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Study on Dyeing Performance of Cationic Water-soluble Sulphur Black on Silk

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Abstract: A novel polyquaternaryammonium cationic sulphur black dye was synthesized and its dyeing behavior on silk was studied. The dye exhibited excellent dyeing fixation of up to 98.2 %, as well as excellent dyeing fastness on silk.

Keywords: Cationic sulphur black, dyeing performance, silk, water-soluble, sulphur dye.

Sulphur dyes are a class of dyes having the best light fastness and low price among the dyes applied to natural fibres. They are well-recognized in the world owing to their non-carcinogenicity，non-irritability and no heavy metal[1]. However, alkali metal thiolate is usually necessary as a reducing agent in the dyeing process of sulphur dyes, which can bring about serious environment pollution[2]. And, the fiber dyed by this water-insoluble dye presents poor wet rub fastness. Moreover, this conventional sulphur dyes generally only be used in the dyeing of cotton. Therefore, many chemists of coloration field have devoted great concerns to improve the performance of the sulphur dye[3~5]. The effort of employing the prepared modified water-soluble sulphur without using sodium thiolate on protein fibres as well as obtaining good light and rub fastness is an application expansion and technology innovation of traditional sulphur dyes with remarkable practical significance.

Herein, cationic reagent 3-chloro-2-hydroxypropyltrimethyl ammonium chloride (CHPTMA) with low cost, good solubility, high reactivity and wide applied range of pH, was employed in the modification of traditional sulphur dyes. Study on the solubility and dyeing properties, such as colour strength (K/S) and dyeing fastness, of the synthesized novel cationic sulphur dyes on silk has been carried out.

Although the structure of C.I. Sulphur Black 1 has been investigated by a number of workers, it has not yet been established till now [6]. Generally, it is believed to be a mixture of compounds bearing similar properties but having very complicated structures or different sulfur contents. The plausible reaction process of nucleophilic substituent reaction between C.I. Leuco sulphur black 1 and CHPTMA is shown in **Scheme 1**[7].

A cationic water-soluble sulphur black containing polyquarternaryammonium groups was prepared by reducing C.I. Sulphur Black **1** to its leuco form with glucose

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followed by reaction with CHPTMA. The starting pH was adjusted to 10-11 with 40%(w/w) sodium hydroxide. It was found that pH value decreased gradually in the reaction process and finally kept almost constant. To a stirred mixture of sulphur black **1** (18 g) and water (10 g) was added dropwise an aqueous solution of glucose (18 g). When the temperature reached 60 °C, CHPTMA solution (65% w/w, 48.5 g) was added dropwise over 30 min, and the reaction mixture was kept stirring and heating at 60 °C for 1-2 h. Afterwards, the reaction product was collected *via* filtration and dried at 70-80 °C until the weight was constant. The λ max of the dye was 628 nm and presented blue light black. This trend is probably resulted from the rupture of disulfur bonds in traditional sulfur dye *via* reduction process as well as the formation of sulphydryl anions. The result of element analysis showed that the nitrogen and sulfur contents of the cationic sulphur dye were 9.5 % and 24.5%, respectively.

The contrast of FT-IR spectrum of cotton dyed with conventional sulphur dye and of silk dyed with cationic sulphur dye is shown in **Figure 1**.

Scheme 1 The suggested reaction equation of the cationic sulphur black

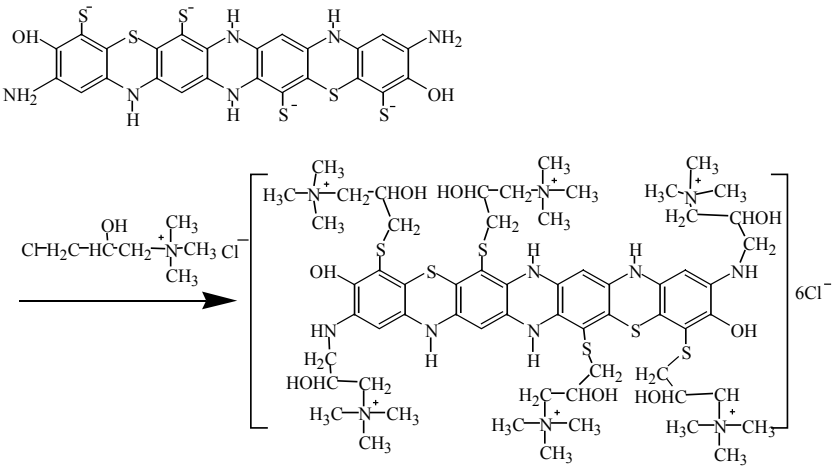

Figure 1 FT-IR spectrum of cotton dyed with conventional sulphur dye **1** and of silk dyed with cationic sulphur dye **2**

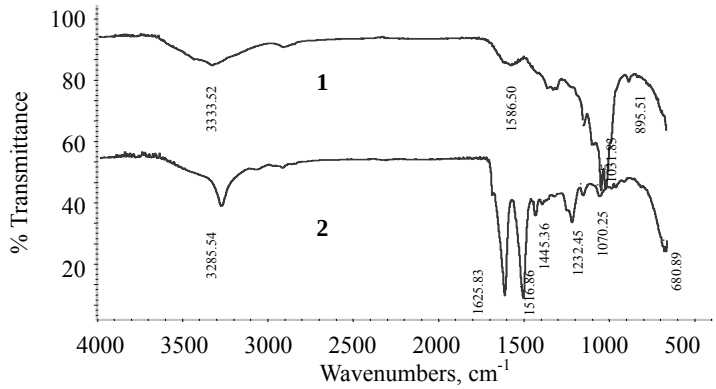

Table 1 Dyeing performance of cationic sulphur dye at various time [a]

No.	Dye	Dyeing time (min)	Fixation (%)	K/S	Fastness (grade)		
					Light	wet rub	dry r
1	Cationic sulphur dye	20	79.3	15.64	—	—	—
2	Cationic sulphur dye	40	84.2	15.75	—	—	—
3	Cationic sulphur dye	60	90.6	16.35	—	—	—
4	Cationic sulphur dye	80	96.5	16.57	—	—	—
5	Cationic sulphur dye	100	98.2	17.48	6	3-4	4-5
6	Cationic sulphur dye	140	97.6	17.26	6	3-4	4-5
7	C.I. Sulphur Black 1	100	69.6	3.48	6	2-3	4
8[b]	C.I. Sulphur Black 1	100	73.8	5.96	6	2-3	4

[a] Conditions: Silk, 0.5 g; dye concentration, 10 % (o.w.f); liquor ratio, 1:40 (v/v); dyeing temperature, 98 °C, dyeing method, exhaust. The dyed fibers were rinsed, soaped and rinsed. And the fixation was calculated by the absorbency of the collection of the residuary solution of rinsed, soaped and rinsed. [b] Sodium thiolate was employed before dyeing. The method for the fixation calculation of sulphur dye was the same as above method.

The dyeing performance of the resulted cationic dye was studied in detail and the results were shown in **Table 1**.

The synthesized cationic sulphur dye exhibited excellent dyeing fixation at 98 °C, and the fixation was 30 percent higher than that of C.I. Sulphur Black 1 dye. The K/S values of the cationic sulphur dye were about 2-4 times higher than that of conventional sulphur dye at the same dyeing condition on silk. The dyeing time has great effect on fixation. The fixation increased with the increase of dyeing time. But beyond 100 minutes, the fixation slightly decreased. The cationic sulphur dye also showed good fastness on silk. Light fastness, wet rub fastness and dry rub fastness of the dyed silk are 6, 3-4 and 4-5 grade, respectively. The results indicate that the novel synthesized dye in this work is not only more suitable for dyeing silk but also has more satisfactory fastness properties compared with conventional sulphur dye.

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