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IMPACT OF HIGH AND ZERO FORMALDEHYDE CROSSLINKERS ON THE PERFORMANCE OF THE DYED COTTON FABRIC

Article Highlights

- Performance of toxic crosslinker DMDHEU and its alternative BTCA was assessed on cotton fabrics
- Shade change of the crosslinker treated dyed fabrics were assessed and compared
- Performance of the alternative catalyst of sodium phosphate for BTCA was also examined
- Both crosslinkers impart similar effect on the easy care and tensile strength retention

Abstract

Performance of colored cotton fabrics dyed with sulphur, vat, direct and reactive dyes was investigated using two crosslinkers. DMDHEU was used as a formaldehyde-based crosslinker and BTCA was assessed as a zero formaldehyde alternative. The shade change of the fabrics treated with both crosslinkers was comparable and in acceptable range apart from all sulphur dyes and two reactive dyes. However, the shade change of the sulphur dyed fabrics was significantly improved when typical sodium hypophosphite based catalyst for BTCA was replaced with sodium phosphate. In addition, tensile strength and easy care performance of the crosslinker treated dyed fabric was also assessed.

Keywords: coloration, formaldehyde based crosslinkers, polycarboxylic acid, shade change, textile easy care performance.

Cotton is among the most imperative apparel fibers of the world due to its numerous end use performance advantages [1,2]. Typically, cotton fabric is first dyed and then finished with easy care crosslinkers to achieve the desired color and wrinkle free performance. Easy care crosslinkers are among the most commonly used finishes for cotton to overcome the drawback of wrinkling of cotton especially after washing [3-5]. Unfortunately, crosslinkers impart negative effect on the shade of the dyed fabric [6-9]. Requirement of acidic pH, metal catalyst, high temperature and longer curing time are some of the major reasons for the observed change in the shade of dyed fabric after easy care crosslinker treatment.

Formaldehyde based crosslinkers are the most commonly used easy care crosslinkers for cotton due to their excellent performance and low cost [10,11]. Unfortunately, formaldehyde has toxic issues associated with its use. Formaldehyde can cause difficulty in breathing, headaches, skin irritation, but most problematic of all, it is a human carcinogen [12-18]. Therefore, zero add-on formaldehyde crosslinkers are gaining importance. Consequently, intensive efforts have been undertaken to develop environmentally friendly finishing systems.

Polycarboxylic acids (PCA) are formaldehyde-free crosslinking agents and BTCA (Butanetetra-carboxylic acid) is the most effective among them [19,20,26]. Sodium hypophosphite (SHP) was identified as being the most effective catalyst from the range of catalysts evaluated [21-23]. However, SHP is a strong reducing agent and consequently has a negative effect on the shade of the dyed fabric [24-25]. Shade change is very prominent in case of sulphur dyes due to the strong reducing nature of SHP.

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Most of the easy care fabrics are first dyed and then finished; therefore, it is necessary for zero formaldehyde crosslinkers to have the least or no deleterious effect on the color of the dyed fabric.

Crosslinkers also tend to impart negative effect on the tensile strength of the finished fabric. However, most research related to tensile strength retention after crosslinker treatment is focused on white fabrics rather than dyed, while in practice, cotton fabrics are first dyed and then finished. There is also no literature available on the effects of different crosslinkers on the crease recovery performance of the range of dyed fabrics.

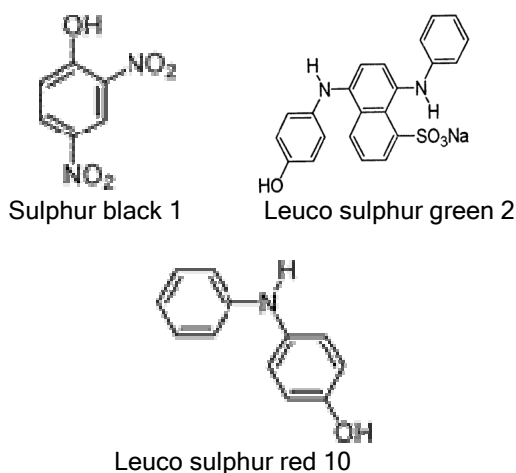
Therefore, this study was conducted to analyze the effect of formaldehyde based crosslinker (DMDHEU) and BTCA as zero formaldehyde crosslinker, on the performance range of dyed cotton fabric.

EXPERIMENTAL

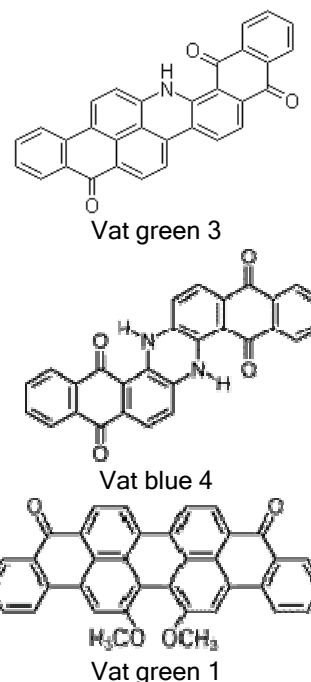
Material

100% Bleached cotton fabric was used in this study. Butanetetracarboxylic acid (BTCA), sodium hypophosphite monohydrate (SHP), sodium phosphate, dimethyloldihydroxyethylene urea (DMDHEU) and $MgCl_2$ were supplied by Aldrich chemicals.

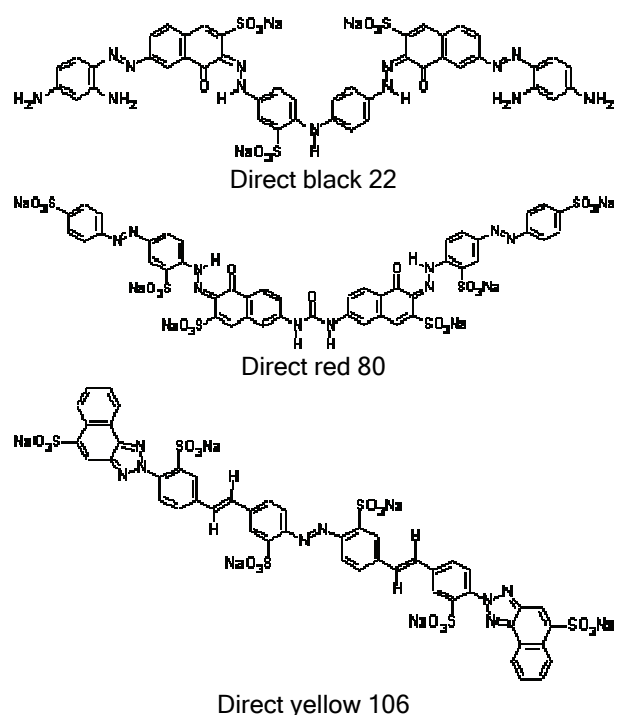
Different commercial dyes were obtained from various sources. Three sulphur dyes used in this research were sulphur black 1 (Diresul black RDT-LS 200%), leuco sulphur green 2 (Diresul green RDT-N) and leuco sulphur red 10 (Diresul bordeaux RDT-6R):



Vat green 3 (Cibanone olive B), vat blue 4 (Cibanone blue RS) and vat green 1 (Cibanone green BF) were among the three vat dyes used:

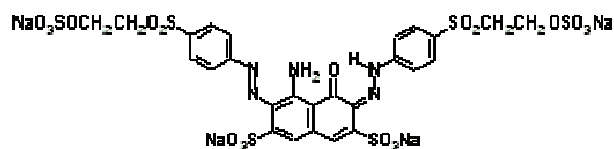


Three direct dyes consisted of direct black 22 (Everdirect black VSF 600%), direct red 80 (Red 3B conc) and direct yellow 106 (Solophenyl yellow ARLE 154%):

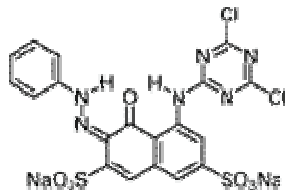


Following nine different commercially available reactive dyes were used: reactive blue 38 (Remazol brilliant green 6B), reactive black 5 (Remazol black B), reactive orange 4 (Procion orange MX-2R), reactive red 2 (Procion red MX-5B), reactive green 12

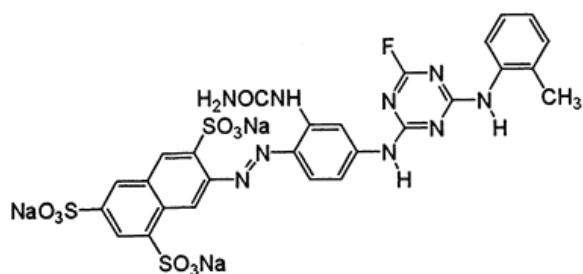
(Drimarene brilliant green X-3G), reactive red 238 (Cibacron red C-R), reactive orange 91 (Cibacron yellow F-3R), reactive red 184 (Cibacron red F-B) and reactive blue 182 (Cibacron blue F-R).



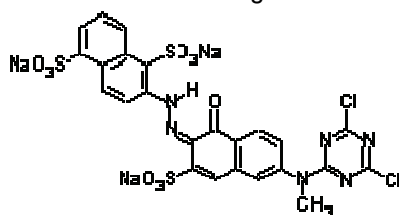
Reactive black 5



Reactive red 2



Reactive orange 91



Reactive orange 4

Chemical structures of Reactive red 238 (mono-azo benzotriazines based), Reactive blue 38 (phthalocyanine based), reactive blue 182 (Formazan copper complex based), Reactive red 184 (Monoazo based) and Reactive green 12 (Phthalocyanine based) are kept confidential by the manufacturer.

Method

Dye concentration used for dyeing was 2% (on the weight of the fabric). The dyeing process was performed according to manufacturer recommendation. After dyeing the fabric, it was padded with the desired crosslinker recipe (50 g/l of the crosslinker) with a wet pick up of 80%. Fabric was dried at 100 °C for 5 min and cured at 160 °C for 3 min in case of DMDHEU and 180 °C for 1.5 min when BTCA was used.

British and European standard BS EN 22313:1992 was used to assess the crease recovery performance of the cotton fabric. BS EN ISO 13934-1:

1999 was used to determine the tensile strength of the treated fabric. Color change rating was given by using spectrophotometer, Spectra Flash 600, on the scale of 1-5 where 1 represents the highest color change and 5 represents the least or no color change.

RESULTS AND DISCUSSION

The crease recovery angle of the cotton fabric without being dyed and finished was only 117°. In addition, the dyeing of the cotton fabric resulted in no significant improvement in the easy care performance of the dyed fabric. The crease recovery angle of the dyed samples range from only 117 to 129°, reflecting the need to apply a crosslinker in order to boost the easy care performance of the dyed fabric.

Effect of crosslinker treatment on shade of the sulphur dyed fabric

Two different crosslinkers, carboxylic acid based BTCA and formaldehyde based DMDHEU, were analyzed on the three sulphur dyed cotton fabrics. Treatment of DMDHEU crosslinker on the sulphur dyed fabrics did change the shade of the dyed fabrics. The color change rating of 4 was achieved when sulphur black 1 and leuco sulphur green 2 dyed fabrics were treated with DMDHEU. However, rating was reduced to 3-4 for leuco sulphur red 10. Nevertheless, 35-40% decrease of in tensile strength was observed while using DMDHEU as a crosslinker.

However, treatment with BTCA and SHP imparted a significant negative impact on the color change of the dyed fabric. The color change rating was as low as 1 with BTCA and SHP, due to the strong reducing nature of SHP. This problem was reported in literature when SHP was used with sulphur dyes [25]. Therefore, catalyst based on SHP was replaced with sodium phosphosphate leading to comparable rating of color change as that of DMDHEU treated fabric, Table 1. In addition, sulphur dyed fabric treated with sodium phosphosphate and BTCA exhibited about 5% better tensile strength retention than DMDHEU treated fabric.

Crease recovery of the dyed fabric was significantly improved by using any of the crosslinkers as compared to the untreated cotton fabric. However, all three sulphur dyed fabrics exhibited different crease recovery angles with both of the crosslinkers. BTCA and SHP treatment on leuco sulphur green 2 dyed fabric demonstrated higher crease recovery than DMDHEU treated fabric (Figure 1). However, DMDHEU treatment on sulphur black 1 dyed fabric exhibited two degrees better crease recovery than BTCA. In contrast, BTCA with SHP, and DMDHEU treatment on

Table 1. Effect of crosslinker treatment on shade of the sulphur dyed cotton fabric; S.D. - standard deviation

C.I. Reference sulphur	Conditions					
	BTCA = 50 g/l; SHP = 40 g/l		DMDHEU = 50 g/l; MgCl ₂ = 10 g/l		BTCA = 50 g/l; sodium phosphate = 40 g/l	
	Color change rating	Tensile strength retention, % (S.D.)	Color change rating	Tensile strength retention, % (S.D.)	Color change rating	Tensile strength retention, % (S.D.)
Sulphur black 1	2	59 (0.43)	4	60 (0.42)	4	64 (0.44)
Leuco sulphur green 2	2-3	65 (0.48)	4	64 (0.51)	4	69 (0.48)
Leuco sulphur red 10	1	62 (0.41)	3-4	65 (0.46)	3-4	70 (0.40)

sulphur red 10 dyed fabric exhibited the same crease recovery angle of 240°.

Sulphur black 1 has the lowest molecular weight of 184 among the three sulphur dyes used in this research. Fabric dyed with this dye and treated with the crosslinker exhibited the highest crease recovery angle than the remaining two sulphur dyes. Leuco sulphur red 10 has the second lowest molecular weight of 186 among the three sulphur dyes and Leuco sulphur green 2 has the highest molecular weight of 433. The crease recovery angle of the lower molecular weight sulphur red 10 was higher than sulphur green 2. It can be concluded that the molecular weight of the dye plays a vital role in the crease recovery angle of the dyed and finished fabric. From Figure 1, a trend could be noticed that greater the molecular weight of the dye lesser will be the crease recovery angle of the dyed and finished fabric; this

might be due to the relatively more fiber pore area occupation by the high molecular weight dye than the lower molecular weight dye, consequently limiting the amount of the crosslinker that gets inside the pores and can crosslink.

It is also observed that when sodium phosphate was used as a catalyst with BTCA for all three sulphur dyed fabrics then crease recovery angle is lower than BTCA with SHP and DMDHEU. However, it is not surprising as SHP is reported to be the most effective catalyst for BTCA [21].

Effect of crosslinker treatment on shade of the vat dyed fabric

Vat dyed fabrics were the second class of dyed fabrics on which crosslinkers performance was analyzed to assess the change in shade of the finished fabric. DMDHEU treated fabric exhibited good rating of color change of 3-4 to 4-5 (Table 2). However,

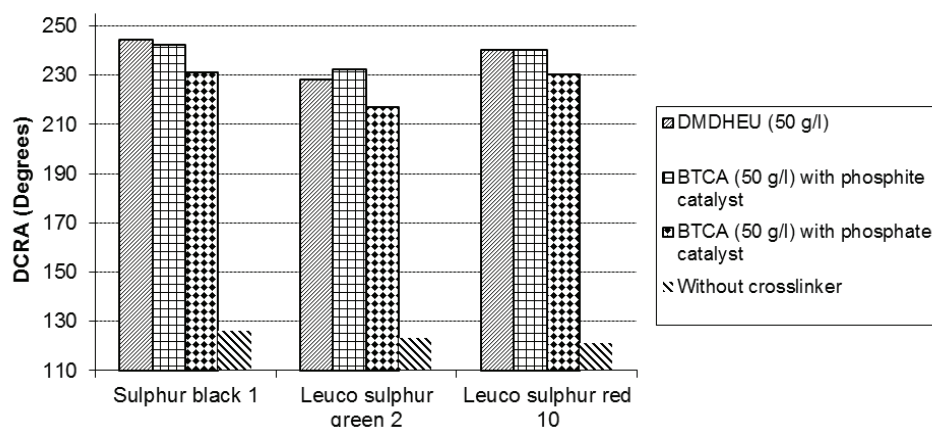


Figure 1. Effect of crosslinkers on the crease recovery angle of the sulphur dyed fabric.

Table 2. Effect of crosslinker treatment on shade of the vat dyed cotton fabric; S.D. - standard deviation

C.I Reference Vat	Conditions			
	BTCA = 50 g/l; SHP = 40 g/l		DMDHEU = 50 g/l; MgCl ₂ = 10 g/l	
	Color change rating	Tensile strength retention, % (S.D.)	Color change rating	Tensile strength retention, % (S.D.)
Vat green 3	4-5	66 (0.53)	3-4	68 (0.52)
Vat green 1	4	60 (0.57)	4	57 (0.56)
Vat blue 4	4-5	71 (0.55)	4-5	69 (0.59)

fabric treated with BTCA and SHP also exhibited the color change rating of 4 to 4-5. Nevertheless, shade change due to the treatment of BTCA with SHP was equal or better than DMDHEU treatment. In addition, vat dyed fabric treated with BTCA and SHP demonstrated similar tensile strength retention as that of the DMDHEU treated fabric.

The order of molecular weight (*MW*) of the vat dyes used for dyeing cotton in this research is vat green 1 (*MW* = 516) > vat green 3 (*MW* = 449) > vat blue 4 (*MW* = 442). The order of dry crease recovery angle of the dyed and finished fabric was vat blue 4 > > vat green 3 > vat green 1 (Figure 2). These results confirm that the greater the molecular size of the dyes, the lower will be the crease recovery angle of the dyed and finished fabric. Therefore, the size of the dye used for dyeing does affect the easy care performance of the vat dyed and finished fabric.

Effect of crosslinker treatment on shade of the direct dyed fabric

The third class of the dye examined for the shade change by the crosslinker treatment was direct dyes. Again DMDHEU treatment on the direct dyed cotton fabric exhibited good color change rating of 3-4 to 4-5. Nonetheless, direct dyed fabric treated with BTCA and SHP exhibited exactly the same color change rating as that of DMDHEU for all three direct dyes (Table 3). In addition, there is hardly any performance difference in terms of tensile strength retention between the two crosslinkers for all the three direct dyed fabrics.

The direct dyes used in this research have relatively higher molecular weight than other dyes; consequently, the crease recovery angle exhibited by the direct dyed and finished fabric is comparatively lower than other dyed fabrics. The lowest molecular weight among direct dyes was of direct black 22 (*MW* = 1119) and therefore, exhibited the highest crease recovery angle than the remaining two higher molecular weight direct dyed fabrics (Figure 3). These results provide further evidence that greater the molecular weight of the dye lesser will be the crease recovery angle of the dyed fabric after crosslinker treatment.

Effect of crosslinker treatment on shade of the reactive dyed fabric

Reactive dyes are an important class of dyes for the coloration of cotton fabrics. Therefore, fabric dyed with various reactive dyes was also examined for the color change due to the crosslinker treatment. DMDHEU treatment on the range of reactive dyed fabrics did exhibit the change in the color of the treated fabrics, Table 4. However, it was in good range of 3-4 to 4-5 for all the reactive dyes used in this research. In addition, most of the reactive dyed fabrics treated with BTCA and SHP exhibited acceptable shade change rating of 3 to 4-5. Nevertheless, reactive black 5 dyed fabric and tertiary color dyed fabric containing mixture of reactive orange 91, reactive red 184 and reactive blue 182 demonstrated poor color change rating of 2. Reactive black 5 is a vinyl sulfone based dye and, consequently, the change in

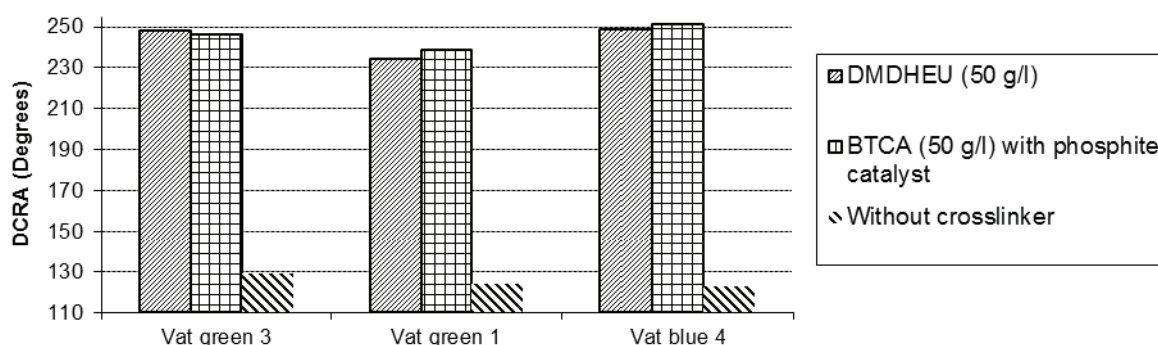


Figure 2. Effect of crosslinkers on the crease recovery angle of the vat dyed fabric.

Table 3. Effect of crosslinker treatment on shade of the direct dyed cotton fabric; S.D. - standard deviation

C.I Reference Direct	Conditions			
	BTCA = 50 g/l; SHP = 40 g/l		DMDHEU = 50 g/l; MgCl ₂ = 10 g/l	
	Color change rating	Tensile strength retention, % (S.D.)	Color change rating	Tensile strength retention, % (S.D.)
Direct black 22	3-4	57 (0.50)	3-4	56 (0.57)
Direct red 80	4-5	70 (0.53)	4-5	72 (0.58)
Direct yellow 106	4-5	59 (0.51)	4-5	61 (0.54)

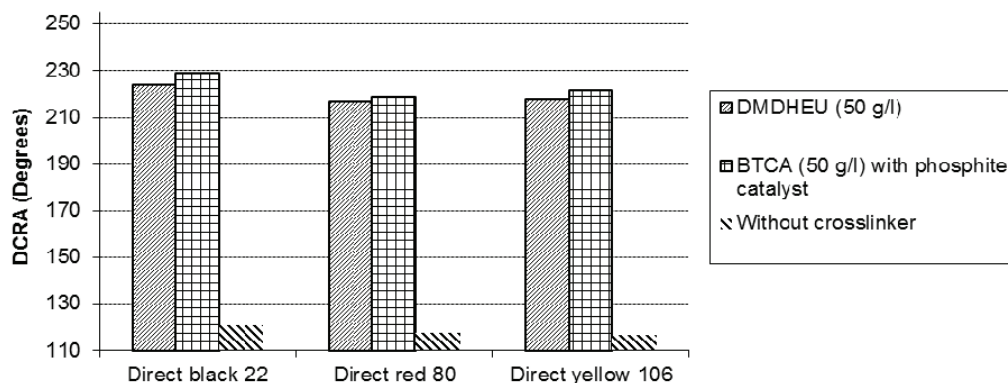


Figure 3. Effect of crosslinkers on the crease recovery angle of the direct dyed fabric.

Table 4. Effect of crosslinker treatment on shade of the reactive dyed cotton fabric; S.D. - standard deviation

C.I. Reference reactive	Conditions					
	BTCA = 50 g/l; SHP = 5 g/l		DMDHEU = 50 g/l; MgCl ₂ = 10 g/l		BTCA = 50 g/l; sodium phosphate = 40 g/l	
	Color change rating	Tensile strength retention, % (S.D.)	Color change rating	Tensile strength retention, % (S.D.)	Color change rating	Tensile strength retention, % (S.D.)
Reactive blue 38	4	54 (0.44)	4	52 (0.45)	-	-
Reactive orange 4	4-5	60 (0.47)	3-4	59 (0.48)	-	-
Reactive red 2	3-4	61 (0.51)	3-4	63 (0.43)	-	-
Reactive red 238	3	69 (0.43)	3-4	72 (0.47)	-	-
Reactive black 5	2	52 (0.46)	4	50 (0.46)	4	57 (0.43)
Reactive green 12	3-4	53 (0.49)	3-4	54 (0.51)	-	-
Reactive orange 91	2	57 (0.50)	4	54 (0.53)	4	63 (0.41)
Reactive red 184						
Reactive blue 182						

color of the dyed fabric using this particular dye and then finishing is due to the reaction between strong reducing catalyst SHP and vinyl sulphone. It is also noticed that reactive blue 182 is among the dyes used in the tertiary shade dyeing of the fabric and reactive blue 182 is based on formazan copper complex. Therefore, in the presence of strong reducing catalyst SHP and copper complex, fabric dyed with this dye and then after treated with BTCA and SHP exhibited the colour change.

However, shade change rating was raised to the rating of 4 for both fabrics; equivalent to the rating of DMDHEU treated fabric, when SHP based catalyst was replaced with sodium phosphate for BTCA. The tensile strength retention of the reactive dyed fabric treated with any of the crosslinker is similar to each other, as it was observed in case of other classes of dyed and finished fabrics.

Seven of the reactive dyed fabrics finished with both the crosslinkers exhibited different crease recovery angle performance. However, it could easily be noticed that the molecular weight of the dye determines the crease recovery performance of the dyed

and finished fabric when crosslinker amount is kept constant. Reactive red 238 has the lowest molecular weight of 366 among the all reactive dyes used in this research and consequently, it has the highest crease recovery angle among the all reactive dyed and finished fabrics (Figure 4). In contrast, reactive green 12 has the highest molecular weight of 1283 and has the lowest crease recovery performance among all reactive dyes used in this research.

CONCLUSION

The shade change of cotton fabric dyed with sulphur, vat, direct and reactive dyes was assessed after the application of DMDHEU and BTCA. Acceptable shade change rating of 3-4 to 4-5 was obtained with the application of DMDHEU. Dyed fabrics after treatment with zero formaldehyde based crosslinker BTCA exhibited similar shade change in most of the cases apart from three sulphur dyed and two reactive dyed fabrics. However, shade change ratings were brought back to the acceptable range by replacing the strong reducing catalyst sodium hypophosphite with

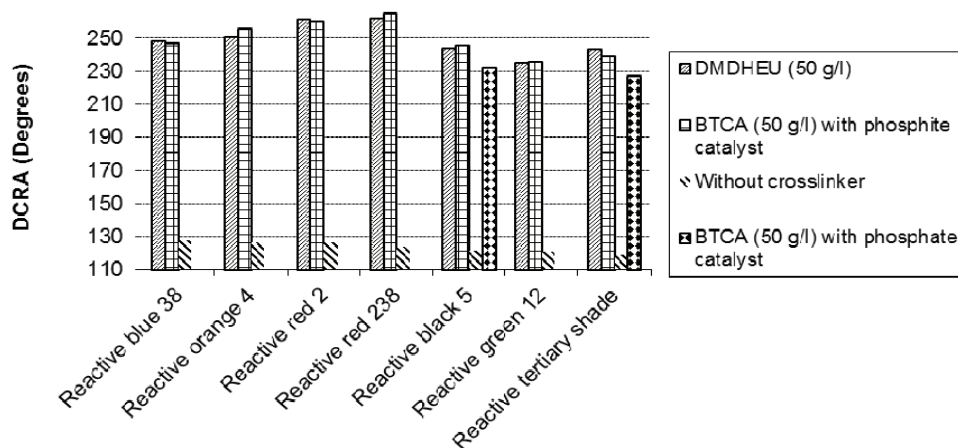


Figure 4. Effect of crosslinkers on the crease recovery angle of the reactive dyed fabric.

sodium phosphate. Nonetheless, easy care performance and tensile strength retention of the BTCA and DMDHEU finished dyed fabric were in the similar range. It was observed that the greater the size of the dye, the lower the crease recovery angle of the finished fabric was. Therefore, the molecular weight of the dye should be considered during the selection of dye for cotton fabric on which easy care treatment has to be performed at the later stage. Overall, it could be concluded that BTCA treated fabric exhibited similar performance as compared to toxic formaldehyde-based crosslinker DMDHEU, thus BTCA could replace DMDHEU treatment for cotton fabric.

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NAUČNI RAD

UTICAJ UMREŽIVAČA SA FORMALDEHIDOM I BEZ NJEGA NA PERFORMANSE OBOJENE PEMUČNE TKANINE

U ovom radu su proučavane performanse pamučnih tkanina obojenih sumpornim, redukcionim, direktnim i reaktivnim bojama uz korišćene dva umreživača: DMDHEU kao formaldehidni umreživač i BTCA kao alternativa bez formaldehida. Promena nijansi tkanine tretirane sa oba umreživača je upoređivana u prihvatljivom opsegu nezavisno od sumpornih boja i dve reaktivne boje. Međutim, promena nijanse tkanine obojene sumporom je značajno poboljšana zamenom tipičnog katalizatora na bazi natrijum-hipofosfita za BTCA sa natrijum-fosfatom. Pored toga, izvršena je i procena zatezne čvrstoće i performansi održavanja obojene tkanine tretirane umreživačem.

Ključne reči: Bojenje, umreživači na bazi formaldehida, polikarboksilna kiselina, promena nijanse, jednostavne performance tekstila.