Effect of the Chemical Modification of Cotton Fabric with Propane Sultone and through Grafting with Acrylonitrile on the Dyeability with Basic Dyes

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Synopsis

The sulfonated cotton fabrics (sulfur content: 0-0.52%), obtained by the treatment with propane sultone, were subjected to graft copolymerization with acrylonitrile. The values of the % graft of the sulfonated cotton fabrics were higher than those of untreated cotton fabrics. The sulfur contents of the sulfonated cotton fabrics, however, affected little the % graft. The sulfonated and grafted cotton fabrics absorbed basic dyes, Methylene Blue, Diamond Green, and Cathilon Red. The color fastness of these dyes towards light from a Xenon lamp and towards ultraviolet radiation was significantly improved by the introduction of polyacrylonitrile onto cotton.

INTRODUCTION

The color fastness of dyes towards light is known to depend much on the substrate fibers. For example, basic dyes have usually low color fastness when used for silk and wool. However, they can show much better color fastness when used for dyeable polyacrylonitrile.[1] It is supposed that polyacrylonitrile gives a favorable medium for dyes to be stable towards light. The purpose of the present study is to see if the light stability of basic dyes is improved by graft copolyerization of acrylonitrile onto cotton. Cotton samples were pretreated with propane sultone before graft copolymerization, in order to give sites for absorption of basic dyes. The effect of the treatment with propane sultone on the graft copolymerization was also studied.

EXPERIMENTAL

The cotton fabrics used were 40's cotton broad. Ammonium cerium (IV) nitrate was obtained from Koso Chemical Co., as a guaranteed reagent. Propane sultone was obtained from Tokyo Kasei Kogyo as a guaranteed reagent. *N,N*-dimethylformamide was obtained from Nakarai Chemicals, Ltd. as a guaranteed reagent. Acrylonitrile was purified by distillation just before use. Methylene Blue (C.I. Basic Blue 9) and Diamond Green (C.I.

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Basic Green 1) were obtained from Tokyo Kasei Kogyo, while Cathilon Red (Aizen Cathilon Red CD-FBLH) was obtained from Hodogaya Chemical Co., Ltd. All dyes were used without further purification.

Treatment with Propane Sultone[2]

The fabrics were dipped in aqueous solution of definite concentration (ranging from 13 to 20%) and preheated to the required temperature in a thermostated water bath for a definite time, followed by pressing between two sheets of filter paper. The alkali-treated samples were then immersed in an aqueous solution of propane sultone of definite concentration (from 2 to 10%) and preheated to the required temperature for definite time. The sulfonated cotton fabrics were then rinsed thoroughly with distilled water till neutrality and dried at room temperature. For control samples (alkali treated only), the fabrics were washed with distilled water till neutrality. The amounts of introduced propylsulfonic acid groups in the cotton was estimated by the sulfur content of the treated fabrics by Schoninger's flask combustion method.[3]

Copolymerization with Acrylonitrile

The chemically modified fabric was hung in a round-bottomed flask and stirred for 30 min at a constant rate by means of a mechanical stirrer in a water solution to which the appropriate amount of Ce^{IV} initiator was added (0.015 mol/L). At this stage, the appropriate amount of freshly distilled acrylonitrile (An) was added and the polymerization reaction was carried out in a preheated water bath at 60°C for 4 h. Nitrogen (gas) was bubbled into the system at a constant rate from the beginning up to the end. When the grafting time was over, the grafted sample was washed thoroughly with distilled water (to remove any residual monomer or initiator) and dried in an oven. The dried sample was then extracted with dimethylformamide (DMF) overnight at room temperature, followed by extraction with a new portion of DMF for 4 h at 50°C to remove any residual homopolymer (on the surface of the fabric). The sample was then extensively washed with distilled water till free from DMF followed by washing with ethanol and dried in the air oven at 60°C for 4 h, and kept in a vacuum desiccator for analysis and dyeing.

The grafting percentage was determined by both the percent increase in weight and by the estimation of nitrogen content by the Kjeldhal method.

Dyeing Method

The chemically treated fabric was immersed at room temperature in a dye bath composed of 0.1% aqueous solution of the dye. The liquor ratio was kept constant for all samples being 100 : 1 and the pH was adjusted to 3–4 by adding 1% acetic acid/sodium acetate solution. The temperature was then gradually raised to 95°C in 30 min and was kept at this temperature

for 50 min. The dye bath was then cooled to 60°C and the fabric was squeezed, rinsed, and dried. The amount of dye on the fabric was measured by the conventional colorimetric method to measure the concentration of dye remained in the dye bath.

RESULTS AND DISCUSSION

Sulfonation of Cotton Fabrics with Propane Sultone and Graft Copolymerization with Acrylonitrile onto Sulfonated Cotton

Cotton fabrics were impregnated in aqueous NaOH of different concentrations, squeezed to about 106% pick-up and treated with aqueous propane sultone (PS). The extent of sulfonation was evaluated from the sulfur content of the treated cotton. A preliminary study showed that the extent of the sulfonation reached maximum value when the concentration of PS was 10 wt % in accordance with some experimental data reported in the literature.[4,5] It is found that the concentration of NaOH affects the extent of sulfonation as shown in Table I and Figure 1. At the concentrations of 13 and 15 wt % of NaOH, the extents of sulfonation were about equal to each other. When the concentration was increased to 17 wt %, a juump in the extent of the sulfonation was observed, and at a higher concentration (20 wt %) the extent of the reaction increased a little. It is possible to distinguish

TABLE I
Effect of Alkali Concentration in the Pretreatment on the Extent of Sulfonation and % Graft in Relation to Sulfur Content and AN Concentration[a]

			Graft copolymerization with acrylonitrile		
				% graft	
Sample no.	NaOH conc (wt %)	% S on fabric	AN conc (g/L)	From wt increase	From N analysis
1	13	None	10	24	29
2	13	0.26	10	60	65
2a	13	0.26	5	16	23
2b	13	0.26	3	8	13
3	15	None	10	28	30
4	15	0.29	10	56	59
4a	15	0.29	5	19	24
4b	15	0.29	3	11	13
5	17	None	10	26	28
6	17	0.45	10	60	58
6a	17	0.45	5	22	25
6b	17	0.45	3	3	9
7	20	None	10	31	34
8	20	0.51	10	56	60
8a	20	0.51	5	21	26
8b	20	0.51	3	4	12

[a] PS treatment; at 50°C for 30 min in 10 wt % solution. All the samples were pretreated with aqueous NaOH solution at 40°C for 40 min.

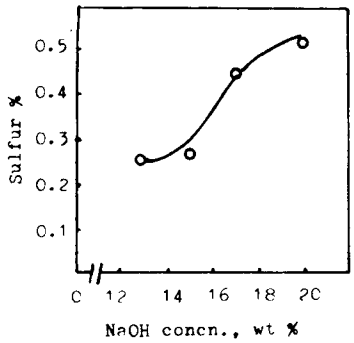

Fig. 1. Relationship between the alkali concentration and the sulfur content on the fabric

clearly between two levels of sulfonation extent, one for the 13 and 15 wt % NaOH and the other for the 17 and 20 wt %. It seems that the structure of the cellulose molecules affects the reaction with the sultone reagent. In fact, the X-ray diffraction patterns of the alkali treated fabrics showed the presence of both cellulose I and cellulose II structures for the cotton treated with 17 and 20 wt % NaOH, while only cellulose I structure was observed in case of the 13 and 15 wt % alkali. The high concentration of alkali increased the reactivity of the cellulose through increasing the degree of swelling and consequently increasing the amorphous region which affects directly the diffusion of the sultone reagent into the fabric.

The effect of the time of impregnation of cotton fabrics in 20 wt % NaOH was studied in the range of 20–60 min while keeping the conditions for the PS treatment constant (Table II). The time of impregnation gave no effect on the extent of sulfonation. The sulfonated cotton fabrics of low extents of sulfonation were obtained when PS of lower concentrations were used for sulfonation (see Table III).

The sulfonated cotton fabrics were subjected to graft copolymerization with acrylonitrile (AN) in the presence of ammonium Ce(IV) nitrate as an initiator (see Tables I–III). Control cotton fabrics were also subjected to graft copolymerization, which were obtained by treatment with aqueous NaOH of different concentrations. The % graft was obtained from both the determination of weight increase and by the Kjeldhal nitrogen analysis. The results reveal that the concentration of NaOH did not affect appreciably the % graft for control cotton fabrics, while the concentration of AN affected much the % graft (Tables I–III).

The effect of the extent of sulfonation on the % graft is shown in Figure 2, at three levels of concentration of AN. The data clearly demonstrate the enhanced increase in the % graft especially for the high AN concentration even with the lowest extent of sulfonation as compared with the only alkali-treated samples (control samples). Thus, while the % graft for sample no. 1 (no PS) is about 30%, the % graft for sample no. 2 (S % = 0.084) is over 60%. However, it was found that an increase in the extent of sulfonation on the fabric is not followed by an increase in the % graft, but rather a nearly constant value of grafting was obtained independent on the extent of sulfonation. On the other hand, the concentration of AN affects the %

TABLE II
Effect of Pretreatment Time on the Extent of Sulfonation and % Graft in Relation to Sulfur Content and AN Concentration

			Graft copolymerization with acrylonitrile		
				% graft	
Sample no.	Time of alkali treatment (min)	% S on fabric	AN Conc (g/L)	From wt increase	From N analysis
9	20	None	10	34	34
9a	20	None	5	7	10
10	20	0.52	10	61	59
10a	20	0.52	5	20	22
10b	20	0.52	3	4	12
7	40	None	10	31	34
7a	40	None	5	6	11
8	40	0.51	10	56	60
8a	40	0.51	5	21	26
8b	40	0.51	3	4	12
11	60	None	10	29	32
11a	60	None	5	3	8
12	60	0.50	10	68	70
12a	60	0.50	5	25	31
12b	60	0.50	3	2	12

[a] PS treatment; 50°C for 30 min in 10 wt % solution. All the samples were pretreated with 20 wt % aqueous NaOH solution at 40° C.

TABLE III
Effect of PS Concentration on the Extent of Sulfonation and % Graft in Relation to Sulfur Content and AN Concentration

Treatment with PS			Graft copolymerization with acrylonitrile		
				% graft	
Sample no.	PS conc (wt %)	% S on fabric	AN conc (g/L)	From wt increase	From N analysis
13	0	None	10	29	31
14	2	0.09	10	57	67
14a	2	0.09	5	25	23
14b	2	0.09	3	0	5
15	4	0.15	10	66	63
15a	4	0.15	5	24	23
15b	4	0.15	3	7	7
16	6	0.12	10	58	68
16a	6	0.12	5	28	27
16b	6	0.12	3	4	8

[a] PS treatment; at 40°C for 40 min. All the samples were treated with 13% aqueous NaOH solution at 30°C for 20 min before the PS treatment.

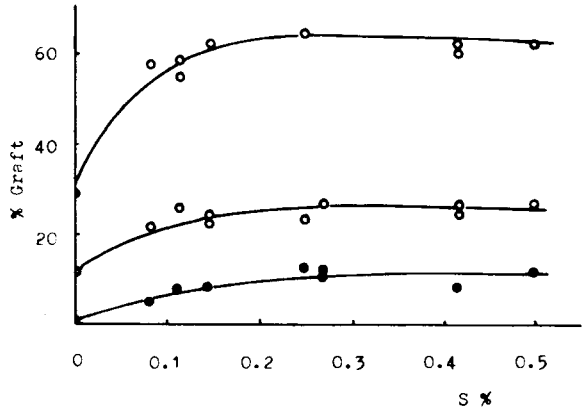

Fig. 2. Variation of the % graft with the increase in sulfur content at various AN concentration. (0.015 mole/1 Ce^{4+}, 375 ml H_2O, temp. 60°C, (○) - 10g/1 AN, (●) - 5g/1 AN, (●) - 3g/1 AN.

graft of the sulfonated cotton significantly, as for control cotton fabrics (Tables I–III). The increase in % graft with increasing monomer concentration may be due to the following reasons: (i) the solubility of the AN monomer in the polymerization medium (H_20) up to the highest concentration used (10 g/L) together with its small molecular size helping its diffusion and (ii) the prior reaction of the fabric with the initiator system which creates sufficient radicals on the cellulosic sites prior to the addition of the monomer, thus minimizing the degree of homopolymerization. Indeed, no sign of homopolymer was observed for the 3 and 5 g/L AN as the reaction medium was almost clear either during or at the end of the grafting process, while a slight turbidity was detected for the highest concentration of the monomer (10 g/L); yet it was impossible to separate it even by centrifugation.

The graft copolymerization onto sulfonated cotton fabrics were studied kinetically. Figure 3 shows that the % graft reaches the maximum in 90

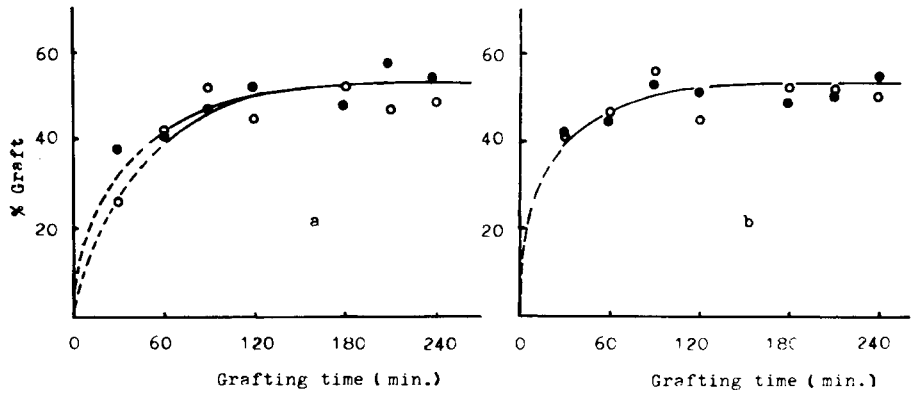

Fig. 3. Variation of the % graft with time of grafting. (0.015 mole/l Ce^{+4}, 10 g/l AN, temp. 60°C, 250 ml H_2O, sample wt., 0.2 – 0.22 g.) Fig. 3a (○) - 13 % NaOh, 2.5 % PS (●) - 15 % NaOH, 2.7 % PS Fig. 3b (○) - 17 % NaOH, 4.18 % PS (●) - 20% NaOH, 5.23 % PS

min. The extent of sulfonation or the concentration of NaOH during the treatment affects a little the rate of graft copolymerization, being slower for the sulfonated cotton fabrics prepared in the presence of 13 and 15 wt % NaOH than those prepared in the presence of 17 and 20 wt % alkali.

The scanning electron microscopic study showed that the diameter of cotton fibers increased in accordance with the increase in the % graft; cracks were found to be developed for the samples of maximum % graft (see Fig. 4). Moreover, the scanning electron microscopic photographs for the low as well as for the high % graft gave an additional experimental proof for the absence of any homopolymer deposit on the surface of the fibers.

Dyeing and Fastness Properties of Sulfonated and Grafted Cotton Fabrics

In order to study the dyeing properties, the sulfonated and grafted cotton fabrics of two levels of extent of sulfonation and three levels of % graft were prepared. For comparison, control cotton fabrics, sulfonated and non-grafted cotton fabrics, and nonsulfonated and grafted cotton fabrics were also prepared (Table IV).

The cotton samples were dyed with three basic dyes, Methylene Blue, Diamond Green, and Cathilon Red. A comparison between the amount of dyes absorbed on different samples for the three dyes is given in Table V. These values were calculated from the concentrations of the dyes in the dye bath before and after dyeing as the dyes in the sulfonated and grafted samples were not removed completely by extraction with aqueous pyridine. From these results, the role of propane sultone (PS) in enhancing the dye uptake is well illustrated. Thus, an increase in the sulfur content on fabric from 0.27% to 0.52% (A-2 and B-2 samples) is followed by an increase in the dye uptake equivalent to 33.2%, 22.9%, and 12.5% for the Cathilon Red, Methylene Blue, and Diamond Green, respectively. The ability of the dye uptake for the cotton fabric of the same extent of sulfonation towards the various investigated dyes is nearly the same. Thus, in spite of the fact that the amount of dye uptake for sample A-2 (only sulfonated sample) as

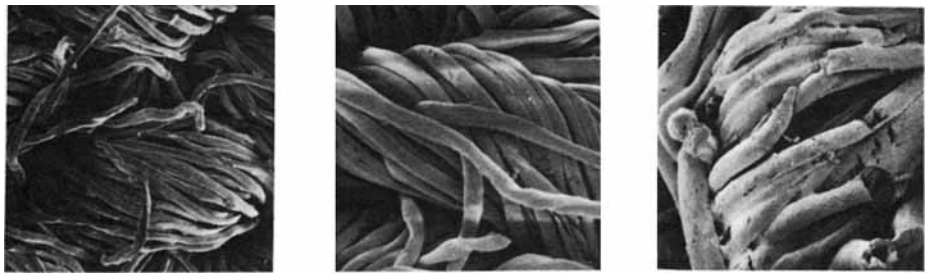

Fig. 4. The scanning electron microscope photographs of 20 % alkali treated fabrics either ungrafted or grafted to different extents. (Sulfur content = 0.51 %).

TABLE IV
Selected Samples of Chemically Modified Cotton Fabrics for Testing Dyeing Properties

Sample code	NaOH conc (wt %)	% S in original fabric	% graft from N analysis	% S after grafting calculated[a]
A-1	13	None	None	0.00 (0.000)
A-2	13	0.27	None	0.27 (0.084)
A-3	13	None	25	0.00 (0.000)
A-4	13	0.27	10	0.25 (0.077)
A-5	13	0.27	24	0.22 (0.068)
A-6	13	0.27	58	0.17 (0.053)
B-1	20	None	None	0.00 (0.000)
B-2	20	0.52	None	0.52 (0.163)
B-3	20	None	31	0.00 (0.000)
B-4	20	0.52	12	0.47 (0.145)
B-5	20	0.52	21	0.43 (0.134)
B-6	20	0.52	59	0.33 (0.102)

[a] Values in parentheses are in mol S/kg fabrics.

reported in g dye/kg fabric is increased in magnitude from Cathilon Red to Methylene Blue and Diamond Green, the values calculated in mol dye/kg fabric for the Methylene Blue and Diamond Green are near the same, being $\sim$ 0.14 mol. Nearly the same results were obtained for the fabric of high extent of sulfonation (B-2 sample) being 0.16 and 0.18 mol/kg fabric for Diamond Green and Methylene Blue, respectively. These results enable one to consider the possibility of 1:1 interaction between the dye molecules and the sulfonate groups in the samples. The chemical formula of Cathilon Red is not disclosed, and the molar amount of this dye absorbed could not be calculated (Table V). The observed increase in dyeability with increasing the sulfur content on fabric is in accordance with the data reported by several workers on the cationic dyeing properties of cellulose chemically modified by introducing acidic groups.[6-10]

TABLE V
Comparison between Amounts of Dyes Absorbed on Modified Cotton Fabrics

Sample code	mol S/kg fabric	g dye absorbed/kg fabric[a]		
		Cathilon Red	Methylene Blue	Diamond Green
A-1	0.0	2.0	3.9 (0.010)	31.6 (0.065)
A-2	0.084	30.7	55.0 (0.147)	68.8 (0.142)
A-3	0.0	5.4	0.9 (0.002)	14.8 (0.030)
A-4	0.077	25.1	23.4 (0.062)	25.5 (0.052)
A-5	0.068	55.9	39.5 (0.105)	60.2 (0.124)
A-6	0.53	35.3	15.8 (0.042)	21.9 (0.045)
B-1	0.0	0.9	1.3 (0.003)	21.1 (0.043)
B-2	0.163	40.9	67.6 (0.180)	77.4 (0.160)
B-3	0.0	5.0	1.3 (0.003)	9.3 (0.019)
B-4	0.145	50.6	67.9 (0.181)	65.8 (0.136)
B-5	0.134	60.4	57.5 (0.153)	65.0 (0.134)
B-6	0.102	55.9	30.8 (0.082)	52.4 (0.108)

[a] Values in parentheses are in mol/kg fabric.

The results reveal also that only grafted samples (nonsulfonated) showed a little tendency for dyeing as compared with the PS-treated fabrics (compare A-3 with A-2 and B-3 with B-2). These results illustrate once more the important role of the acidic groups on the fabric for this class of dyes. For samples treated with PS and grafted, an increase in % graft from 9.8 to 24.0 (A-4 and A-5 sample) is followed by an increase in the dye uptake for the three dyes, while a dramatic drop in the amount of dye absorbed was observed for the 57% grafted sample (A-6 sample). These results correlate well with the important role played by the sulfonate moiety towards these ionic dyes. This is simply because an increase in % graft on the fabric is followed by a decrease in the real amount of sulfonate groups on the fabric. Taking this into consideration, the value of the sulfur content for the A-group samples was found to change from 0.27% to 0.25%, 0.22%, and 0.17% for the A-4, A-5, and A-6 samples, respectively (Table IV). Thus, the sulfur content of the high grafted sample (A-6 is about 2.3 of that of the ungrafted one (A-2), and it is reasonable that the amount of dye uptake is lowered in this case. The same is true for the 20% alkali treated samples (B-group samples) as the value of sulfur was changed by changing the % graft from 0.52% to 0.47%, 0.43%, and 0.33% for the B-4, B-5, and B-6 samples, respectively. For this an increase in the % graft for B-group samples is followed by a decrease in the dye uptake.

The stabilities of these dyes in water towards UV light from a low pressure mercury lamp were studied. The time of irradiation was up to 5 h, while the temperature of irradiation was about 100°C. Figure 5 shows that these dyes degrade according to the first-order kinetics with respect to the concentration of the dyes. Diamond Green was the least stable, and Methylene Blue the most stable.

Light color fastness of the dyed cotton fabrics towards Xenon lamp were

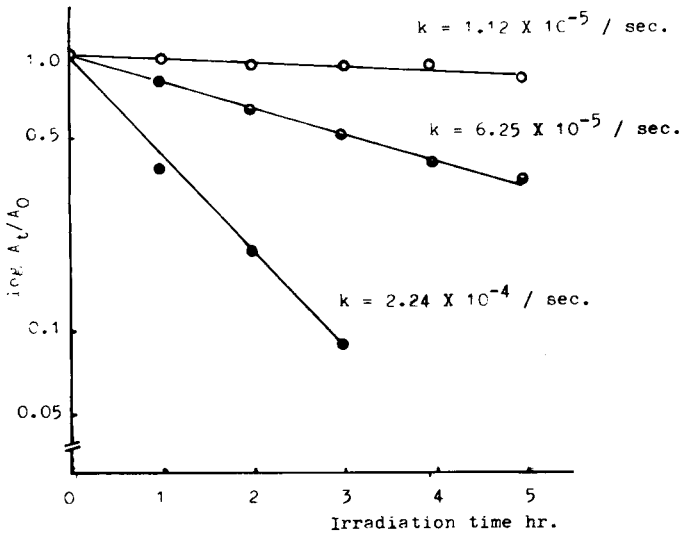

Fig. 5. Decomposition of dyes as a function of irradiation time. Light source: low pressure Hg lamp. (◐) - Cathilon Red, (○) - Methylene Blue, (●) - Diamond Green.

TABLE VI
Light Fastness of Dyed Fabrics Exposed to Xenon Lamp Based on the Blue Scale[a]

Sample code	Cathilon Red	Methylene Blue	Diamond Green
A-1	1>	1	1>
A-2	1	4–5	1–2
A-3	2–3	1–2	3
A-4	3	6	4
A-5	5	7	4–5
A-6	5	7–8	6
B-1	1>	1	1
B-2	2	4–5	4
B-3	2–3	3	3–4
B-4	5	8	6
B-5	8	8	6
B-6	8	8	7

[a] Exposure time up to 3 days.

studied according to the procedure standardized by JIS L 0824, and the evaluation of the results was according to the method L 0842 based on matching with the blue scale. The results of the light fastness after 3 days exposure of the different samples under controlled conditions of humidity and temperature to a Xenon lamp are shown in Table VI. The results show that the introduction of polyacrylonitrile onto cotton significantly improves the color fastness. The higher the % graft, the better the color fastness (compare samples A-2 and B-2 with A-4, A-5, and A-6, and B-4, B-5, and B-6, respectively). The sulfonated and nongrafted cotton fabrics appeared to show better color fastness than control cotton. This is, however, not exactly true since the color concentrations of these samples were too much different.

TABLE VII
UV Fastness of Dyed Fabrics Exposed to Low Pressure Mercury Lamp[a]

Sample code	Cathilon Red	Methylene Blue	Diamond Green
A-1	VP	VP	VP
A-2	P	M	P
A-3	P	P	P
A-4	M	M	G
A-5	G	G	G
A-6	G	G	G
B-1	VP	VP	VP
B-2	M	G	M
B-3	M	P	P
B-4	VG	VG	VG
B-5	VG	VG	VG
B-6	VG	VG	VG

[a] VG=very good, G=good, M=moderate, P=poor, VP=very poor. Test conditions: temperature was about 100°C; distance from the source was 7.5 cm. Exposure time: up to 40 min.

The UV color fastness of the dyed cotton fabrics towards low pressure mercury lamp were also studied. Table VII represents the values of the UV color fastness of the different dyed samples after 40 min exposure. The temperature of irradiation was about 100°C, while the distance from the source was 7.5 cm. The results show the improvement of the UV fastness with the extent of sulfonation (compare A-2 with B-2 sample) but much more pronounced with the increase in the % graft onto sulfonated cotton fabrics (compare samples A-2 and B-2 with A-4, A-5, and A-6, and B-4, B-5 and B-6, respectively). These results are in good accordance with those reported by the light color fastness test.

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