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The Use of Thiourea Dioxide as Reducing Agent in the Application of Sulphur Dyes

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ABSTRACT

Thiourea dioxide was applied as reducing agent during the dyeing of cellulosic fibres with eight commercial sulphur dyes. The same dyes were also applied from dyebaths containing sodium sulphide. It was found that the intensity and fastness properties of the dyeings by both methods were similar, although in some cases slight differences in shade were observed. Analysis of the exhausted dyebaths indicates that thiourea dioxide may be considered as a more environmental friendly substitute for sodium sulphide during the application of sulphur dyes.

1 INTRODUCTION

Traditionally, the main use of sulphur dyes is in the dyeing of cellulosic fibres and blends of these fibres with various synthetic fibres. Sulphur dyes are characterized by their moderate cost, and, taking into consideration their fastness properties, they fall into a position midway between vat and reactive or direct dyes. It could be considered that sulphur dyes are

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of prime importance for dyeings of black, navy, green and brown colours, especially when heavy depth, good fastness properties and economy are needed.[1]

The conventional method of application of these dyes is from a dyebath containing sodium sulphide as reducing agent. This chemical can cause ecological and toxicological problems and alternative reducing agents would be advantageous. In a review of sulphur dyes by Guest and Wood,[2] reducing agents such as sodium sulphydrate, sodium polysulphide, sodium dithionite (hydrosulphite), glucose and thiourea dioxide are mentioned. In the more recent literature, derivatives of bivalent ferrous compounds[3,4] and *o*-hydroxy carbonyl compounds[5] have also been reported.

Our interest was directed towards thiourea dioxide, since for some time this has been recommended for wool bleaching, dyeing with vat dyes, dye stripping and reduction clearing of dyed polyester and polyester–cellulose blends.[6,7] Little information concerning the application of this reducing agent in the dyeing with sulphur dyes is readily available, except for some Japanese patents.[8]

The purpose of this present work was to examine the possibility of the application of thiourea dioxide during dyeing with sulphur dyes both from a practical and ecological point of view.

2 EXPERIMENTAL

Eight commercial samples of sulphur dyes—C.I. Sulphur Yellow 1, C.I. Sulphur Orange 1, C.I. Sulphur Brown 10, C.I. Sulphur Brown 12, C.I. Sulphur Brown 14:1, C.I. Sulphur Blue 11, C.I. Sulphur Black 1 and C.I. Solubilized Sulphur Black 1 (Boruta Dyestuff Industry Works, Poland) were used. Dyeings on cotton fabric were carried out on a Linitest laboratory dyeing machine at a fabric-to-liquor ratio of 1:30. Alkaline dyebaths contained dye, wetting agent and sodium sulphide or thiourea dioxide as reducing agents. Oxidation of the dyed fabric was carried out in a bath containing hydrogen peroxide and acetic acid. Fastness properties of all the dyes were determined according to Polish Standards, which correspond with British Standards.[9]

3 RESULTS AND DISCUSSION

From visual examination of the samples dyed during initial trials, it was found that, as in the case of sodium sulphide, the necessary amount of thiourea dioxide depends on the structure of the dye used. Therefore, the required amount of the reducing agent had to be estimated experimentally in a series of dyeings. Taking into consideration that the reducing properties of thiourea dioxide are higher in alkaline solution, an addition of sodium hydroxide to the dyebath was also necessary. It was also observed that addition of sodium sulphate (Glauber's salt) did not significantly improve the depth and shade of the dyeings, and therefore it was not used in the dyebath. A more detailed description of the dyebath composition has been given elsewhere.[10]

The resulting dyeings were comparable in depth to those from the sodium sulphide method, but were slightly different in shade. In the majority of cases, the dyeings obtained using the thiourea method were brighter, except for C.I. Sulphur Brown 12 and C.I. Sulphur Brown 14:1. The colour value of the first dye was markedly diminished, probably due to its over-reduction, as has been previously reported in the case of dyeing with this dye in the presence of sodium dithionite.[2] In contrast, C.I. Sulphur Brown 14:1 gave dyeings much stronger in depth and bluer in shade when compared with dyeings using sodium sulphide. During the dyeing on brown shades, thiourea dioxide must, therefore, be used with care, in order to obtain comparable results.

Fastness properties of all dyeings were similar using both methods. Table 1 shows the results obtained in the case of three dyes, viz. C.I. Sulphur Brown 10, C.I. Sulphur Blue 11 and C.I. Sulphur Black 1.

It is apparent that some fastness values of the dyeings obtained using thiourea dioxide are slightly better than those using sodium sulphide.

TABLE 1

Fastness Properties of Cotton Fabric Dyed with Some Sulphur Dyes with the Use of Sodium Sulphide and Thiourea Dioxide (TDO)

Fastness	*C.I. Sulphur Brown 10 (5%)*		*C.I. Sulphur Blue 11 (10%)*		*C.I. Sulphur Black 1 (10%)*	
	Na_2S	*TDO*	*Na_2S*	*TDO*	*Na_2S*	*TDO*
Light (Xenotest)	3	3–4	6	6	5–6	6
Water	5, 5, 5	5, 5, 5	5, 5, 5	5, 5, 5	4–5, 5, 5	5, 5, 5
Washing (60°C)	4–5, 4, 5	4–5, 3–4, 5	4, 1, 5	4–5, 2, 5	3–4, 3, 5	4, 3, 5
Perspiration (acid)	5, 5, 5	5, 5, 5	5, 4, 5	5, 4–5, 5	4–5, 5, 5	5, 5, 5
Perspiration (alkaline)	5, 4–5, 5	5, 5, 5	5, 2–3, 4–5	5, 4, 5	4, 4, 5	5, 4, 5
Dry rubbing	4	3	2	2	2–3	2–3
Wet rubbing	2–3	2–3	2	2	2	2

TABLE 2
Analysis of Exhausted Dyebaths after Dyeing Cotton Fabric with Some Sulphur Dyes with the Use of Sodium Sulphide and Thiourea Dioxide (TDO)

	C.I. Sulphur Yellow 1 (3%)		*C.I. Sulphur Blue 11 (10%)*	
	Na_2S	*TDO*	*Na_2S*	*TDO*
Colour	Yellow	Yellow	Blue	Blue
pH	10·2	11·4	11·2	9·1
Density at 20°C (g/cm^3)	1·050	1·040	1·100	1·060
Permanganate oxidation value (mg O_2/dm^3)	937	433	1 375	850
Dichromate oxidation value (mg O_2/dm^3)	1 853	965	2 769	1 692
Residue after drying at 100°C (mg/dm^3)	7 720	6 416	13 500	8 255
Residue after backing at 600°C (mg/dm^3)	6 612	4 924	12 495	7 130
Weight loss after backing at 600°C (mg/dm^3)	1 108	1 492	1 005	1 125
Chlorides (mg Cl^-/dm^3)	Traces	Traces	Traces	Traces
Sulphates (mg SO_4^{2-}/dm^3)	3 439	933	5 813	1 382
Sulphides (mg S^{2-}/dm^3)	128	Not found	72	Not found
Alkalinity ($mval/dm^3$)	43	80	70	77

However, more definitive conclusions would require more detailed investigations.

Thiourea dioxide can be regarded as less toxic and less hazardous than other reducing agents. It was, therefore, interesting to estimate the properties of exhausted dyebaths both after dyeing with sodium sulphide and thiourea dioxide. The analyses were carried out according to corresponding Polish Standards. Table 2 shows data obtained for C.I. Sulphur Yellow 1 and C.I. Sulphur Blue 11.

It is seen that the residual liquors after dyeing with the use of thiourea dioxide are much less hazardous to the environment. The major improvement is in the decrease of the oxidant amount required for chemical degradation of the effluent. For example, in the case of C.I. Sulphur Yellow 1, chemical oxygen demands, expressed as permanganate and dichromate oxidation values, are decreased by half. Similar observations were made in the case of the second dye. A further advantage is the large decrease in the sulphate ion content, due to elimination of sodium sulphate from the dyebath.

The results indicate that thiourea dioxide may be considered as a useful, although probably more expensive, substitute for sodium sulphide during the application of sulphur dyes. The cost of the alternative reducing agent has to be balanced against the cost of treating waste liquors containing sodium sulphide.

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