

# Concurrent Dyeing and Finishing Of Cotton Fabric with Natural Color and Maleic Anhydride

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**Abstract:** Cotton fabric was simultaneously modified with maleic anhydride and *Allium cepa* and maleic anhydride and *Terminalia arjuna* in presence of sodium citrate as esterification catalyst and potassium peroxodisulfate as free radical polymerization catalyst using a dip-dry-iron-cure technique. Treatment of cotton with 8% maleic anhydride, 8% sodium citrate, 0.5%  $K_2S_2O_8$  and any of the above mentioned dyes with subsequent tumble drying at 70°C followed by ironing of dried fabric at 70°C and curing of ironed fabric at 140°C for 5 minutes produced most balanced improvements in respect of depth of shade, wrinkle recovery, colorfastness properties and strength. IR analysis indicated that, treatment of cotton with maleic anhydride and either of the above dyes under dual influence of esterification catalyst and free radical polymerization catalyst led to some degree of cross-linking of chains polymers of cotton.

**Keywords:** dye process, fabric, finishes, natural dyes, natural fibre, textiles, color.

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## 1. INTRODUCTION

Natural dyes have recently evoked immense interest for coloration of cotton, silk etc (Sarkar and Seal, 2003). in view of their environment friendly character, identified medicinal value and low energy consumption during their production and use (Sarkar and Seal., 2003; Chen and Burns., 2006). They have enough potential to be included for sustainable development of materials related to textiles if harvesting of such dyes are done sensibly, without posing threats to the environment (Fletcher, 2008). Most of the natural dyes are found to contain hydroxyl groups in their structures and are reported to be capable of being esterified with compounds containing carboxylic acid group (Nema *et al.* 2012).

Polycarboxylic acid compounds such as butane-tetra-carboxylic acid, cyclopentane-tetra-carboxylic acid, citric acid, etc. on the other hand offer an alternative to the use of toxic formaldehyde condensate resin as a cross-linking agent in view of its environment friendly non-toxic and safe character (Welch and Andrews, 1989). However, sodium salts of phosphorus containing mineral acids used as esterification catalyst with such polycarboxylic acids are not environmental friendly, in view of their reported odd and adverse effect on aquatic environment and soil (Choi *et al.* 1993). Also finishes based on such non-polymeric polycarboxylic acid cannot retain or improve strength and moisture regain characteristics of cotton. Moreover, most of such polycarboxylic acids are too expensive for practical exploitation. It is also reported in the literature that, most of the natural dyes are having - OH groups in their structure and they can be esterified with a non-polymeric polycarboxylic acid such as, citric acid (Das & Shah., 2011; Das *et al.*, 2014; Nema *et al.* 2012). Also, recently there are growing trend and emphasis in fashion and related clothing industries for coloration and finishing of garment instead of fabric as it depends more on technologies that can be used for short production run, encourages less inventory and are able to respond to fast changes encountered by such industries (Das and Shah, 2011). However, report of concurrent dyeing and finishing of cotton garment employing natural dyes and a carboxyl containing vinyl monomer

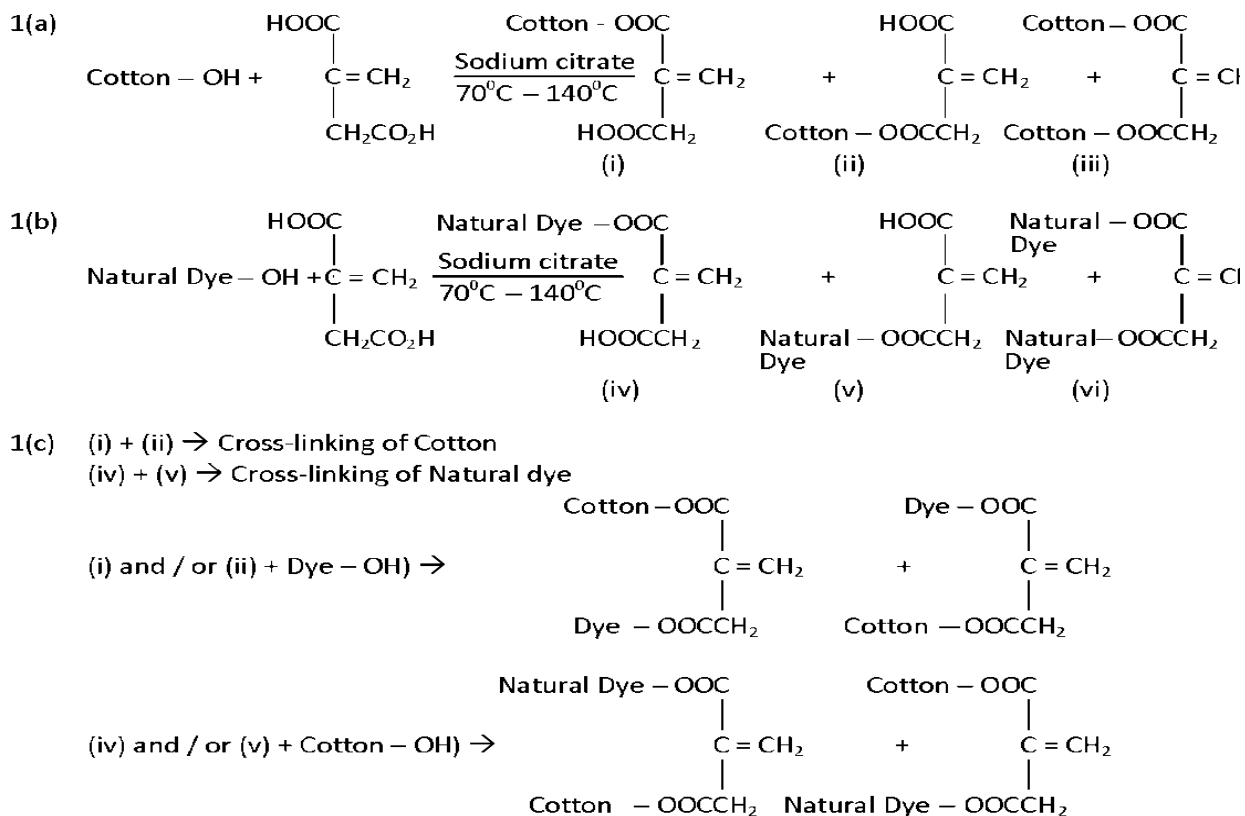
obtained from natural source, such as, maleic anhydride under the dual influence of free radical polymerization catalysts and a phosphorus -free esterification catalyst following a dip-dry-iron-cure technique is not available or scanty. In view of above, we thought, it is of interest to investigate, if use of maleic anhydride could prove to be worthy and efficient in bringing about esterification and graft copolymerization with the hydroxyl groups of cotton and also with that of the natural dyes in a manner that would lead to improvement in color yield and all round fastness properties, in addition to improvement of wrinkle recovery of cotton fabric, when the cotton fabric is dyed with *Allium cepa* and *Terminalia arjuna* in presence of maleic anhydride under the influence of sodium citrate as phosphorus free esterification catalyst and potassium peroxydisulfate as a free radical polymerization catalyst following a dip-dry-iron-cure technique. *Allium cepa* is edible papery skin of onion and is obtained as a waste product during consumption of onion as a food product. It contains pelargonidin (tetrahydroxy anthocyanidin) as coloring pigment with no carboxyl group in its structure. *Terminalia arjuna* is obtained from the leaves and barks of the plant Arjuna having Arjunic acid (terpenoids saponins) as the chief coloring components that contain hydroxyl groups and carboxyl groups in their structures (Nema *et al.*, 2012). *Allium cepa* and *Terminalia arjuna* have been selected for our study as natural dyes in view of their abundant availability, chemical structures with phenolic OH groups typical of majority of natural dyes and absence and presence of additional carboxyl groups respectively, in them.

In this context, it would be useful if we consider the mechanism of intended modification of cotton by *Allium cepa* and *Terminalia arjuna* with maleic anhydride following dip-dry-iron-cure technique under the influence of  $K_2S_2O_8$  (potassium peroxydisulfate) used as the free radical polymerization catalyst and sodium citrate used as esterification catalyst. Hydroxyl groups of cotton and phenolic OH groups commonly present in both the natural dyes mentioned above are expected to bring about intended modifications of cotton and of such dyes under the sequence of reactions shown in Figure 1. Such intended modification of cotton fibre and natural dyes ultimately would lead to notable gain in weight, color yield and changes in the chemical nature and physical properties of cotton during the overall process. Reaction 1(a) and 1(b) producing maleic anhydride esters of cotton and natural dye respectively would be the direct consequences of action of sodium citrate used as esterification catalyst. The said esterification reaction would also expectedly lead to cross-linking of dye and that of cotton as mentioned in the reaction scheme 1(c). However maleic anhydride esters of cotton and dye as shown by the structures (i), (ii) and (iv), (v) may then react further with hydroxyl groups of dye and cotton respectively leading subsequently to linking of cotton and dye via an ester bridge formed by the maleic anhydride moiety as shown by reaction 1(c) during the drying and curing step. Direct consequence of esterification of cotton under the influence of esterification catalyst is therefore likely to enhance ester group or carboxylic acid group and/or both such functional groups of cotton particularly in view of the reaction products as shown in reactions 1(a) of Figure 1.

Influence of free radical catalyst ( $K_2S_2O_8$ ) on the other hand in dip-dry-iron-cure technique would cause graft copolymerization of maleic anhydride under the treatment condition ultimately leading to grafting of poly (maleic acid) chain on the chain molecule of cotton and also on the dye molecules under the treatment condition with ultimate cross-linking of cotton and dye; linking of dye and cotton as grafted via poly (maleic acid) chain molecules shown in equation 2(e) (in addition to peroxydisulfate induced free radical homo polymerization of maleic anhydride ; not shown in the scheme) is another distinct possibility. Such peroxydisulfate induced graft copolymerization and cross-linking would cause enhancement of carboxylic group content of the maleic anhydride modified cotton as well as binding of natural dye with cotton via maleic anhydride and improvement in wrinkle recovery of cotton in consequent to expected cross-linking of polymeric chains of cotton. Under the influence of two catalysts taken together for the maleic anhydride curing of cotton in presence of *Allium cepa* and *Terminalia arjuna* dyes, all the reactions shown and discussed above are likely to take place simultaneously or successively leading to weight gain for the fabric system. Moreover, additional reactions leading to further graft copolymerization and esterification with consequent eventual complex network formation involving further unreacted hydroxyl groups of cotton and that of dye and also carboxyl groups and unsaturation of poly (maleic acid) moieties duly grafted to either dye or cotton may also take place under the treatment condition leading to i) binding of natural dye via poly (maleic acid) and ii) improved wrinkle recovery of maleic anhydride finished cotton.

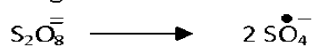
Keeping above scope in view, this work is aimed at establishing optimum condition for application of maleic anhydride in presence of natural dyes on cotton fabric and evaluating attainable changes or improvements in the cotton fabric properties and in the dyeing behavior of cotton fabric with natural dyes. Changes in the cotton fabric properties in respect of tensile strength, wrinkle recovery, flexibility and moisture regain and changes in dyeing behavior in respect of color

yield and color fastness properties on such treatments have been assessed. Also, changes in chemical nature of cotton fabric on such modification have been studied by IR spectroscopy and reported in the article.

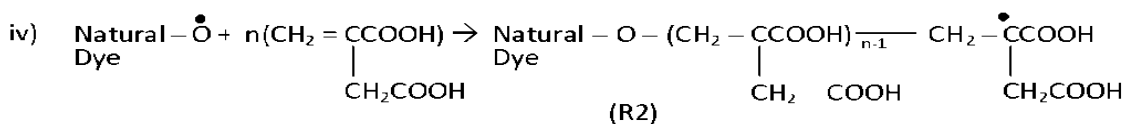
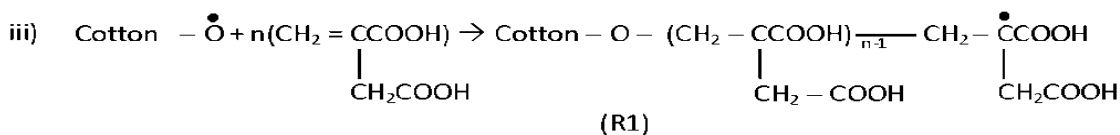


## 2. Persulphate-induced free radical graft copolymerization (30°C – 140°C)

### a) Radical generation:



### Chain initiation & propagation



### v) Chain termination

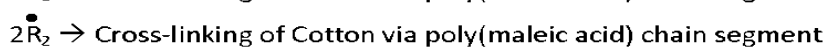


Figure (1): Reaction scheme showing modification of cotton with maleic anhydride in presence of natural dye under the catalytic influence of sodium citrate and potassium persulphate

## 2. MATERIALS AND METHODS

### 2.1 Materials:

Bleached plain weave cotton fabric with 380 ends  $\text{dm}^{-1}$  and 300 picks  $\text{dm}^{-1}$ , 14 tex warp and 15 tex weft and average area density of  $106 \text{ g m}^{-2}$  was used for the present study. Commercial grade maleic anhydride obtained from M/s Macromols India Ltd. was used without any treatment or purification. *Allium cepa* and *Terminalia arjuna* natural dyes in the form of aqueous extract having 50% solid content were obtained from M/S Eco-N-Viron, Serampore, West Bengal, India. All other chemicals used were of laboratory reagent grade.

### 2.2 Method:

#### 2.2.1 Desizing and scouring of mill-bleached cotton fabric:

To remove the sizing chemicals from the surface of the mill-bleached cotton fabric, the later was desized and scoured prior to chemical modification. Desizing of the bleached cotton fabric (250-300 g) was performed in a steel bowl using 0.25 NHCl solution at a temperature of  $50^{\circ}\text{C}$  for 2 hour at a fabric-to-liquor ratio of 1:20 (w/v). The desized fabric was washed successively with hot and cold water prior to scouring.

Scouring of the desized cotton fabric was performed by pad-steam technique. Application of sodium hydroxide was made by padding the fabric with 10% NaOH solution containing 1.5%-2% of an anionic detergent in a two-bowl padding mangle, adjusting the squeeze pressure to enable a wet pickup of 100%. The fabric was subsequently steamed in a laboratory steamer at  $100^{\circ}\text{C}$  for 10 min. The scoured fabric was washed with water, neutralized with dilute acetic acid, further washed with water and finally dried in air.

#### 2.2.2 Application of natural dyes on cotton:

Dyeing of cotton with aqueous solutions of *Allium cepa* and *Terminalia arjuna* dyes was done at a fabric: liquor ratio of 1:20. The dye bath temperature was kept at  $90^{\circ}\text{C}$  for 1 hr. The pH of the dye bath was adjusted to 4 by the addition of acetic acid and sodium acetate buffer. The cotton fabrics were selectively presoaked with aqueous solutions of  $5 \text{ g L}^{-1}$  of aluminium sulphate and ferrous sulphate as mordants separately prior to dyeing. Soaping of all dyed fabric samples was done using  $2 \text{ g L}^{-1}$  of non-ionic detergent at a temp of  $60^{\circ}\text{C}$  for 10 min. Finally the fabric samples were cold washed and dried.

#### 2.2.3 Concurrent dyeing and finishing of cotton with natural dyes and Maleic anhydride:

Cotton fabrics were dyed and finished simultaneously following exhaust -dry-iron-cure technique. Cotton fabric was presoaked with a solution containing 5g/L of potassium peroxodisulphate and subsequently dipped and worked in aqueous bath containing different specified concentrations of natural dye, maleic anhydride, and sodium citrate. Treatment was carried out at a MLR 1: 20 at  $70^{\circ}\text{C}$  for 30 min. The treated fabrics were then tumble dried at  $70^{\circ}\text{C}$  for 15 min. The dried fabrics were then ironed at  $70^{\circ}\text{C}$  and finally cured in a hot air oven at  $140^{\circ}\text{C}$  for 5 min. The cured fabrics were subsequently washed in cold water and dried in air. *Allium cepa* and *Terminalia arjuna* at the common concentrations of 20% on the weight of cotton were used separately with maleic anhydride. The finished cotton fabrics obtained after curing were subjected to soaping following a method mentioned before.

#### 2.2.4 Measurement of K/S:

Dye receptivity of the cotton fabrics as estimated in terms of K/S (Welch and Andrews, 1989) was determined employing a Macbeth 2020-plus reflectance spectrophotometer attached to a computer loaded with appropriate software.

#### 2.2.5 Assessment of color fastness to washing:

Color fastness to washing of cotton fabrics dyed with *Allium cepa* and *Terminalia arjuna* was assessed by washing the test fabrics in a Launder-O-Meter in accordance with the method prescribed in IS: 3361-1984 (ISO-II). Assessment of changes of shade and staining were done employing grey scales for change of shade and staining having numbers ISO105-AO2:1993 and ISO105-AO3:1993 respectively.

### 2.2.6 Assessment of color fastness to light:

Color fastness to light of cotton fabrics dyed with *Allium cepa* and *Terminalia arjuna* were assessed on a Shirley Mercury Bulb Tungsten Filament (MBTF) light fastness tester, Bradford, UK following a method prescribed in IS: 2454-1984 against standard blue wool references having numbers ISO:105 BOIC LFS1 - LFS8.

### 2.2.7 Assessment of color fastness to rubbing:

It was determined using a Shirley Digital Crockmeter following a method prescribed in IS: 766-1984. Assessment was done in accordance with a grey scale for staining having number ISO105-AO3:1993.

### 2.2.8 Determination of weight gain:

For the determination of gain in weight of a known weight of fabric after modification, the dry weight of each sample was recorded before ( $W_2$ ) and after ( $W_1$ ) a specific treatment and the weight gain data is expressed as percentage of initial dry weight. The weight gain percentage was then calculated on the basis of initial dry weight of cotton fabric using the following relationship (Das and Munshi, 2008) :  $\text{weight gain (\%)} = (W_1 - W_2)/W_2 \times 100$

### 2.2.9 Measurement of tensile strength:

Tensile strength of selected unmodified/modified cotton fabric samples as specified was measured according to a method prescribed in IS: 1969-1968 using a Zwick/Roell Z010 CRT universal tensile testing machine. The test strip specimens were ravelled to a size of 50 mm x 20 mm between the jaws of the machine and the tests were performed with a traverse speed of 300 mm min<sup>-1</sup> at a pre-tension of 2N.

### 2.2.10 Determination of fabric stiffness:

Fabric stiffness, as expressed by the bending length of the selected fabric samples, was measured as per IS: 6490-1971 (Cantilever test) in a SASMIRA stiffness tester with a specimen size of 25 mm x 200 mm.

### 2.2.11 Measurement of wrinkle recovery angle:

The wrinkle recovery angle (warp + weft) of the selected fabric samples was measured using a SASMIRA wrinkle recovery tester in accordance with IS: 4681-1972.

Results given for assessment of different properties mentioned above are the average of 10 tests.

### 2.2.12 IR spectroscopy:

IR spectra of desized, scoured and selectively modified cotton samples were obtained following a KBr pellet technique using Perkin-Elmer FT-IR spectrometer. The dried fibre samples were crushed to a size finer than 20 mesh before pelletising with KBr. About 0.003 g of each of crushed fibre samples was considered for pelletisation and test KBr pellets contained about 1% powdered fibre (Das *et. al.*, 2011).

## 3. RESULTS & DISCUSSIONS

### 3.1 Role of dual catalyst:

In order to study the role of esterification catalyst and free radical polymerization catalyst for dip-dry-iron-cure technique of cotton fabric with maleic anhydride in presence of natural dye, the cotton fabric was treated with maleic anhydride in absence of either of the two catalysts (see Table 1). In each experiment maleic anhydride and natural dye dose levels were maintained at 8% and 20% (w/w) respectively. Treatment of cotton fabric in presence of peroxodisulfate as the free radical polymerization catalyst only, resulted in poor weight gain, wrinkle recovery angle and depth of shade assessed in terms of K/S value with retention of high order of tensile strength, commonly for use of both the dyes. Such effects appear to be the consequence of only graft copolymerization induced by potassium peroxodisulfate (as shown in reaction scheme 2 in Figure 1 in the introduction section) and limited self catalyzed esterification reaction effected only at high temperature of drying and curing. Cotton fabric finished with maleic anhydride in presence of only esterification catalyst also resulted in poor weight gain with only marginal improvement in depth of shade and wrinkle recovery angle with high retention of tensile strength in consequent to establishment of ester linkages under the influence of esterification catalyst (as shown in reaction scheme 2 in Figure 1) with limited thermally induced graft copolymerization of maleic anhydride in

absence of free radical polymerization catalyst. Under the influence of two catalysts taken together (Potassium peroxydisulphate and sodium citrate) for the maleic anhydride cure of cotton, weight gain and wrinkle recovery angle achieved are much enhanced with attainment of high order of K/S value commonly for application of both the natural dyes. Retention of tensile strength however suffers for maleic anhydride cure of cotton under the influence of dual catalyst system in presence of the two dyes used in our study. Peroxydisulphate induced graft copolymerization of maleic anhydride is likely to take place within a temperature range of 30<sup>0</sup>C to 140<sup>0</sup>C (reaction 2 in Figure 1) while esterification reaction assumes prominence only at high temperature of drying (95<sup>0</sup>C) and curing (140<sup>0</sup>C) (shown in reaction 1 in Figure 1). Initial peroxydisulphate induced graft copolymerization / homopolymerization of maleic anhydride at ambient temperature and further polymerization of free poly(maleic acid) or cotton and / or dye bound maleic anhydride during the subsequent drying and curing period in presence of sodium citrate as the esterification catalyst caused an overall change in environment and proximity of the hydroxyl groups of cotton and dye and carboxyl groups of unbound or cotton bound poly(maleic acid) in a manner that finally caused an enhanced degree of sodium citrate catalyzed esterification leading partly to (i) cross-linking of chain polymers of cotton as evident from high wrinkle recovery angle of the treated sample and (ii) much enhanced effective linking of dye with cotton as evident from high K/S value of the maleic anhydride treated fabrics under the dual catalytic influence of sodium citrate and potassium peroxydisulphate. Weight gain, K/S value and wrinkle recovery as a consequence of the maleic anhydride curing of cotton fabric under such dual catalyst system are also found to be much superior to those of the cotton samples cured in absence of any one of the two catalysts as evident from Table 1. Consequent esterification reaction effected employing sodium citrate as the esterification catalyst as shown in reactions 1 (a) and 1 (b) of Figure 1 and initial peroxydisulphate induced free radical graft polymerization under treatment condition shown in reaction 2(a) therefore appear to be dependent on each other as results clearly show that, retention or improvements in weight gain, dye uptake assessed in terms of K/S value, wrinkle recovery angle and tensile strength are optimal on dip-dry-iron-cure of cotton with maleic anhydride under the influence of dual catalyst system (Table 1).

**Table (1): Effect of dual catalyst system for maleic anhydride cure of cotton**

Cotton fabric treated with	Potassium Peroxo-disulphate (%)	Sodium citrate (%)	Weight gain (%)	K/S ( $\lambda=420$ nm)	Wrinkle recovery angle (w+f) <sup>o</sup>	Tensile Strength retained (%)
<i>Maleic anhydride and Allium cepa</i>	0.5	0	4.83	3.96	179	97
	0	8	10.06	7.02	181	94
	0.5	8	15.14	10.35	246	80
<i>Maleic anhydride and Terminalia arjuna</i>	0.5	0	5.37	3.21	174	98
	0	8	9.35	8.32	183	90
	0.5	8	14.08	10.02	250	82

### 3.2 Effect of Maleic anhydride application level:

Cotton fabrics were separately dyed with *Allium cepa* and *Terminalia arjuna* dyes following the dip-dry-iron-cure technique in the presence of varying concentration of maleic anhydride as specified maintaining a dose ratio of maleic anhydride to sodium citrate catalyst fixed at 1:1 weight by weight according to the procedure described in the experimental section (see Table 2 and Table 3). Peroxydisulfate application dose level was maintained at 0.5% on weight of cotton fabric commonly for all such application levels of maleic anhydride. For the application of *Allium cepa* and *Terminalia arjuna* dyes following the dip-dry-iron-cure technique it appears that with increasing dose level of maleic anhydride, shade depth (expressed in terms of K/S and wrinkle recovery angle (WRA) of the cotton fabric followed a common increasing trend with a final leveling off effect commonly at an maleic anhydride application level of 8% on weight of cotton fabric. It is interesting to note that weight gain data followed a common increasing trend with increase in the dose level of maleic anhydride for applications of both the dyes and the values for weight gain in both the cases were

observed to be substantially higher than the respective maleic anhydride application levels (Table 2 and Table 3). Such high weight gains achieved at such maleic anhydride application level of 8% is the consequence of improved uptake of both the dyes considered in our study, which is much higher than that achieved when cotton was dyed in the absence of maleic anhydride as is evident from the weight gain and K/S data of the corresponding dyed cotton fabrics.

Retention of tensile strength of cotton fabric however followed a common dropping trend with increasing dose of maleic anhydride upto 8% application level of the said acid after which the retention of tensile strength levels off commonly or even increases marginally with further increase of application dose of maleic anhydride. Such dropping trend in tenacity with increasing dose level of maleic anhydride is the consequence of cross-linking of chain molecule of cotton to some degree by poly (maleic acid) under the treatment condition as evident from the improvement of wrinkle recovery angle of the fabric. Such dropping trend of tenacity appear to be more than compensated by the contribution of poly (maleic acid) incorporated into the structure of cotton for application dose level of maleic anhydride beyond 8%. The fall in tensile strength of cotton fabric for 8% application level of maleic anhydride is considered to be low and of little practical significance for the application of dyed fabric in the area of apparel where wrinkle recovery property is of importance. The higher shade depth and wrinkle recovery attained for the fabric dyed with *Allium cepa* and *Terminalia arjuna* in the presence of maleic anhydride than that dyed with these dyes in the absence of such acid is the consequence of graft copolymerization and esterification reactions that possibly took place between the maleic anhydride, natural dyes and cotton fibre in a manner that ultimately led to the establishment of linkages between the dyes, polymeric chains of cotton and also between dye and cotton.

**Table (2): Effect of maleic anhydride application level on dye receptivity and mechanical properties of cotton fabric dyed with *Allium cepa***

Maleic anhydride (%)	Sodium citrate (%)	Weight gain (%)	K/S ( $\lambda=420$ nm)	Wrinkle recovery angle (w+f) <sup>o</sup>	Tensile Strength retained (%)	Bending length (cm)
0	0	5.34	2.11	180	98	1.6
2	2	7.85	4.06	196	96	1.5
4	4	10.56	6.18	231	92	1.5
6	6	12.21	8.51	245	90	1.5
8	8	14.08	10.02	250	87	1.4
10	10	14.74	10.87	251	82	1.4

**Table (3): Effect of maleic anhydride application level on dye receptivity and mechanical properties of cotton fabric dyed with *Terminalia arjuna***

Maleic anhydride (%)	Sodium citrate (%)	Weight gain (%)	K/S ( $\lambda=420$ nm)	Wrinkle recovery angle (w+f) <sup>o</sup>	Tensile Strength retained (%)	Bending length (cm)
0	0	5.14	2.27	180	98	1.6
2	2	7.32	4.53	198	95	1.5
4	4	9.85	7.16	220	92	1.5
6	6	12.62	8.97	232	88	1.5
8	8	15.14	10.35	246	80	1.4
10	10	15.88	11.08	248	86	1.4

### 3.3 Effect of variation of sodium citrate dose level:

Effect of variation of dose level of sodium citrate as the esterification catalyst for 8% application of maleic anhydride against a constant common dose of 0.5% potassium peroxodisulphate as the free radical polymerization catalyst for dyeing of cotton with *Allium cepa* and *Terminalia arjuna* was also studied (see Table 4). For the application of *Allium cepa* and *Terminalia arjuna* following a dip-dry-iron-cure technique a higher dose of sodium citrate as catalyst commonly produced higher K/S values and wrinkle recovery angle in view of consequent higher degree of esterification. A higher dose of sodium citrate evidently caused a higher degree of linking between dye and the cotton fibre by esterification via maleic anhydride moieties in addition to cross-linking of polymeric chain of cotton that resulted in enhanced K/S value and wrinkle recovery angle with reduced tensile strength for the cotton fabric.

**Table (4):Effect of variation in potassium sodium tartrate dose level on dye receptivity and mechanical properties of cotton fabric dyed with *Allium cepa* and *Terminalia arjuna*; maleic anhydride: 8%; potassium peroxodisulphate :0.5%.**

Cotton fabric dyed with	Sodium citrate (%)	Weight gain (%)	K/S ( $\lambda=420$ nm)	Wrinkle recovery angle (w+f) <sup>o</sup>	Tensile Strength retained (%)	Bending length (cm)
<i>Allium cepa</i>	0	4.83	3.96	179	97	1.4
	2	6.76	4.82	196	97	1.4
	4	10.46	6.63	223	92	1.4
	6	13.39	8.65	243	89	1.4
	8	14.08	10.02	250	87	1.4
	10	14.62	10.61	253	84	1.4
<i>Terminalia arjuna</i>	0	5.37	3.21	174	98	1.4
	2	6.93	4.17	184	96	1.4
	4	11.47	6.01	219	93	1.4
	6	14.23	8.92	239	91	1.4
	8	15.14	10.35	246	80	1.4
	10	15.73	10.66	247	80	1.4

Fabric stiffness expressed in terms of bending length of cotton fabric dyed with above mentioned dyes in presence of maleic anhydride and sodium citrate catalyst remains unaltered, however, for almost all the dose levels of sodium citrate. Maleic anhydride finish of cotton caused moisture regain of the cotton to improve (Table 5) and it is such enhanced bound moisture of maleic anhydride treated cotton contributed significantly to retain the flexibility of the substrate (Das *et. al.*,2011). Considering all data for dyed cotton fabric (Table 4) including K/S value, wrinkle recovery angle, weight gain, tensile properties and fabric stiffness it appears that the application of 8% maleic anhydride with 8% sodium citrate as esterification catalyst and 0.5% potassium peroxodisulfate as free radical; polymerization catalyst, each on the basis of fabric weight produced optimum or the most balanced improvements in the properties of the cotton fabric.

### 3.4 Comparison of properties of cotton fabric dyed with *Allium cepa* and *Terminalia arjuna* in the presence of inorganic salts and maleic anhydride:

A comparison of the properties of cotton fabric dyed with *Allium cepa* and *Terminalia arjuna* following a commonly practiced exhaust dyeing technique in (i) the absence and (ii) the presence of inorganic salts as mordants with those of the cotton fabrics dyed with the above mentioned dyes following dip-dry-iron-cure technique in the absence and presence of maleic anhydride was studied (see Table 5). It clearly indicates that dyeing of cotton fabrics with both the dyes following a dip-dry-iron-cure technique in presence of maleic anhydride produced much overall improvement in the fabric quality in each case; maleic anhydride under the dual catalytic influence of  $K_2S_2O_8$  and sodium citrate specifically and commonly imparts higher K/S (color yield) value and higher wash and light fastness rating with appreciably improved wrinkle recovery for the respective dyed cotton fabrics. From the visual assessment of perceived color difference in different portions of all the dyed samples, it appears that the applied colors are uniform; instrumental assessment of the same gives a  $\Delta E$  value of  $\leq 0.2$  for all the samples. Maleic anhydride under the influence of dual catalyst system introduces linkage between the cotton and the dye molecules via graft copolymerization and esterification in a manner described before in addition to establishment of cross-linkages between the polymeric chains of cotton and that between the dye molecules.



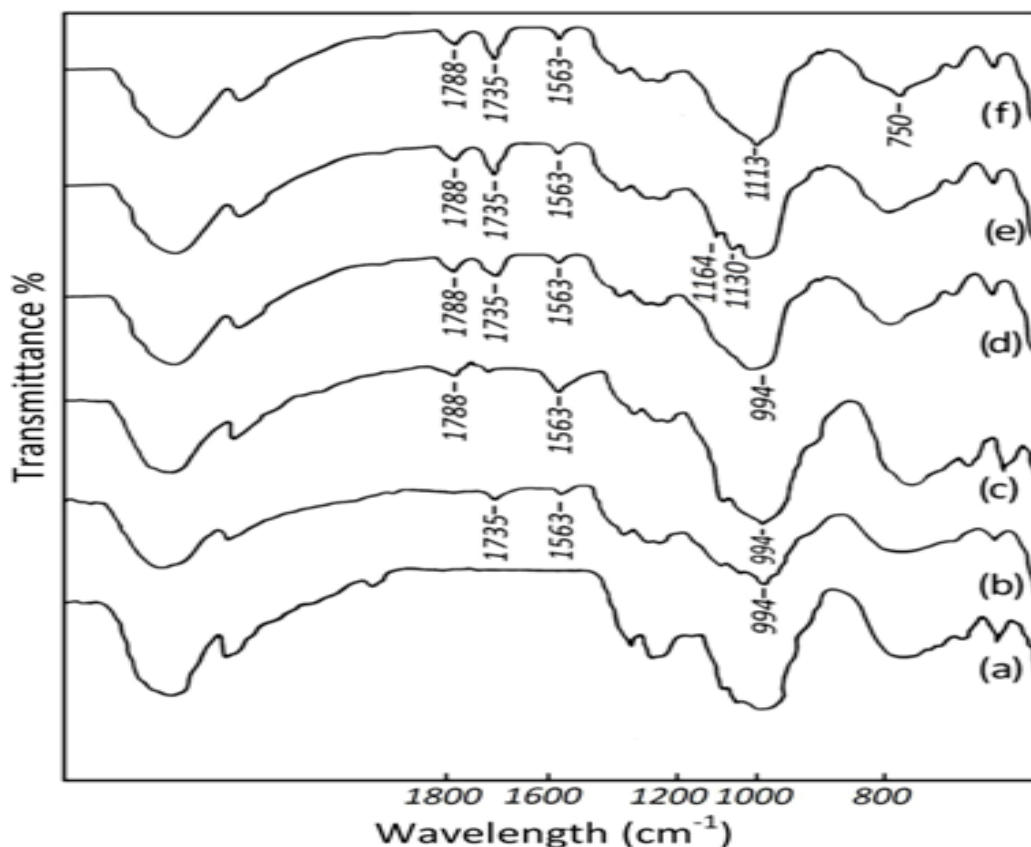
Such cross-linked dye molecules and chemically linked dye molecules to the cotton fabrics offers high resistance to the action of washing, leading to improvements in fastness to washing of the dyed fabrics. Moisture regain of natural dyed cotton fabric in presence of maleic anhydride also appears to be increased when cotton dyed with natural dyes in presence of maleic anhydride. Such additional moisture duly bound to the incorporated maleic anhydride in cotton is responsible for retaining the flexibility as revealed by bending length of the cotton fabric (Das *et. al.*, 2011) as shown in Table 3. The high level of light fastness exhibited by the cotton fabric dyed in the presence of maleic anhydride is explained by the fact that, the diffusion of oxygen becomes difficult in the cross-linked structure of the cotton which is reported to be responsible for initiation of the photo fading mechanism in polymer medium (Allen., 1987). Reduction of surface area per unit volume (specific surface) of the dye molecules in consequent to joining of two or more dye molecules by segments of poly (maleic acid) is also responsible for such improved light fastness property of natural dyed cotton in presence of maleic anhydride. Such chemical linkages of poly (maleic acid) with dye molecules and cotton leading eventually to the (i) cross-linking of cotton fibroin (ii) joining of two dye molecules together and (iii) joining of cotton and the dye molecule via poly (maleic acid) make all the differences in the properties of the correspondingly dyed fabrics including color yield / depth of shade, wrinkle recovery, moisture regain and color fastness to wash and light.

**Table (5): Comparison of properties of cotton fabric dyed with *Allium cepa* and *Terminalia arjuna* in the presence of Inorganic salts and maleic anhydride**

Cotton fabric dyed with	Dyeing technique followed	In the presence of	Weight Gain (%)	K/S ( $\lambda=420$ nm)	W F	L F	R F	Moisture regain (%)	Wrinkle recovery angle (w+f) <sup>o</sup>
<i>Allium cepa</i>	Exhaust	Nil	4.72	3.21	3	3	4	6.38	176
		5% Ferrous Sulfate	6.72	4.75	4	4	4-5	6.34	176
		5% Aluminium Sulfate	10.16	4.11	3	3	4	6.35	178
	Dip-dry-iron-cure	Nil	2.84	1.24	3	3	4-	6.34	179
		8% maleic anhydride, 8% Sodium citrate and 0.5% Potassium peroxy-disulphate	14.08	10.02	5	5	5-4-	9.04	250
<i>Terminalia arjuna</i>	Exhaust	Nil	5.46	4.71	3	3	4	6.38	176
		5% Ferrous Sulfate	7.95	5.82	4	4	4-5	6.34	176
		5% Aluminium Sulfate	11.53	4.94	3	3	4	6.35	178
	Dip-dry-iron-cure	Nil	3.19	1.83	3	3	4-	6.30	180
		8% maleic anhydride, 8% Sodium citrate and 0.5% Potassium peroxy-disulphate	15.14	10.35	5	5	5-4-	9.12	246

### 3.5 IR analysis:

Infrared spectra of unmodified cotton fibre and of the cotton fibres modified with maleic anhydride in absence and presence of catalysts and natural dyes are given in Figure 2 (a-f). A broad absorption band over 3400 – 3000 cm<sup>-1</sup> characteristic of hydrogen bonded O–H stretching vibration is common to all the spectra.



**Figure (2): IR spectra of a) unmodified cotton and cotton modified with maleic anhydride in presence of (b) sodium citrate c) potassium peroxodisulphate, d) sodium citrate and potassium peroxodisulphate, e) sodium citrate, potassium peroxodisulphate and *Allium cepa* and f) sodium citrate, potassium peroxodisulphate and *Terminalia arjuna*.**

Maleic anhydride finishing of cotton in absence of natural dye under the influence of only esterification catalyst sodium citrate (spectrum b in Figure 2) results in appearance of a strong absorption band  $1735\text{cm}^{-1}$  characteristic of ester stretching vibration; absorption band at  $994\text{cm}^{-1}$  characteristic of vinyl unsaturation present in the maleic anhydride with appearance of weak absorption of band  $1563\text{cm}^{-1}$  characteristic of carboxyl anion as expected in the said spectrum. Such trend of change of functional group pattern appears to be in line with the reaction mechanism proposed in reaction 1 (a). Maleic anhydride finish of cotton in the presence of potassium peroxodisulphate catalyst only (Spectrum c in Fig. 2) results in sharp intensification of absorption band at  $1563\text{cm}^{-1}$  for carboxylate anion and retention of weak absorption band at  $1735\text{cm}^{-1}$  characteristic of ester stretching vibration with substantial weakening of the band at  $994\text{cm}^{-1}$  characteristic of unsaturation due to polymerization of maleic anhydride under the treatment condition. Maleic anhydride finish of cotton under the influence of dual catalyst system mentioned above results in weakening of absorption band at  $1563\text{cm}^{-1}$  for carboxylate anion and appearance of strong absorption band at  $1735\text{cm}^{-1}$  characteristic of ester stretching with almost disappearance / substantial weakening of the absorption band at  $994\text{cm}^{-1}$  characteristic of vinyl unsaturation. Such trend of change of function group pattern is in accordance with the set of reactions given in reactions 1a, 2 (iii), part of 2 (v) of the reaction scheme of Figure 1. Maleic anhydride finish of cotton in presence *Allium cepa* under the influence of dual catalyst system (spectrum e in Fig. 2) however results in further intensification of bands at  $1735\text{cm}^{-1}$  characteristics of ester stretching and retention of band at  $1563\text{cm}^{-1}$  characteristics of carboxylate anion with appearance of new weak absorption bands at  $1130\text{cm}^{-1}$  and  $1164\text{cm}^{-1}$  characteristic of phenolic-OH vibrations of flavone and quercetin (Maciej *et. al.*, 2001) in accordance with the set of reactions shown in 1(b), 2b (iv) and 2b (v) of Figure 1. Intensification of ester stretching vibration in the said spectrum as expected is due to the additional esterification reaction that took place between unreacted carboxylic acid groups of cotton bound and/or unbound maleic anhydride and phenolic -OH groups of *Allium cepa*. Also, phenolic -OH vibrations in the spectrum of cotton modified with maleic anhydride in presence of *Allium cepa* accounts for unreacted phenolic OH groups of *Allium cepa* that are duly incorporated into cotton under the treatment conditions employed. Maleic anhydride finish of cotton in presence of *Terminalia arjuna* results in

similar intensification of band at  $1735\text{cm}^{-1}$  characteristic of ester stretching and retention of band at  $1563\text{ cm}^{-1}$  characteristic of carboxylate anion. Maleic anhydride finish of cotton in presence of *Terminalia arjuna* also results in appearance of new bands at  $1113\text{ cm}^{-1}$  characteristic of phenolic OH stretching for terpenoids and at  $750\text{ cm}^{-1}$  characteristics of substitute benzene present in *Terminalia arjuna* (Nema *et. al.*, 2012). The results of IR analysis is supportive to the mechanism proposed.

#### 4. CONCLUSION

The appropriate maleic anhydride finish of cotton following a dip-dry-iron-cure technique in the presence of natural dye establishes a cleaner formaldehyde and phosphorus free route for achieving simultaneous dyeing and finishing of cotton with high scope for incorporation of much improved physical and physio-chemical properties of cotton. The major property advantages that can be derived from such maleic anhydride finish in presence of natural dyes under the dual influences of esterification catalyst and free radical polymerization catalyst are substantial improvements in (i) wrinkle recovery (ii) depth of shade / dye uptake (iii) colorfastness properties to light wash and rubbing of natural dyed cotton and moisture regain property with retention of flexibility of the cotton fabric. Mechanistic consideration and IR spectroscopy indicate that changes and improvements in the properties of the natural dyed and finished cotton as mentioned above, are the direct consequences of esterification of cotton and dye with poly (maleic acid) and notable cross-linking of chain molecules of cotton via poly (maleic acid) with associated linking of natural dye and cotton through segments of poly (maleic acid) during such dip-dry-iron-cure process.

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