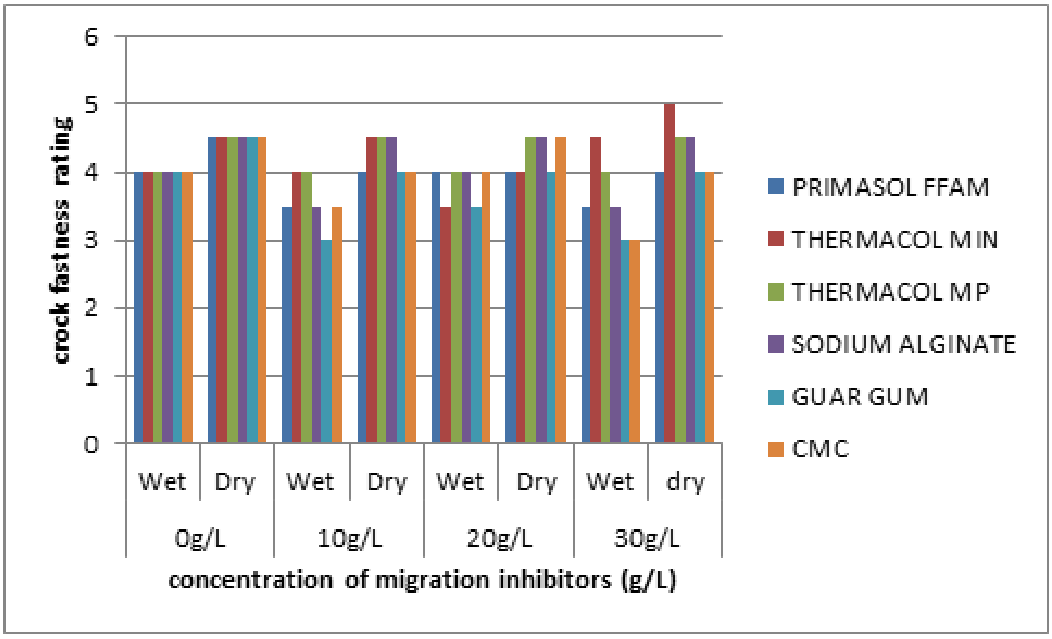


Figure 10. Effect of migration inhibitors on crock fastness

The results in table and figure shows that effect of migration inhibitors on crock fastness is not seen and they do not affect the crocking properties of the fabric. Poor Crock fastness is due to the poor fixation of dye, as migration inhibitors do not take any part in the fixation of dye so they do not affect the crock fastness values of fabric.

3.3.2.3. Effect of Migration Inhibitors on Wash Fastness [26]

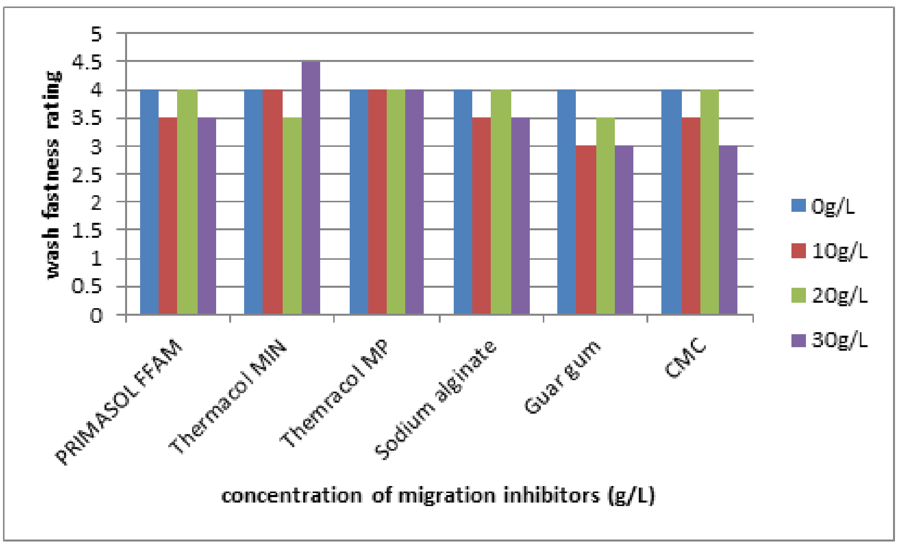


Figure 11. Effect of migration inhibitors on wash fastness

The results in table and figure shows that effect on wash fastness by migration inhibitors is not seen, because migration inhibitors have no any role in the fixation of dye as dye fixation is the key factor in wash fastness, more the dye fixation better the wash fastness, however synthetic migration treated fabric has better wash fastness as compared to natural migration inhibitors.

3.3.2.4. Effect of Migration Inhibitors on CV-SUM

The results of application of different migration inhibitors are given below. The following table shows the effect of migration inhibitors on the CV-SUM of the samples.

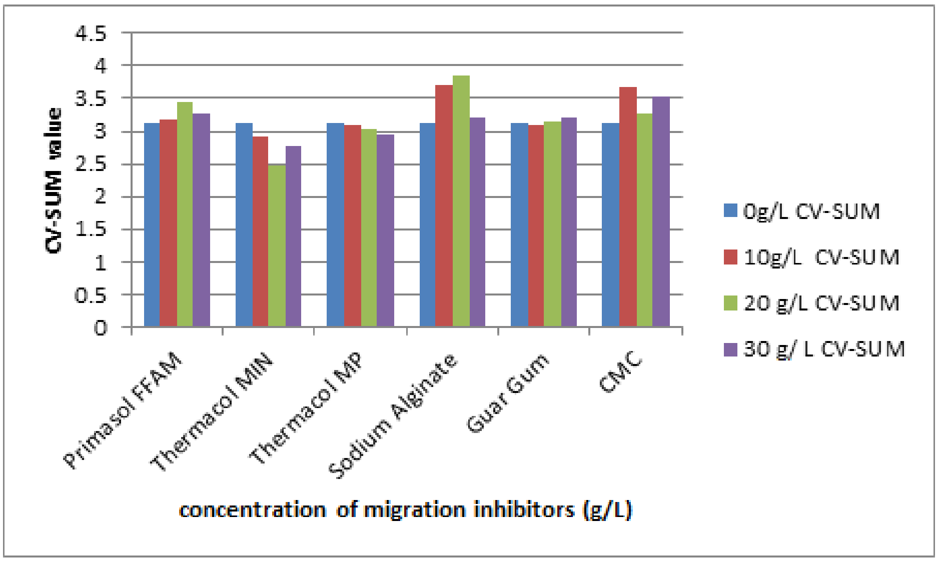


Figure 12. Effect of migration inhibitors on CV-SUM

The results in table and figure shows that migration inhibitors has no any significant impact on CV-SUM, however, CV-SUM of natural migration inhibitors is comparatively more than synthetic migration inhibitors due the fact that natural migration inhibitors have cellulose components in its polymer structure, so dye is more attracted to the cellulose component, resulting in better CV-SUM value of natural migration inhibitors.

3.3.2.5. Effect of Migration Inhibitors on % Strength

The results of application of different migration inhibitors are given below. The following table shows the effect of migration inhibitors on the % strength of the samples.

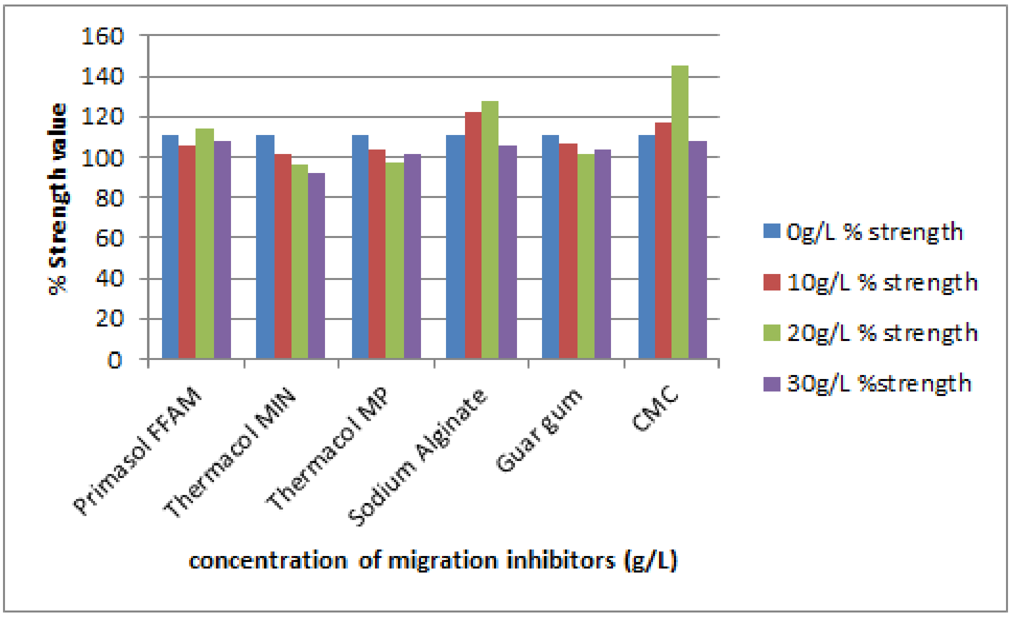


Figure 13. Effect of migration inhibitors on % strength

The results in table and figure shows that natural migration inhibitors show good % strength then synthetic migration inhibitors, due the fact that natural migration inhibitors have cellulose components in its polymer structure, so dye is more attracted to the cellulose component, resulting in better % Strength value of natural migration inhibitors.

3.3.2.6. Effect of migration Inhibitors on Bending Length

Bending length of the dyed fabric was measured using cantilever test method.

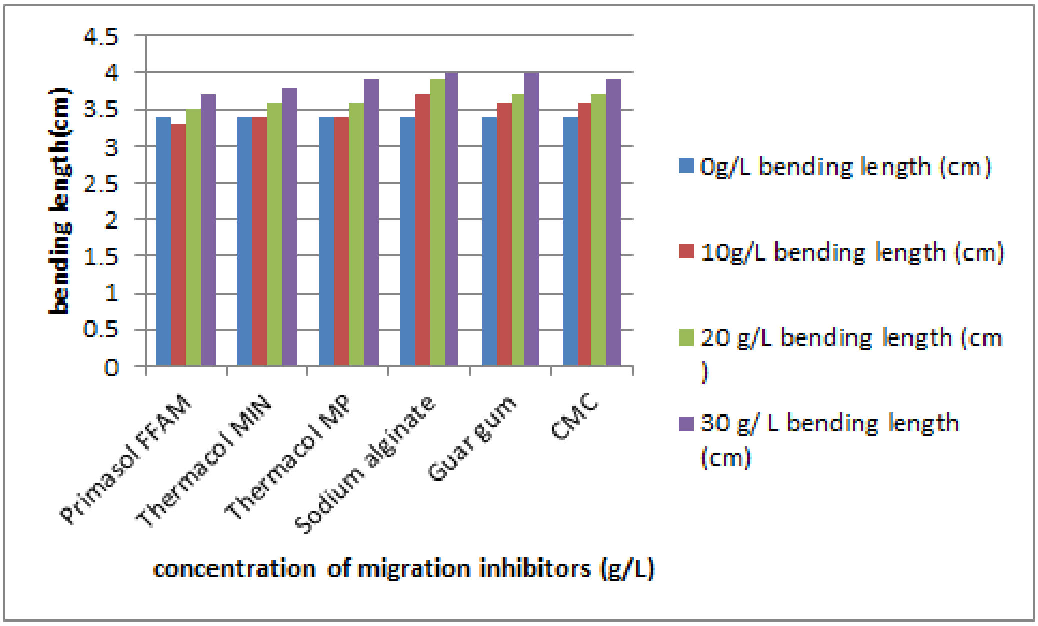


Figure 14. Effect of migration inhibitors on Bending Length

From the above table and graph it is shown that bending length of fabric treated with natural and synthetic migration inhibitors has increased, however natural migration inhibitor treated fabric has more bending length as compared to synthetic migration inhibitor treated fabric due to the fact that they give more stiffness to the fabric.

4. Conclusions and Future Work

4.1. Conclusions

Following conclusions are drawn after the project:

- Synthetic migration inhibitors efficiently restrict dye particle movement during drying but along with the environmental concern.
- Natural migration inhibitors are environmental friendly but do not restrict dye particles movement efficiently.
- Migration inhibitors have no any effect on wash fastness as they have no any role in dye fixation.
- Migration inhibitors also not have any impact on crock fastness properties of dyed fabric.
- Synthetic migration inhibitors do not cause stiffness in fabric while natural cause to little extent.
- Synthetic migration inhibitors also effect on Tensile/ Tear strength of fabric while natural migration inhibitors do not effect strength of fabric.
- CV-SUM and % strength of natural migration inhibitors is better than synthetic migration inhibitors because cellulosic component in natural migration inhibitors have more dye affinity then acrylic based synthetic migration inhibitors.

4.2. Future Work

Although I tried my best to achieve the goal of the project. I did this project on pad-dry-cure method in future pad-dry-steam method could be used. In future research could be done on the new generation of migration inhibitors which are now available in market and desired properties obtained by new generation of migration inhibitors could be compared with natural.

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