Dyes and Pigments, Vol. 37, No. 3, pp. 197–204, 1998

Printed in Great Britain
PII: S0143-7208(97)00055-7 0143-7208/98 $19.00+0.00

Iron Complexed Afterchrome Dyes

Wojciech Czajkowski & Małgorzata Szymczyk

Institute of Dyes, Technical University of Łódź, Zwirki 36, 90-924 Łódź, Poland

(Received 22 April 1997; accepted 30 May 1997)

ABSTRACT

The possibility of elimination of chromium in dye effluents during application of afterchrome dyes has been investigated. Eight commercially available azo mordant dyes were used in dyeing of wood fabric and aftertreated with iron (II) and iron (III) salts. Colour and lightfastness of received dyeings was compared with those obtained with the use of traditional chromium-aftertreated method. The structure of some complexes formed on wool fibre was characterised by negative ion fast atoms bombardment spectroscopy (FAB) and HPLC analysis. It was found that mordant dyes with ortho, ortho′*-hydroxyazo chelate system aftertreated with iron salts form metal–dye complexes of 1:2 type. © 1998 Elsevier Science Ltd*

Keywords: afterchrome dyes, dye effluents, iron–dye complexes.

INTRODUCTION

It is well known that the introduction of metal ion into a dye molecule improves the fastness properties of the dye, especially its fastness to light and washing fastness. These properties in most cases are accompanied by a bathochromic shift of the colour of the dye.

Chromium complexes of monoazo dyes formed on wool by the afterchrome method have been especially useful in the dyeing of wool in dark shades with high fastness properties. Ecological problems can arise with these types of dye, with resulting high chromium salt content in the exhausted dyebath. This problem can be partially solved by optimising the pH value of the dyebath and by employing new dyeing auxiliaries [1].

There has now developed a growing interest in environmentally friendly dyes. In the area of metal-complex dyes this term applies to premetallized 1:2 iron complexes. Iron analogues of some 1:2 Cr and 1:2 Co commercial azo dyes, as well as formazan dyes, were applied in dyeing wool and nylon in violet, brown and black shades exhibiting high lightfastness [2, 3]. Iron complexes of disazo resorcinol-based dyes have also been described for use in the dyeing of leather in brown colours [4].

The objective of this work was to examine the possibility of the replacement of chromium salts during the dyeing of wool by monoazo mordant dyes by commercially available iron salts. It was anticipated that the iron complexes of these dyes, obtained by treating of dyed fibres by iron salts, would yield brown to black shades with good fastness properties.

EXPERIMENTAL

Commercially available samples of azo mordant dyes (Boruta SA Works, Poland) were used. All these dyes were of the monoazo type and their structures are shown in Table 1.

The dyeing of the wool fabric was carried out on a Rotec (Roaches, England) laboratory dyeing machine by the conventional two-stage afterchrome method recommended in dye manufacturer catalogue [5]; composition of dyebath: dye, *x*%; Glauber's salt 10%; acetic acid, 3%. The dyeing process was started at 40–50°C and over 30 min the bath was gradually heated to the boil and dyeing carried out for 30–45 min at this temperature. The bath was

TABLE 1
Chemical Structure of Investigated Afterchrome Dyes

CI name	*CI number*	*Diazo component*	*Coupling component*
Mordant Yellow 1	14025	3-nitroaniline	salicylic acid
Mordant Orange 37	18730	2-aminophenol-4-sulfonic acid	1-phenyl-3-methylpyrazolone-5
Mordant Red 7	18760	1-amino-2-naphthol-4-sulfonic acid	1-phenyl-3-methylpyrazolone-5
Mordant Red 9	16105	anthranilic acid	R acid
Mordant Black 17	15705	1-amino-2-naphthol-4-sulfonic acid	2-naphthol
Mordant Green 17	17225	2-amino-4-nitrophenol	H acid (alkaline)
Mordant Brown 15	14870	2-amino-6-chloro-4-nitrophenol	1-naphthol-5-sulfonic acid (0.61) 1-(4'-sulfophenyl)-3-methylpyrazolone-5 (0.39)
Mordant Black 11	14645	1-amino-6-nitro-2-naphthol-4-sulfonic acid	1-napthol

then cooled to 70°C and an appropriate amount of potassium dichromate was added, and the bath then heated to the boil and the dyeing process continued for 30–40 min. The dyed fabric was then rinsed and dried. Following manufacturer's recommendations, dye concentrations varied for different dyes, from 1.5% for light colours to 6% in the case of CI Mordant Black 11. Recommended quantities of potassium dichromate were approximately 50% of the amount of applied dye, and not less than 0.1% and not more than 2.5% on fibre weight. In the case of iron aftertreated dyes the same procedure was applied, but in the second stage of dyeing, instead of potassium dichromate, an equimolar amount of iron salts such as iron (II) sulphate heptahydrate (analytical and technical grade), iron (III) sulphate and iron (III) chloride were used. In order to more easily compare the manufacturer's data with the experimental results, we also used various other dye concentrations as shown in Tables 2 and 3.

TABLE 2
Colour Properties of Wool Fabric Dyed with Some Afterchrome Dyes without and After Treatment with Chromium or Iron Salts

Dye	*% Dyeings*	*Colour of wool fabric*		
		No treatment	*Cr-complexed*	*Fe-complexed*
CI Mordant Yellow 1	1.5	yellow	yellow	yellow–brown
CI Mordant Orange 37	1.5	yellow	orange	olive–brown
CI Mordant Red 9	3.0	orange	red	brown–red
CI Mordant Red 7	4.0	red	bordeaux	light brown
CI Mordant Black 17	2.0	violet	navy blue	violet–brown
CI Mordant Green 17	1.5	violet	green	violet–brown
CI Mordant Brown 15	3.0	brown	brown	brown
CI Mordant Black 11	6.0	black	black	black

TABLE 3
Lightfastness Properties of Wool Fabric Dyed with Some Afterchrome Dyes without and After Treatment with Chromium or Iron Salts

Dye	*% Dyeings*	*Lightfastness (Xenotest) of wool fabric*[a]		
		Without treatment	*Cr-complexed*	*Fe-complexed*
CI Mordant Yellow 1	1.5	4–5	6	5–6
CI Mordant Orange 37	1.5	3	6	6–7
CI Mordant Red 9	3.0	5–6	6–7	6
CI Mordant Red 7	4.0	3–4	4–5	4
CI Mordant Black 17	2.0	2–3	5–6	4
CI Mordant Green 17	1.5	4	6	6
CI Mordant Brown 15	3.0	2–3	6	6
CI Mordant Black 11	6.0	3–4	6–7	5–

[a] In 8-grade scale; 1, the lowest; 8, the highest lightfastness.

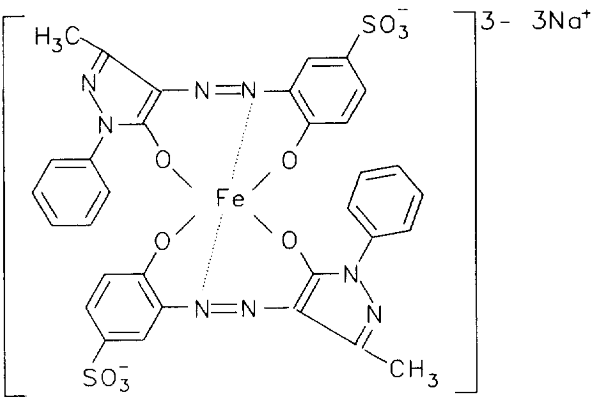

Fig. 1. CI Mordant Orange 37, 1:2 Fe complex.

Additionally, in order to compare the colour and fastness properties of the dyeings, several model dyes, i.e. iron complexes of the parent afterchrome dyes, were synthesised using the conventional methods. For example, the 1:2 iron complex of CI Mordant Orange 37 (Fig. 1) was prepared by diazotization of 2-aminophenol-4-sulfonic acid followed by coupling with 1-phenyl-3-methylpyrazolone-5, and converting the metal-free monoazo dye to 1:2 Fe complex using Fe(II) sulphate at slightly acidic pH. Thus 3.79 g (0.02 mol) 2-aminophenol-4-sulfonic acid was dissolved in 50 ml of hot (50°C) water with the addition of 2 g Na_2CO_3. The solution was poured into a mixture of 30 g crushed ice and 6 ml 30% HCl. To the resulting suspension, 5 ml 4N $NaNO_2$ was added with stirring at such a rate as to maintain a reaction temperature at 0–5°C and a slight excess of nitrous ions in the reaction mixture. The liquor was then stirred for a further 30 min and the excess nitrite was removed by the addition of a small amount of sulfamic acid. The diazonium salt was added to a solution of 3.49 g (0.02 mol) 1-phenyl-3-methyl-5-pyrazolone in 50 ml of water with addition of 2 ml 30% NaOH and 3 g Na_2CO_3 and the reaction mixture was stirred for 4 h at 0–5°C. After this time no presence of diazonium salt was detected (test with resorcinol solution on filter paper). By addition of 4 g Na_2CO_3, the pH of the reaction mixture was adjusted to 7.5–8.0. After heating to 60°C the intermediate dye was salted out with NaCl (20 vol.%) and filtered. The wet cake was dissolved in 50 ml H_2O and the solution heated to 60°C and 2.78 g $FeSO_4{\cdot}7H_2O$ was then added during 15 min (foaming). After 30 min the pH was adjusted to 7–7.5 with 1 N NaOH and the reaction mixture then stirred for 1 h at 60–70°C. After this time TLC analysis (Merck Kiesegel 60 plates and *n*-propanole:ethyl acetate:water = 6:3:1 as eluent were used) showed only a single spot of the 1:2 Fe complex ($R_f = 0.74$) and no presence of unmetallized dye ($R_f = 0.81$). The final dye was isolated by evaporating the water from reaction mixture to give 14.6 g of a dark powder.

The other model dyes were prepared in a similar way except for the iron complexes of CI Mordant Yellow 1 and CI Mordant Red 7. In these two dyes, which contain an *o*-hydroxsyazo-*o*′-carboxy chelating system, iron complex formation proceeds with difficulty and the complex formation was carried out in formamide at 120–125°C for 5 h. The structures of the 1:2 complex type dyes were confirmed for some representative dyes using negative ion FAB mass spectrometry. FAB spectra were recorded on a Finningam Mat MAT94 (Switzerland) spectrometer in a 3-nitrobenzylalcohol matrix. The same method was used for the analysis of the products extracted from the dyed fiber. HPLC reverse phase analysis was carried out on a Milton Roy 3100 Chromatograph (Column 0.46×25 cm, Vydac C_{18}, 5 μ particle size, solvent $A =$ water and 0.05% CF_3COOH, $B = 90\%$ acetonitrile, 10% water and 0.038% CF_3COOH, detection at 310 or 360 nm). The 1:2 type dyes were used for colouring wool fabric by a dyeing process typical for acid dyes. Lightfastness data were determined with the use of Heraeus Xenotest 150s according to the method recommended by Polish Standards which correspond with British Standards [6].

RESULTS AND DISCUSSION

It was found that iron (III) chloride was a less useful complexing agent than iron sulphates. The resulting dyeings were weaker in depth and duller in shade, probably due to the oxidising properties of this compound in the acidic dyebath. Both iron (II) sulphate and iron (III) sulphate gave good and comparable results. From a practical point of view, iron (II) sulphate heptahydrate is more convenient due to its better solubility in water and its more facile oxidation to iron (III) salts during the dyeing process.

Table 2 shows the colour properties of wool fabrics dyed with the afterchrome dyes studied without aftertreatment, and by aftertreating them with sodium dichromate or iron (II) sulphate heptahydrate.

The treatment of the acid chrome dyes on wool with iron salts gave, as expected, various brown hues, and black colour in the case of Mordant Black 11 (6% dyeings). Similar results were obtained during the dyeing of wool with 1:2 iron complexes of the parent mordant dyes. The latter dyeings were, however, much weaker in depth, probably owing to their different affinity for the fibre.

It can be presumed that, as in the case of chrome dyed wool [7], the iron complexes formed on wool also have a 1:2 type structure. This assumption was confirmed for some of the investigated dyes containing a *o*,*o*'-dihydroxyazo chelating system, by HPLC and FAB analysis of products extracted from the dyed fibre with pyridine/water azeotrope. Figures 2 and 3 and Table 4 show the results of the FAB analysis of CI Mordant Orange 37.

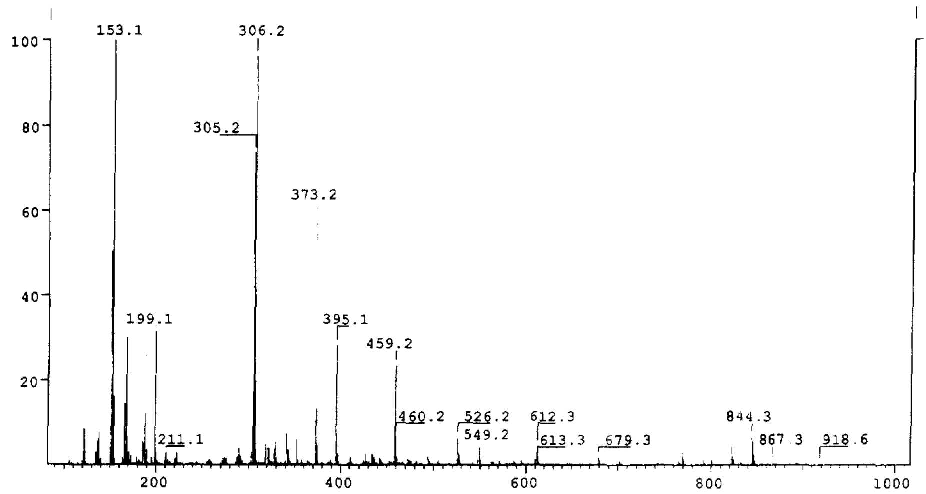

Fig. 2. Negative ion FAB mass spectroscopy of 1:2 Fe complex of CI Mordant Orange 37 (nitrobenzyl alcohol as the matrix).

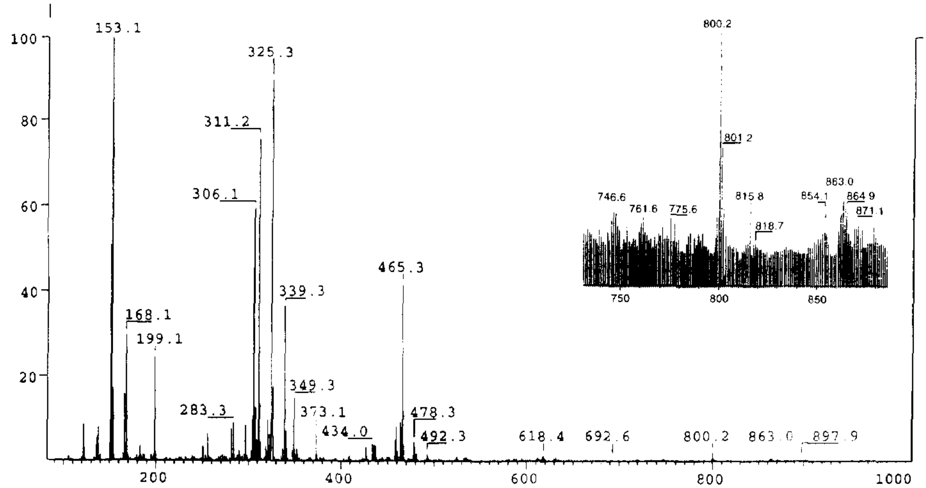

Fig. 3. Negative ion FAB mass spectroscopy of products extracted from wool dyed with CI Mordant Orange 37 and aftertreated with iron (II) sulfate (nitrobenzyl alcohol as the matrix).

These results confirm the structure of the model dye, although the intensity of the peaks concerned with the 1:2 Fe complex are rather low. The same phenomenon has been previously reported in the case of Fe-complex dyes containing sulfonic acid groups [2] and in the case of azo dyes containing a large number of sulfonate and phosphonate groups [8]. This effect is especially apparent in samples extracted from wool, probably owing to the additional presence of pyridine which, as a strong base, could both partially

TABLE 4
Relative Abundance[a] of Molecular Ion Species in the FAB Mass Spectra of CI Mordant Orange 37

Dye	*Assignment*[b]	m/z	*Relative abundance*
1:2 Fe complex	D^-	867	0.67
	$[D - Na]^-$	844	6.79
	$[D\text{-}Na+H]^-$	845	5.80
	$[D\text{-}2Na+H]^-$	822	4.52
	$[D\text{-}3Na+2H]^-$	800	1.38
	B^-	396	7.30
	$[B\text{-}Na]^-$	373	60.92
	$[B\text{-}Na+H]^-$	374	13.44
Extract from dyed wool	$[D\text{-}3Na+2H]^-$	800	1.73
	$[D\text{-}3Na+3H]^-$	801	0.93
	$[B\text{-}Na]^-$	373	6.84

[a] Ion abundances are expressed relative to the base peak $m/z = 153$ (3-nitrobenzyl alcohol).
[b] B, unmetallized dye; D, 1:2 metal complex.

decompose the complex and form different salts with the dye and products of its decomposition. Nevertheless the presence of pseudomolecular ions [D-3Na+2H] m/z 800.2 and [D-3Na+3H] m/z 801.2 in the extracted dye confirms the existence of the 1:2 Fe complexed dye.

The HPLC results give further support to this assumption. The uncomplexed dyes give a single peak with a retention time of 20.0 min. The 1:2 Fe complex contains two peaks of comparable intensity, viz., the first with retention time of 7.49 min relatable to the with 1:2 Fe complex, and the second with retention time 20.25 min which relates to the uncomplexed dye appearing on the column, probably as the result of decomposition of the complex in the presence of trifuoroacetic acid.

The pyridine extract from the dyed fibre showed also only two strong peaks with almost the same retention times as above, viz., 7.63 and 19.95 min, related to the presence of the 1:2 complex dye and uncomplexed dye.

Similar results were obtained in the case of Mordant Green 17. The structure of the 1:2 complex was confirmed by FAB spectroscopy, viz., the presence of a molecular ion D^- m/z 1131, as well as of pseudomolecular ions $[D\ \text{-Na}]^-$ and $[D\text{-}Na+H]^-$ m/z 1108 and 1109, respectively. FAB analysis of the product extracted from dyed wool did not give a clear answer of its structure, but again HPLC analysis was more helpful. The uncomplexed dye gave a single peak with retention time 15.94 min. The 1:2 Fe complex again contained two peaks, the first one a strong intensity peak with retention time 3.37 min connected with 1:2 Fe complex, and the second a weak intensity peak with retention time 16.02 min; which is the uncomplexed dye, the result of decomposition of the complex on the column. The pyridine extract from the dyed fibre also showed only two peaks with almost the same retention times as above, i.e. 3.34 and 16.10 min, connected with the presence of 1:2 complexed dye and uncomplexed dye.

The above assumption has not yet been confirmed in the case of CI Mordant Yellow 1 and CI Mordant Red 9, dyes with an *o*-hydroxy-*o′*-carboxy chelating system. It can be seen from the Tables 2 and 3 that the complex formation during aftertreatment with iron salts give both a change of colour and improvement of lightfastness. However, FAB analysis of model dyes and extracts from dyed fibres did not give evidence for the existence of a 1:2 type complex. This problem requires further investigation.

As mentioned before, one of the important application properties of metal-complexed dyes is their fastness to light. Table 3 shows the lightfastness of wool fabric dyed with the investigated afterchrome dyes. From the data shown, it can be seen that the introduction of an iron atom into the dye molecule in all cases increases the lightfastness of the dyed fabric. As has already been reported in the case of other 1:2 Fe metallized dyes [2], the lightfastness of iron complexes is usually somewhere lower than that of Cr analogs, but generally much better than their metal-free analogs. As replacements for more conventional metal-complex dyes [9], iron salts may be considered as an environmentally friendly substitute for chromium salts in the application of afterchrome dyes, although this requires much more detailed investigations of a more practical nature.

REFERENCES

1. Zollinger, H., *Color Chemistry*, Verlag Chemie, 1987, p. 126.
2. Sokolowska-Gajda, J., Freeman, H. S. and Reife, A., *Textile Res. J.*, 1994, **64**, 388.
3. Sokolowska-Gajda, J., Freeman, H. S. and Reife, A., *Dyes and Pigments*, 1996, **30**, 1–20.
4. Sandoz, Ger. pat 4133166 and 4133167, 1991.
5. *Acid Chrome Dyes*, ed. Boruta Dyestuff Industry Works, Poland.
6. *Standard Methods for the Determination of the Colour Fastness of Textiles and Leather*. Society of Dyers and Colourists, Bradford, 1978.
7. Bird, C. L., *The Theory and Practice of Wool Dyeing*. Society of Dyers and Colourists, Bradford, 1972, p. 95.
8. Monaghan, J. J., Barber, M., Bordoli, R. S., Sedgwick, R. D. and Tyler, A. N., *Organic Mass Spectrometry*, 1983, **18**, 75.
9. Sewekow, U., *Textile Chemist and Colorist*, 1996, **28**, 21–27.