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Study on chemical bonding of Polycarboxylic acid Black on cotton and its dyeing and finishing properties

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Abstract

Polycarboxylic acid Black was applied to dyeing of cotton and acted as wrinkle resistant finishing agent through the bonding between the cotton and the dye. Thermal gravimetry and FT-IR spectroscopy were used to investigate the dyeing mechanism and methods of color stripping, fiber dissolving in cuprammonia and fiber oxidation were employed to indirectly testify the ester linkage of the fiber and the dye. Dyeing properties were examined to show that Polycarboxylic acid Black could realize high fixation, good fastness properties and improved wrinkle resistance on cotton. Also, Polycarboxylic acid Black can be completely utilized by cycle dyeing due to the stability of the dye.

Keywords: Polycarboxylic acid dye; Cotton; Ester linkage; Dyeing; Finishing

1. Introduction

Cotton, which is comfort-wear and ventilate, is usually dyed with reactive dyes to obtain good wet fastness by formation of covalent bonds between fiber and dye. But effluent impact of reactive dyes on environment, resulted from dye hydrolyzation and low fixation, has all along been a problem urgent to solve. In our study, cotton dyed with polycarboxylic acid dye can also achieve good wet fastness. As multiple stable carboxylic groups exist in polycarboxylic acid dye, dye hydrolyzation is avoided and cycle dyeing can be employed to achieve high fixation of the dye, which greatly reduces the environmental pollution and shows the priority of polycarboxylic acid dye in dyeing of cotton.

The idea of application of carboxylic groups as the reactive groups in dyeing of cotton is derived from finishing effect of polycarboxylic acid [1–3]. The finishing mechanism of tetrabutyl carboxylic acid on cotton is that adjacent carboxylic groups form intramolecular anhydride and then react with hydroxyl groups of cotton to form ester linkage [4–6]. The finishing property of the cotton dyed with polycarboxylic acid dye, when the carboxylic groups of polycarboxylic acid dye do not link to adjacent carbons, has not yet been reported. So the purpose of this paper is to prove the dyeing mechanism of ester linkage by dehydrating esterification in dyeing of cotton with Polycarboxylic acid Black, to evaluate finishing and other fastness properties of the dyed fabrics, and to investigate the dyeing properties in cycle dyeing of the dye.

2. Experimental

2.1. Materials

The desized, scoured and mercerized cotton poplin ($40 \times 40/120 \times 60$) was purchased from Dalian Printing Co. Ltd. Dicyandiamide and sodium hydroxide were chemical pure, and imidazole, copper sulphate and ammonia were analysis pure. Polycarboxylic acid Black used in the experiment was synthesized by Wang and Yang [7].

2.2. Dyeing procedure

Pad-dry process was used in dyeing of cotton with Polycarboxylic acid Black. Dyeings were carried out at liquid ratio of

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10:1 and the concentration of the dye was 80 g/l. Cotton was padded two dips and two nips using TFO/S 350 (Roaches Co., UK) laboratory pad mangle, the pressure on the mangle was adjusted to give 80% pickup. The dyed cotton then pre-dried at 80 °C for 3 min followed by baking on a rapid ager for 10 min.

Finally the dyed cotton was washed thoroughly, soaped in 2 g/l nonionic detergent at 95 °C for 15 min, then washed and dried.

2.3. Dye fixation

The dye fixation F was calculated by the following equation, and the absorbance was determined using HP 8453 UV–vis spectrophotometer, wherein A_0, A_1 and A_2 of the dye liquors were measured with the same volume.

$$F = (A_0 - A_1 - A_2)/(A_0 - A_1) \times 100\%$$

A_0 – absorbance of the initial dyebath,
A_1 – absorbance of the dyebath after dyeing process,
A_2 – absorbance of the soap bath after the soaping step.

2.4. Measurements

The wrinkle-recovery angle of the cotton dyed with Polycarboxylic acid Black was tested according to GB/T3819-1997 using YG541A wrinkle-recovery tester (Darong Standard Textile Apparatus Co. Ltd., Wenzhou). Wash fastness of the dyed cotton was tested according to GB/T3921-97 using S-1002 two bath dyeing and testing apparatus (Roaches Co., UK). Water fastness was tested according to GB-5713-97 using YG(B) 631 perspiration fastness testing apparatus and Y902 perspiration fastness testing oven (Darong Standard Textile Apparatus Co. Ltd., Wenzhou). Rub fastness was tested according to GB/T3920-97 using Y(B)571-II crockmeter. Light fastness was tested according to GB8427-87 using Xenotext 150s Weatherometer (Heraeus Co., Germany). Thermal analysis of Polycarboxylic acid Black was tested using TGA/SDTAe851 (Mettler-Toledo Co., Swiss). IR spectra of the dyed fiber were recorded using NEXUS FT-IR Spectrometer (KBr pellets) (Thermo Nicolet Co., USA).

3. Results and discussion

Under suitable conditions, carboxylic groups of Polycarboxylic acid Black can react with hydroxyl groups of cotton by dehydrating esterification and the dye was fixed on fiber through ester linkage (see Scheme 1).

$$\text{D-COOH} + \text{Cell-OH} \xrightarrow{-H_2O} \text{D-COO-Cell}$$

Scheme 1.

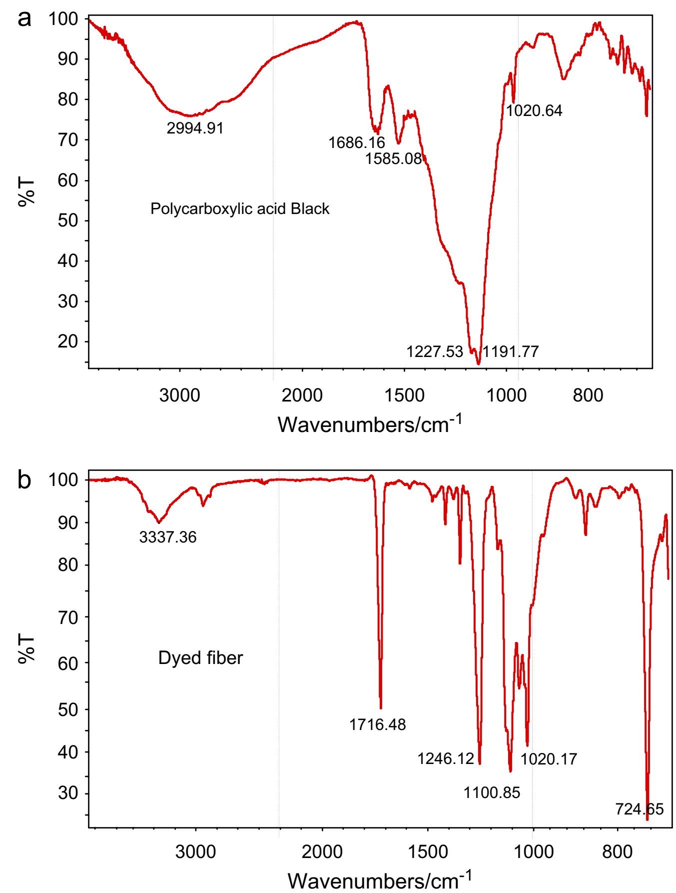

Fig. 1. IR spectra of Polycarboxylic acid Black and the dyed fiber.

Chemical linkage between the Polycarboxylic acid Black and fiber was testified by a series of direct and indirect methods.

3.1. Direct methods for testing the ester linkage

3.1.1. IR spectra analysis

Since multiple carboxylic groups exist in Polycarboxylic acid Black, ester linkage may form between it and the fiber, which would show characteristic adsorption in IR spectrum of the dyed fabrics. The IR spectra of Polycarboxylic acid Black and the dyed fiber are shown in Fig. 1.

Fig. 1(a) is the IR spectrum of Polycarboxylic acid Black. The broad band at 2500–3400 cm^{-1} was attributed to the stretching vibration of carboxyl hydroxyl groups, and band at 1686 cm^{-1} was due to the stretching mode of carboxyl carbonyl groups. Fig. 1(b) is the IR spectrum of the fiber dyed

Table 1
Effect of dehydrating agents on thermal gravimetry, baking temperature and dyeability of Polycarboxylic acid Black

	Onset (°C)	Endset (°C)	DTG peak temperature (°C)	Baking temperature (°C)	Fixation (%)	*K/S*
D	214.6	295.4	267.3	220	59.4	6.3
D + B	194.7	286.4	250.2	200	99.9	12.6
D + A	174.8	206.7	191.1	190	99.7	12.4

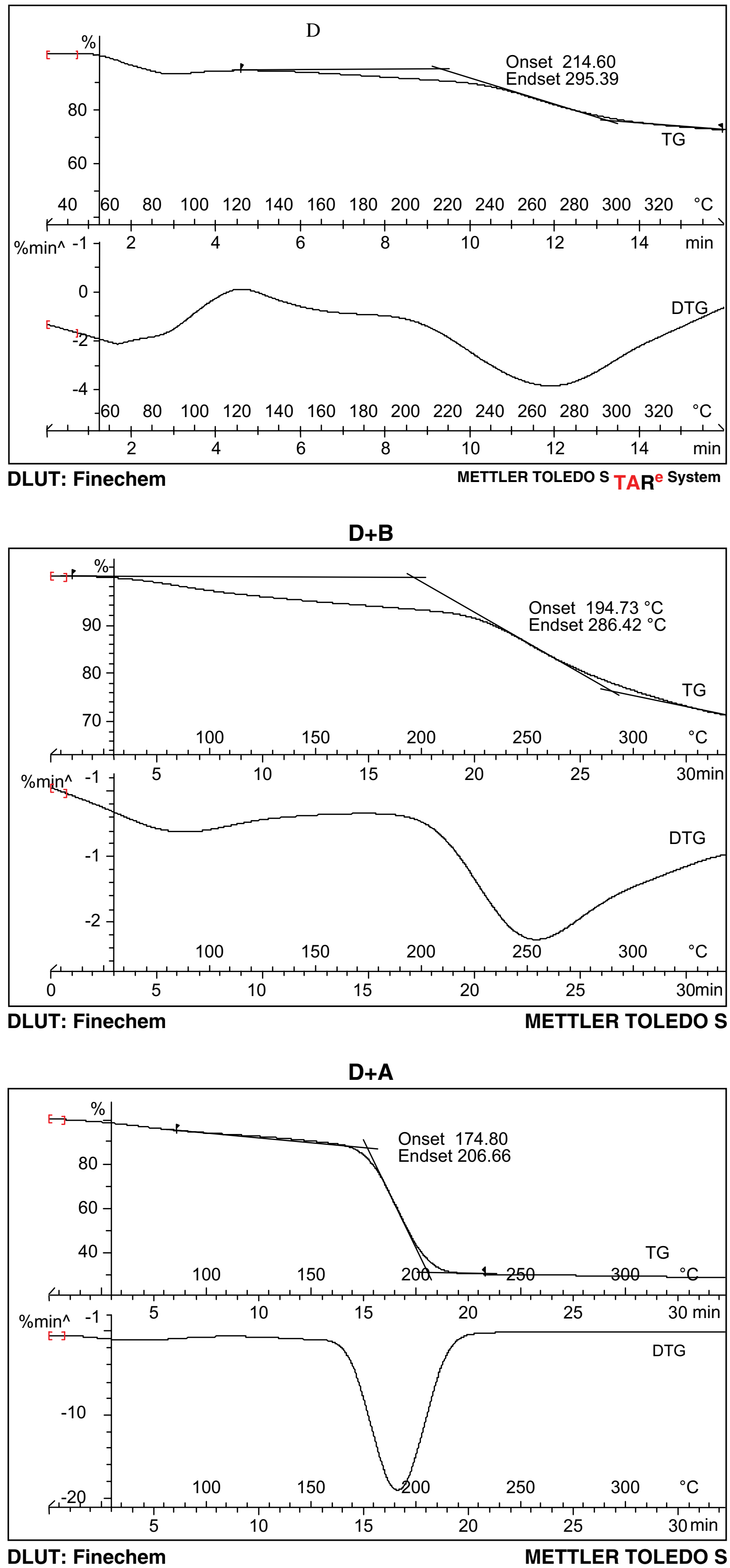

Fig. 2. Thermal gravimetry of D, D + A and D + B.

with Polycarboxylic acid Black, the bands at 1716 cm^{-1} and 1246 cm^{-1}, respectively, represented ester carbonyl groups and carbon–oxygen bonds of ester groups, which demonstrated that esterification reaction happened when the cotton was dyed with Polycarboxylic acid Black.

3.1.2. Thermal analysis

If ester linkage formed between fiber and Polycarboxylic acid Black, weight loss would happen in the process of dehydration esterification, so thermal gravimetry (TG) was applied to study the dyeing mechanism of Polycarboxylic acid Black on cotton. As dicyandiamide and imidazole were reported to be effective dehydrating agents, they were added in dyebath of Polycarboxylic acid Black to investigate their effect on dyeing. The relationship between the baking temperature in dyeing process and the weight loss of the dye was tested and the results are listed in Table 1 and are illustrated in Fig. 2, wherein (A) is imidazole, (B) is dicyandiamide and (D) is Polycarboxylic acid Black.

The thermal analysis showed that weight loss existed no matter whether dehydrating agent was added or not. But it was observed that when no dehydrating agents were added in the dyebath, low fixation of 59.4% and low *K*/*S* of 6.3 were obtained even at heating temperature as high as 220 °C; whereas addition of imidazole or dicyandiamide which can reduce the dehydration temperature was beneficial to dyeability of Polycarboxylic acid Black at lower baking temperature. Imidazole showed priority in decreasing the dehydrating temperature, at baking temperature of 190 °C, dye fixation of 99.7% and color strength of 12.4 were obtained. For dicyandiamide, 200 °C was needed to acquire almost the same results. The addition of dehydrating agents lowered the temperature at the maximum rate of weight loss of the dye and made the dehydrating esterification between the carboxylic groups of the dye and the hydroxyl groups of the cotton become much easier. Therefore it was concluded that ester linkage formed between Polycarboxylic acid Black and the fiber during the dyeing procedure.

3.2. Indirect methods for testing the ester linkage

3.2.1. Color stripping of the dyed fiber

Polycarboxylic acid Black can slightly dissolve in water under acidic condition, and can well dissolve in water under neutral and alkaline condition. But if covalent bonds form between Polycarboxylic acid Black and fiber, the dye is difficult to be removed from fiber even under neutral and dilute alkaline conditions. This method is actually a common test for indirectly proving the existence of covalent bond between fiber and dye. The color stripping results of the dyed fiber under various conditions are shown in Table 2 and Fig. 3.

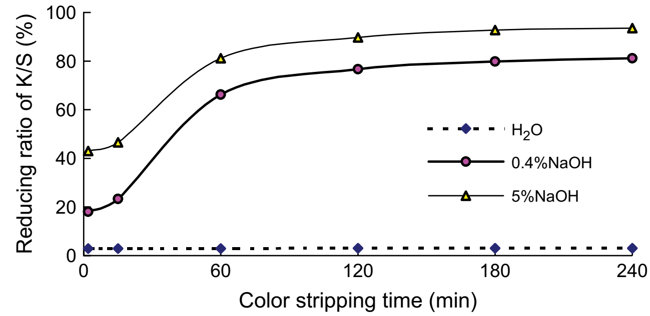

Fig. 3. Reducing ratio of *K*/*S* of the fiber dyed with Polycarboxylic acid Black at 90 °C with different decolorizing times.

Table 3 showed that when 10% acetic acid was used for color stripping, little dye was removed off no matter whether baking step proceeded, which was mainly owing to the dissolubility of the dye in acidic condition. By wash of neutral water and 0.4% sodium hydroxide, if without baking procedure, the reducing ratio of *K*/*S* was about 90% and most of the dye was removed from the fiber; whereas for dyeing with baking process, hardly any color was stripped off. This indicated that covalent bonds formed between Polycarboxylic acid Black and the cotton, at baking step, by dehydrating esterification. Figures in Table 3 also show that under both conditions of baking, *K*/*S* of the dyed fiber treated with 5% sodium hydroxide decreased greatly. This was mainly attributed to the breakage of ester linkage under this condition. In Fig. 3, when the treatment temperature increased to 90 °C, reducing ratio of *K*/*S* was always low and kept constant within the time range of color stripping for neutral washing. But for alkaline washing with 0.4% sodium hydroxide, the reducing ratio of *K*/*S* exceeded 80% after 240 min treatment, which didn't happen in treatment at room temperature. At 90 °C, the tendency of reducing ratio of *K*/*S* for both 0.4% and 5% sodium hydroxide washing was the same and 5% sodium hydroxide had more effect on color stripping, which demonstrated that at 90 °C, ester linkage broke gradually with the increase of washing time and concentration of alkali.

3.2.2. Dissolution of the dyed fiber in cuprammonia

The viscosity of cuprammonia increased when cotton was dissolved in it. It was found that when the fiber was dyed

Table 2
Color stripping results of the fiber dyed with Polycarboxylic acid Black (25 °C)

Solution used	$K/S_{unbaked}$			K/S_{baked}		
	Before curing	After curing	Reducing ratio (%)	Before curing	After curing	Reducing ratio (%)
10% HAc	10.2	9.9	2.94	10.7	10.4	2.80
H_2O	10.6	1.2	88.68	10.8	10.5	2.77
0.4% NaOH	10.4	0.9	91.35	10.5	10.2	2.86
5% NaOH	10.5	0.5	93.33	10.1	1.8	82.18

Table 3
Relative viscosity of the copper ammonia solution dissolving different fibers

No.	Fiber dissolved in cuprammonia	Relative viscosity
1	–	1.00
2	Cotton dyed by exhaust method	1.11
3	Cotton dyed by pad-dry method ($F = 99.9\%$)	1.16
4	Cotton dyed by pad-dry method ($F = 65.4\%$)	1.42
5	Unbaked dyed fiber	1.51
6	Undyed fiber	1.54

Table 4
Effect of content of aldehyde groups of the oxidized fiber on dye fixation

$NaIO_4$ (mol/L)	Content of aldehyde groups (mmol/g)	Fixation (%)
0	–	99.18
0.01	28.85	98.22
0.02	89.64	88.98
0.04	135.80	79.31
0.06	261.03	67.86

with Polycarboxylic acid Black, the solubility of it in cuprammonia changed. Table 3 presents the relative viscosity of cuprammonia, which dissolved the cotton dyed with different dyeing processes.

It showed that the cuprammonia, which dissolved the undyed fiber and the unbaked dyed fiber, gave higher relative viscosity, they were 1.54 and 1.51, respectively. But for the fiber dyed with both pad-dry method and exhaust method, the relative viscosity of the cuprammonia obtained was low, which was presumably due to the covalent bond—ester linkage formed between the dye and the fiber, so the dyed fiber was difficult to dissolve in cuprammonia. Compared with the dyed fiber with fixation of 65.4%, the dyed fiber with higher fixation of 99.9% showed lower relative viscosity when it was dissolved in cuprammonia, their relative viscosity was 1.42 and 1.16, respectively. These results were obtained owing to the fact that more ester linkages were formed between the dye and the fiber (for the dyed fiber with high fixation) which prevented the fiber from dissolving in cuprammonia and led to lower viscosity.

3.2.3. Fiber oxidation method

To testify the ester linkage between Polycarboxylic acid Black and cotton, the hydroxyl groups of the fiber were partially oxidized before dyeing to examine the influence of it on dye fixation. In Table 4, the effect of content of aldehyde groups of the oxidized fiber on dye fixation is listed.

From Table 5, it is observed that with the increase of concentration of oxidation agent, more hydroxyl groups were oxidized to aldehyde groups and the fixation of Polycarboxylic acid Black on fiber decreased evidently. This indicated that ester linkage formed during dyeing process, so when some hydroxyl groups were oxidized, they can no longer react with the carboxylic groups of the dye and thus the dye fixation was reduced.

3.2.4. Oxidation of the dyed fiber

If covalent bonds existed between the dye and the cotton, partial hydroxyl groups of the fiber had reacted with the carboxylic groups to form the ester linkage. Higher the dye fixation was, more will be the hydroxyl groups reacted and less will be the residual hydroxyl groups that could be oxidized to aldehyde groups after dyeing process under the same oxidation condition. Therefore the method of oxidation of the dyed fiber was employed to indirectly testify that esterification reaction happened in the dyeing procedure.

Fig. 4 shows that higher the dye fixation was, lower will be the amount of aldehyde groups contained in fiber by oxidation of the dyed fiber. This indicated that in dyeing process, some hydroxyl groups of the fiber reacted with the dye, they then lost the reactivity to be oxidized. So the dyed fiber with high fixation led to lower content of aldehyde groups by oxidation procedure.

3.2.5. Recoverability of the dyed fiber

If Polycarboxylic acid Black was linked to cotton by covalent bonds, the recoverability of the dye fiber may be improved. So the angle of recovery of the cotton before and after dyeing was investigated and the results are shown in Fig. 5.

Fig. 5 shows that the angle of recovery of cotton was distinctly increased after dyeing, and the higher the dye fixation was, larger was the angle of recovery of the dyed fiber. It was also found that if bake procedure was not included in the dyeing process, the angle of recovery obtained was almost the same as that of the undyed fiber. This presumably resulted from the reason that no covalent bonds formed between the dye and the fiber, so the recoverability was not improved.

3.2.6. Evaluation of effect of dyeing and finishing

Comparison of dye fixation, fastness properties and angle of recovery of the cotton dyed with Polycarboxylic acid Black

Table 5
Fastness properties and angle of recovery of the cotton dyed with different dyes

			Undyed	Polycarboxylic acid Black	Reactive Black KN-B	Sulphur Black
Fixation (%)			–	98.8	–	–
Light fastness			–	6	5	5
Wash fastness	Change		–	4	3–4	4
	Staining	Cotton	–	4–5	4–5	4–5
		Wool	–	4–5	4–5	4–5
Rub fastness	W	Dry	–	4	4–5	4
		Wet	–	2–3	3	2
	F	Dry	–	4	4–5	4
		Wet	–	2–3	3	2
Water fastness	Change		–	4–5	4–5	4–5
	Staining	Cotton	–	4–5	4–5	4–5
		Wool	–	4–5	4–5	4–5
Angle of recovery	W		165	179	164	168
	F		131	155	132	133

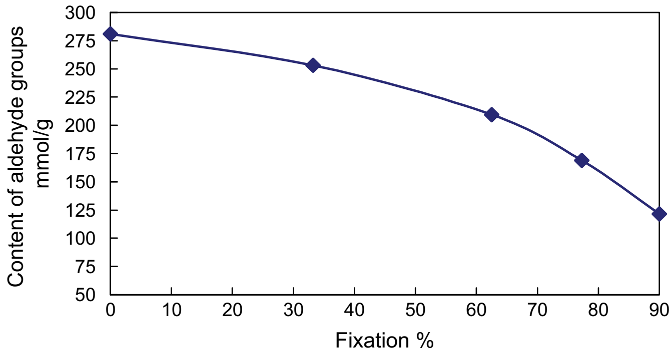

Fig. 4. Content of aldehyde groups by oxidation of the dyed fiber with dye fixation.

with those of Reactive Black KN-B and Sulphur Black was investigated. The results are shown in Table 5.

The figures presented show that the fixation of Polycarboxylic acid Black on cotton could reach 98.8%. This was attributed to more reactive carboxylic groups existing in the dye compared with the reactive groups in Reactive Black KN-B. The light fastness and wash fastness were excellent in comparison with that of Reactive Black KN-B, and the rub fastness was better than that of Sulphur Black. The recoverability of the fiber dyed with Polycarboxylic acid Black also showed priority, which demonstrated that dyeing and finishing effect could be realized in the same dyeing procedure for Polycarboxylic acid Black.

3.2.7. Utilization of the Polycarboxylic acid Black by cycle dyeing

Although Polycarboxylic acid Black showed high fixation, dye utilization should be further improved. This was due to the fact that both the carboxylic groups of Polycarboxylic acid Black and hydroxyl groups of the fiber were negatively charged in the dyebath, so charge repulsion existed between them and resulted in low dye–fiber affinity. As carboxylic groups of the dye were much stable in aqueous solution, cycle dyeing was applied in dyeing of Polycarboxylic acid Black to enhance its utilization. Fig. 6 shows that after seven times dyeing, the dye of certain amount could be completely utilized.

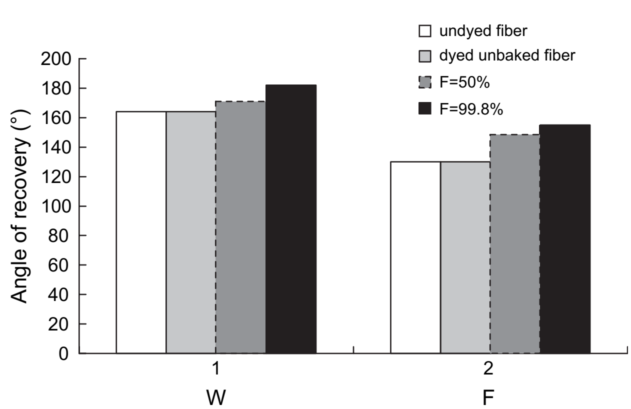

Fig. 5. Angle of recovery of the cotton before and after dyeing.

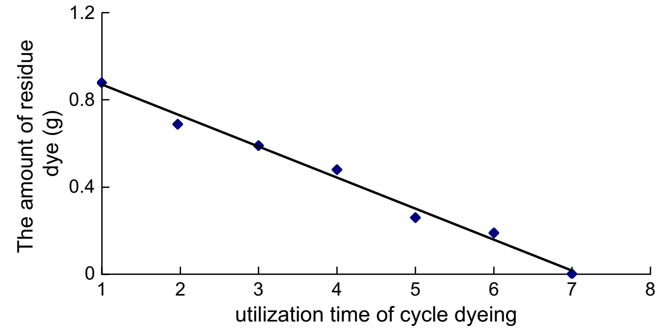

Fig. 6. Amount of residue dye with the utilization time of cycle dyeing.

Cycle dyeing by addition of certain amount of dye each time to keep concentration constant in the dyebath was attempted to enhance the utilization of Polycarboxylic acid Black. The results are shown in Table 6.

A certain amount of dye was added to keep the concentration of the dye constant and dye fixation, color strength and fastness properties of the dyed cotton were almost kept the same even after nine times cycle dyeing procedure. Cycle dyeing increased the dye utilization, lowered the cost, reduced the effluent released and was proved to be an effective method in dyeing of Polycarboxylic acid Black.

4. Conclusions

Polycarboxylic acid Black was used for dyeing of cotton, and realized high fixation of over 98.0%. Thermal gravimetry and FT-IR spectroscopy were employed to testify the dyeing mechanism of dehydrating esterification of this dye on cotton. Methods of color stripping, fiber dissolving in cuprammonia and fiber oxidation were applied to indirectly prove the ester linkage between the fiber and the dye. The light fastness of the fiber dyed with Polycarboxylic acid Black was higher than that of Reactive Black KN-B and Sulphur Black, the wash fastness was comparable with that of the dyes above mentioned, and the rub fastness was better than that of Sulphur Black. Testing on recoverability of the cotton dye with the Polycarboxylic acid Black showed that this dye also acted as anti-wrinkle finishing agent at the same time of dyeing. Due to the stability of this dye, cycle dyeing was realized and satisfactory dyeability and

Table 6
Effect of cycle dyeing of Polycarboxylic acid Black

Cycle time	Dye applied each time (g)	Dye added (g)	Rub fastness		Fixation (%)	*K/S*
			Dry	Wet		
1	2.56	0	4	2–3	98.8	19.2
2	2.81	0.78	4	2–3	98.6	19.1
3	2.42	0.48	4	2–3	97.9	18.2
4	2.61	0.64	4	2–3	99.1	19.1
5	2.44	0.50	4	2–3	98.9	19.8
6	2.57	0.65	4	2–3	99.0	19.6
7	2.40	0.57	4	2–3	98.5	18.9
8	2.15	0.48	4	2–3	98.8	19.0
9	2.56	0.78	4	2–3	98.6	18.9

fastness properties were obtained in the cycle dyeing to improve the utilization of Polycarboxylic acid Black.

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