Dyes and Pigments, Vol. 30, No. 1, pp. 1–20, 1996
Elsevier Science Ltd
Printed in Great Britain
0143-7208/96 $15.00 + 0.00

0143-7208(95)00048-8

Synthetic Dyes Based on Environmental Considerations. Part 2: Iron Complexed Formazan Dyes*

Jolanta Sokolowska-Gajda,† Harold S. Freeman‡ & Abraham Reife

Department of Textile Engineering, Chemistry, and Science,
North Carolina State University, Raleigh, NC 27695-8301, USA

(Received 2 May 1995; accepted 9 June 1995)

ABSTRACT

This paper is concerned with the synthesis and evaluation of some 1:2 iron complexed formazan dyes for use on wool and nylon. The chemical structures of these new dyes were confirmed with the aid of negative ion FAB mass spectrometry, a technique which also proved instrumental in establishing the nature of the products obtained when unsymmetrical 1:2 iron complexed formazan dyes were synthetic targets. It is clear from the fastness properties obtained that certain of the title compounds could have utility in applications requiring high lightfastness.

INTRODUCTION

It is evident from the open literature that manufacturing and application processes involving the treatment of metallizable dyes with Co(II), Cr(III) and Cu(II) ions (each of which is considered to be a priority pollutant by the US Environmental Protection Agency) have become areas of considerable concern in the associated industries. Interestingly, little has been published about the suitability of iron complexes as environmentally friendly alternatives to currently used Cr(III) and Co(II) metal complexed acid dyes for wool and nylon. Although iron complexes of azo dyes (1:1 and 1:2 type) have been claimed in the patent literature, they are not

---

* Part 1 published in *Textile Research Journal*.

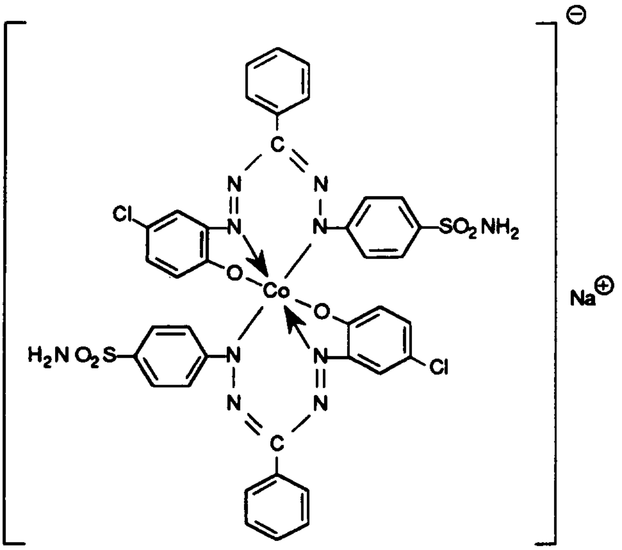
† Permanent address: Institute of Dyes, Technical University (Politechnika), Lodz, Poland.

‡ Corresponding author.

often used in the coloration of textile fibers. Perhaps their lack of use as textile dyes can be traced to the general belief that iron complexed azo dyes are inferior in fastness to Cr and Co complexed azo dyes and usually produce olive-brown, brown, and black-brown shades on the fabric. As a part of continuing research[1,2] aimed at developing an approach to synthetic dyes based on toxicological considerations, a group of iron complexed formazan dyes was synthesized as potential alternatives to certain Co and Cr metallized acid dyes used at present.

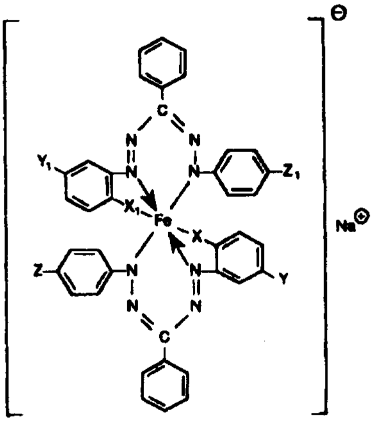
Historically, formazans have been used in a number of different areas. For instance, because they produce very fast and intense color reactions with many metal ions they are often used as analytical reagents. Since water-soluble, colorless tetrazolium salts can be reduced to water-insoluble, deeply colored formazans, they have found practical application as bio-indicators in biochemistry and cytochemistry. Also, the conversion of tetrazolium salts into metallized formazan dyes is used in color photography. Water-soluble formazan complexes containing sulfonamide, alkylsulfonyl or sulfonic acid groups possess a high affinity for protein and polyamide fibers, and can be used for dyeing or textile materials. An example is CI Acid Black 180 (1).

The patent literature provides a few examples of 1:2 metallized formazan dyes.[3–6] All of them are 1:2 Co complexed formazan compounds and are used for dyeing protein and polyamide fibers from neutral or weakly acidic baths. Some of them[7] are used separately or in combination with



1

other dyes and are recommended for dyeing leather.[8] The most important formazan dyes are the 1:1 Cu complexed formazan reactive dyes used for dyeing and printing cellulose fibers. The largest group of these dyes is derived from cyanuric chloride[9–15] or cyanuric fluoride.[16,17] Some of the formazan reactive dyes also contain 5-chloro-2,4,6-trifluorpyrimidine[27–21] as the reactive system. A large number of the formazan reactive dyes



Dye	X	X₁	Y	Y₁	Z	Z₁
2b	O	O	SO_2NH_2	SO_2NH_2	H	H
3b	O	O	Cl	Cl	SO_2NH_2	SO_2NH_2
4b	O	O	NO_2	NO_2	SO_2NH_2	SO_2NH_2
5b	O	O	H	H	SO_2NH_2	SO_2NH_2
6b	COO	COO	H	H	SO_2NH_2	SO_2NH_2
7b	O	O	Cl	Cl	SO_3Na	SO_3Na
8b	O	O	NO_2	NO_2	SO_3Na	SO_3Na
9b	COO	COO	H	H	SO_3Na	SO_3Na
10	O	O	SO_2NH_2	H	H	SO_2NH_2
11	O	O	SO_2NH_2	Cl	H	SO_2NH_2
12	O	O	H	Cl	SO_2NH_2	SO_2NH_2
13	O	O	NO_2	Cl	SO_2NH_2	SO_2NH_2
14	O	O	NO_2	Cl	SO_3Na	SO_3Na

Fig. 1. Dyes prepared and evaluated in this investigation. Dyes **10–14** are statistical mixtures of unsymmetrical and symmetrical molecules, though not specified here.

contain a vinylsulfonyl group,[22-26] sometimes also in combination with cyanuric chloride which affords bifunctional reactive dyes.[27,28] The patent literature also contains examples of 1:1 Cu or Ni complexed formazan disperse dyes for dyeing polyamide fibers,[29-32] and water-soluble metal complexed formazan cationic dyes for dyeing polyacrylonitrile fibers.[33] Iron is also claimed as one of the metals used for metallization.[33]

The focus of the present paper is the synthesis of dyes **2–14**, and the determination of their fastness properties. The dye structures are shown in Fig. 1.

RESULTS AND DISCUSSION

The target iron complexed formazan dyes were prepared in the manner outlined in Figs 2 and 3. The unmetallized dyes were prepared by conventional diazotization of either 2-aminophenol derivatives or anthranilic acid followed by coupling with either benzaldehyde phenylhydrazone, benzaldehyde phenylhydrazone-4-sulfonamide, or benzaldehyde phenylhydrazone-4-sulfonic acid in aqueous pyridine. Benzaldehyde phenylhydrazone-4-sulfonamide and its 4-sulfonic acid analog were synthesized via the condensation of benzaldehyde with phenylhydrazine-4-sulfonamide or

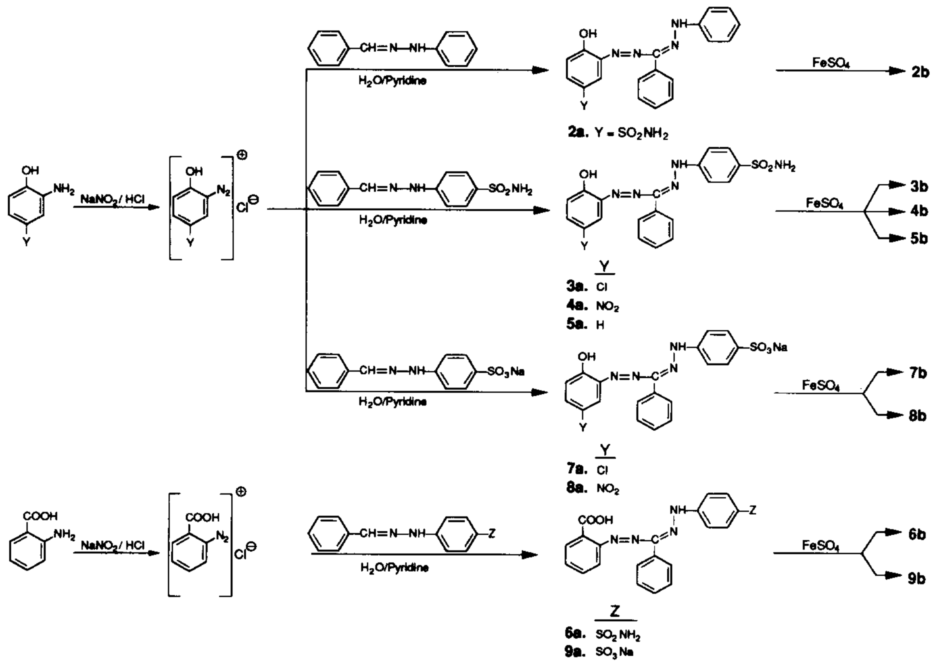
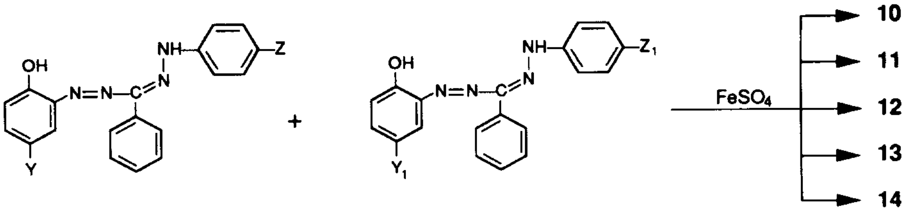


Fig. 2. Synthesis of symmetric dyes **2–9**.



	Y	Z		Y_1	Z_1
2a	SO_2NH_2	H	**5a**	H	SO_2NH_2
2a	SO_2NH_2	H	**3a**	Cl	SO_2NH_2
5a	H	SO_2NH_2	**3a**	Cl	SO_2NH_2
4a	NO_2	SO_2NH_2	**3a**	Cl	SO_2NH_2
8a	NO_2	SO_3Na	**7a**	Cl	SO_3Na

Fig. 3. Synthesis of asymmetric dyes **10–14**.

phenylhydrazine-4-sulfonic acid. The latter two compounds were obtained by reduction of the corresponding diazonium salts with Na_2SO_3.[34] The target symmetric dyes (Fig. 2) were synthesized in high yield and purity by the conversion of unmetallized formazan dyes to their 1:2 Fe complexes using $FeSO_4 \cdot H_2O$ at pH = 7 and 60–70°C. Using two molecules of different formazan dyes (Fig. 3) and the same metallization conditions, the

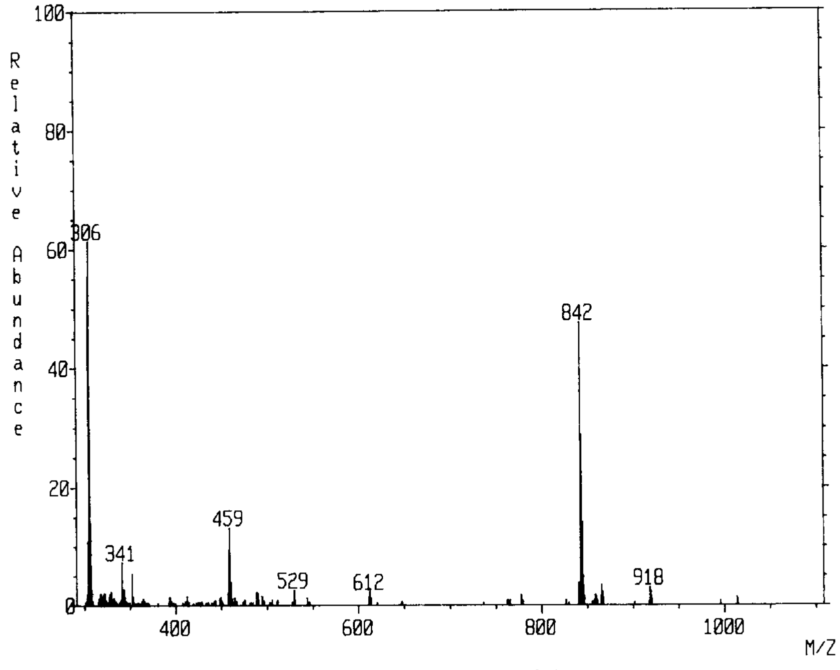


Fig. 4. FAB mass spectrum of dye **2b**.

synthesis of unsymmetrical dyes was attempted. However, the products obtained were statistical mixtures of the target unsymmetrical and corresponding symmetrical dyes.

The chemical structure of each unmetallized and metallized dye prepared in this investigation was verified using negative ion FAB mass spectrometry. Although FAB spectrometry is known to be an effective ionization procedure for a number of non-volatile hydrophilic dyes,[35–37] papers published so far do not demonstrate the suitability of this technique for generating molecular weight information on formazan dyes and their 1:2 medially complexed analogs. In most cases, 3-nitrobenzyl alcohol was used as the matrix.[38–39] In the case of unmetallized dyes containing sulfonic groups, diethanolamine was found to be more useful than 3-nitrobenzyl alcohol. In the spectra of the dyes investigated, we detected the molecular ion M^{-} and/or the pseudomolecular ion $[M—Na]^{-}$ formed by the loss of a sodium cation from either a sulfonate moiety or a counterion of 1:2 Fe complexed dyes. In the case of unmetallized dyes, the $[M—H]^{-}$ ion was usually observed. The relative abundances of the molecular ions are summarized in Table 1, while examples of the spectra recorded are given in Figs 4–7. It is worthwhile to note that in the FAB spectra of formazan dyes containing sulfonic groups the spectra were characterized not only

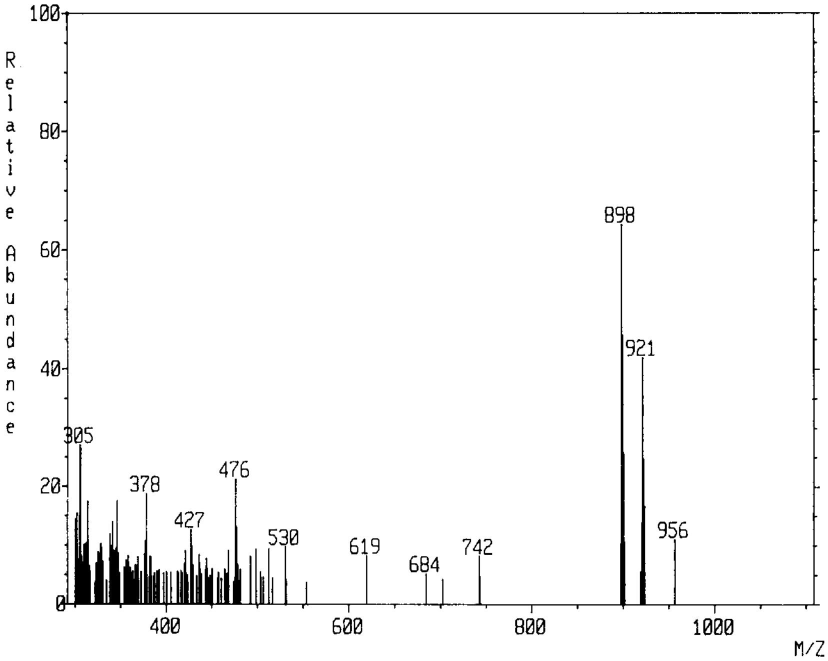


Fig. 5. FAB mass spectrum of dye **6b**.

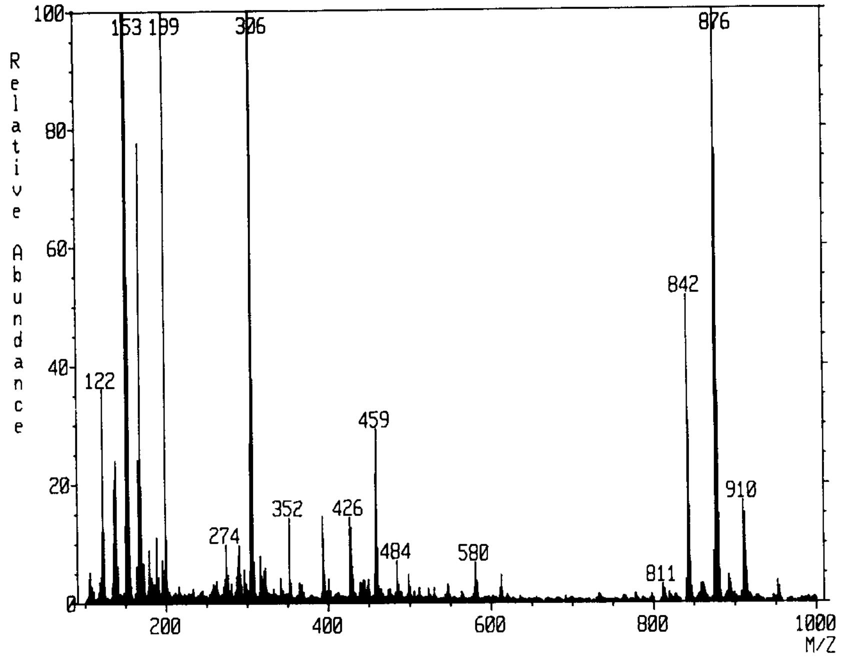


Fig. 6. FAB mass spectrum of dye **11**.

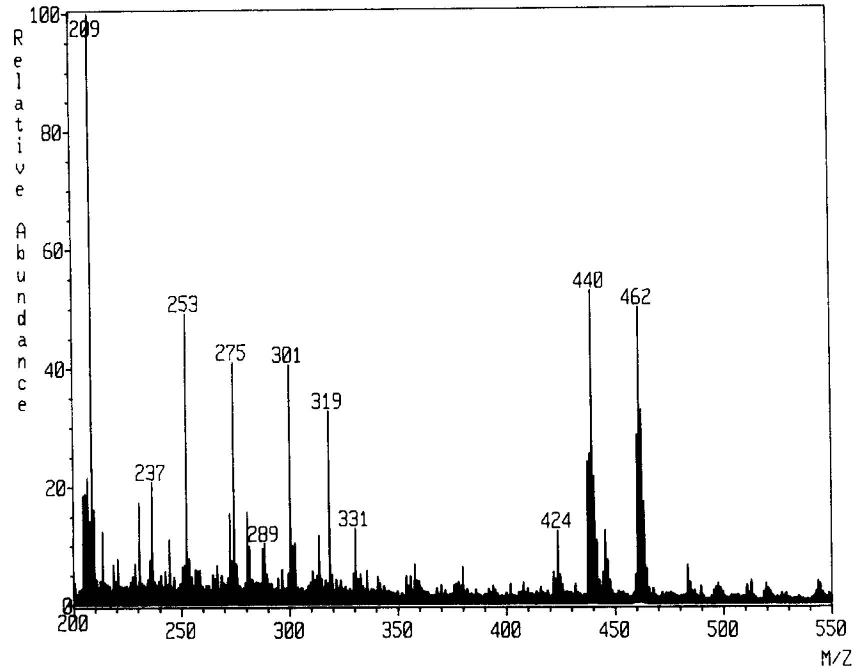


Fig. 7. FAB mass spectrum of dye **8a**.

by $[M-H]^-$ and $[M-Na]^-$ ions but also by key daughter ions that were important in establishing the structures involved. To confirm which fragments originate directly from $[M-Na]^-$ ions, B/E linked scanning with collisional activation[40] was carried out using this type of species as the parent ion. As an example, the B/E linked scan of the $[M-Na]^-$ ion of dye **8a** is reported (cf. Fig. 8), which confirmed the formation of the fragments shown in Fig. 9.

FAB mass spectrometry was also very useful in explaining the interesting behavior of Fe metallized formazan dyes observed during their synthesis. Surprisingly, we found that the synthesis of pure unsymmetrical 1:2 formazan dyes by the reaction of a 1:1 Fe complexed dye with a structurally different unmetallized formazan dye was unsuccessful, in that the isolated product was a mixture of three different 1:2 metallized dyes. In addition, we found that heating a mixture of the two symmetrical 1:2 Fe formazan dyes **4b** and **5b** under conditions identical to those normally employed in the synthesis of 1:2 Fe formazan dyes afforded the unsymmetrical product mixture **13** (*m/z* 921) again (Fig. 10). This provides evidence for the interchange of dye molecules under the aforementioned conditions, and explains our difficulties with the stepwise synthesis of pure unsymmetrical 1:2 Fe formazan dye.

The synthesized formazan dyes were applied to nylon and wool fabric

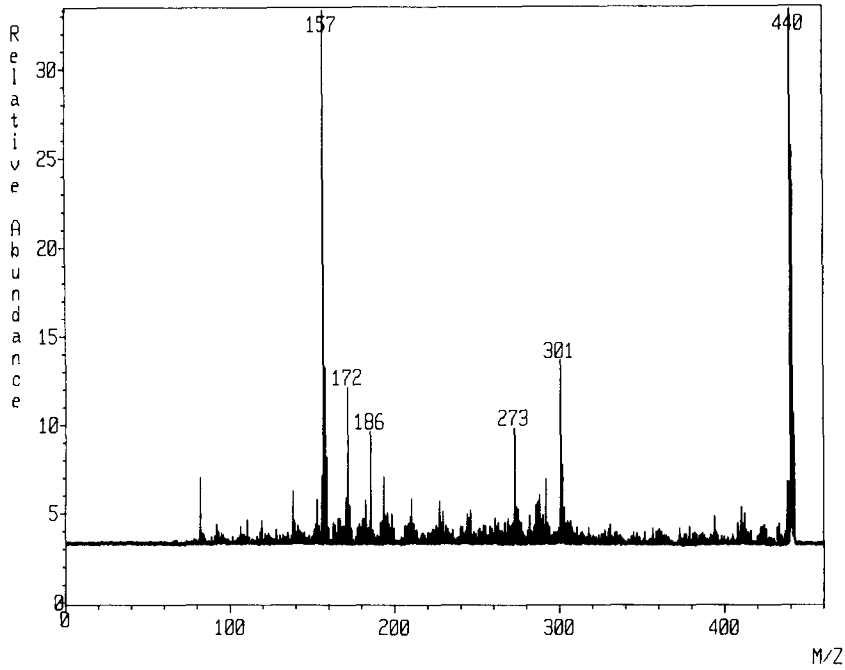


Fig. 8. B/E linked scan of dye **8a**.

TABLE 1

Relative Abundance[a] of Molecular Ion Species in the FAB Mass Spectra of 1:2 Fe Metallized Dyes

Dye	*Assignment*	*m/z*	*Relative abundance*
2a	$[\mathrm{M}-\mathrm{H}]^-$	394	50·94
2b	$[\mathrm{M}-\mathrm{Na}]^-$	842	44·44
3a	$[\mathrm{M}-\mathrm{H}]^-$	428	100·00[b]
3b	$[\mathrm{M}-\mathrm{Na}]^-$	911	14·17
4a	$[\mathrm{M}-\mathrm{H}]^-$	439	35·42
4b	$[\mathrm{M}-\mathrm{Na}]^-$	932	12·04
5a	$[\mathrm{M}-\mathrm{H}]^-$	394	100·00
5b	$[\mathrm{M}]^{-\cdot}$	865	4·20
	$[\mathrm{M}-\mathrm{Na}]^-$	842	27·81
6a	$[\mathrm{M}-\mathrm{H}]^-$	422	100·00[c]
6b	$[\mathrm{M}]^{-\cdot}$	921	42·15[b]
	$[\mathrm{M}-\mathrm{Na}]^-$	898	65·19
7a	$[\mathrm{M}-\mathrm{Na}]^-$	429	57·57[d]
	$[\mathrm{M}-\mathrm{H}]^-$	451	30·95
7b	$[\mathrm{M}-\mathrm{Na}+\mathrm{H}]^-$	958	3·89[e]
8a	$[\mathrm{M}-\mathrm{H}]^-$	462	50·50[f]
	$[\mathrm{M}-\mathrm{Na}]^-$	440	55·49
8b	$[\mathrm{M}]^{-\cdot}$	956	5·62[e]
	$[\mathrm{M}-\mathrm{Na}+\mathrm{H}]^-$	978	6·87
9a	$[\mathrm{M}-2\mathrm{Na}+\mathrm{H}]^-$	423	82·67[f]
	$[\mathrm{M}-\mathrm{Na}]^-$	445	79·60
9b	$[\mathrm{M}-2\mathrm{Na}+2\mathrm{H}]^-$	922	11·11
10	$[\mathrm{M}-\mathrm{Na}]^-$	842	71·40
11	$[\mathrm{M}-\mathrm{Na}]^-$	876	100·00
	2b	842	50·00
	3b	910	15·00
12	$[\mathrm{M}-\mathrm{Na}]$	876	40·00
	5b	842	19·75
	3b	910	27·00
13	$[\mathrm{M}-\mathrm{Na}]^-$	921	62·03
	4b	932	100·00
	3b	910	27·00
14	$[\mathrm{M}-\mathrm{Na}+\mathrm{H}]$	967	13·05

[a] Ion abundances are expressed relative to the base peak *m/z* = 152 (3-nitrobenzyl alcohol, 100%) unless otherwise indicated.

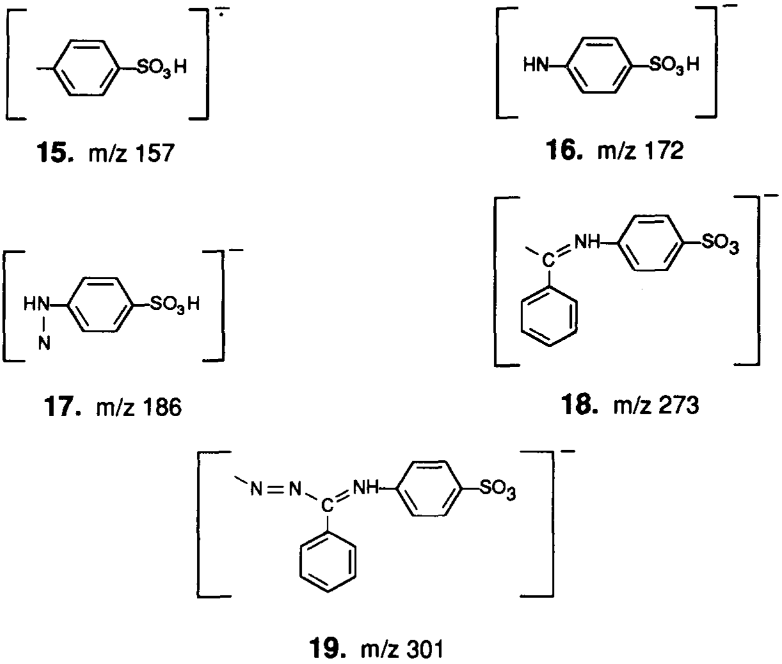
[b] Ion abundances are expressed relative to the base peak *m/z* = 306 (3-nitrobenzyl alcohol, 30%).

[c] Ion abundances are expressed relative to the base peak *m/z* = 152 (3-nitrobenzyl alcohol, 80%).

[d] Ion abundances are expressed relative to the base peak *m/z* = 104 (diethanolamine, 100%).

[e] Ion abundances are expressed relative to the base peak *m/z* = 306 (3-nitrobenzyl alcohol, 100%).

[f] Ion abundances are expressed relative to the base peak *m/z* = 104 (diethanolamine, 75%).


15. m/z 157

16. m/z 172

17. m/z 186

18. m/z 273

19. m/z 301

Fig. 9. Daughter ions (**15**–**19**) arising from the MS analysis of dye **8a**.

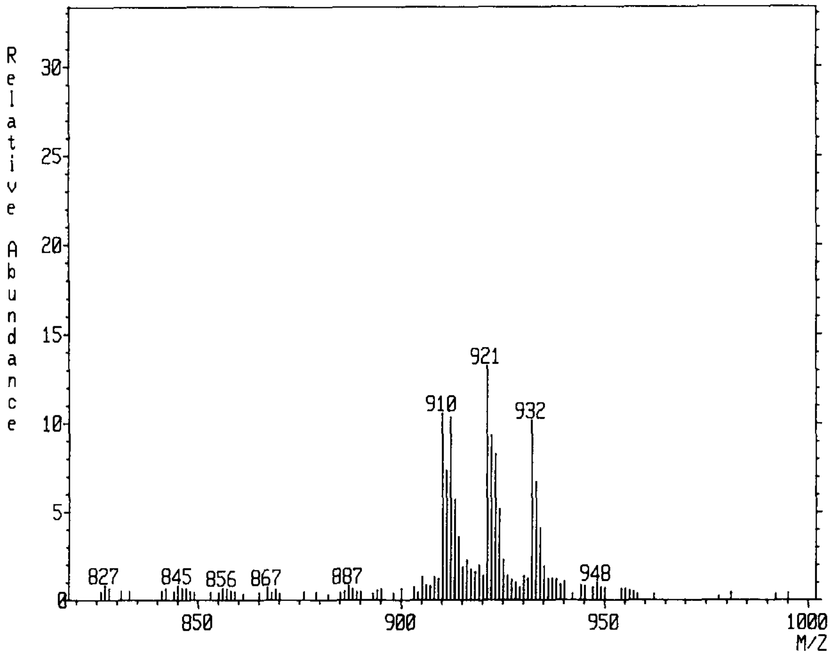


Fig. 10. FAB mass spectrum arising from heating a mixture of **4b** and **5b**.

TABLE 2
Fastness Properties of Dyes **2–14**

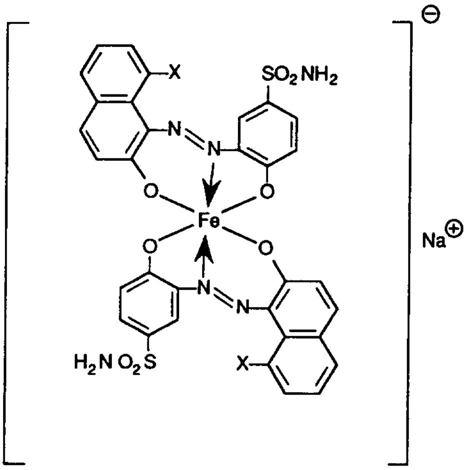
Dye	Depth of shade (%)	Color on fabric	Lightfastness				Washfastness						Crockfastness	
			Wool		*Nylon*		*Color change*		*Fiber staining*[a]				*Wool*	*Nylon*
			40 h	*80 h*	*40 h*	*80 h*	*Wool*	*Nylon*	*Dyed wool*		*Dyed nylon*			
									A	*B*	*A*	*B*		
2b	2	Reddish violet	2–3	2	3–4	2	5	5	4–5	4	4–5	4	4–5	5
3b	2	Blue	3–4	3	4–5	4	5	5	5	4–5	5	4–5	5	5
4b	2	Reddish black	5	4–5	4–5	3–4	5	5	5	4	5	4–5	5	5
	6	Black	4–5	4–5	4–5	4–5	5	5	5	4	5	4–5	4–5	4–5
5b	2	Bluish violet	4–5	4–5	4–5	4	5	5	5	5	5	4–5	5	5
6b	2	Brown	4	3–4	4–5	4	5	5	4–5	4	4–5	4–5	5	5
7b	2	Violet	2–3	1–2	3	2	5	5	4	4	4	4	5	5
8b	2	Violet	3–4	3–4	3	2	4	4	4	4	4	4	5	5
	6	Black	4–5	4–5	4	2–3	4	4	4	4	4	4	5	5
9b	2	Brown	4–5	4	3–4	3	4	4	3–4	3–4	4	4–5	5	5
10	2	Violet	2	1	1–2	<1	5	5	5	4–5	5	4–5	4–5	4–5
11	2	Bluish violet	3	2	3–4	2	5	5	5	4	4–5	4–5	5	5
12	2	Blue	3	2	4	3	5	5	5	4–5	5	4–5	5	5
13	2	Black	4–5	4–5	4–5	4	5	5	4–5	4	4–5	4–5	5	5
	6	Black	5	5	4–5	4–5	5	5	4–5	4	4–5	4	4–5	5
14	2	Violet	3–4	2–3	3–4	2–3	4–5	4–5	4–5	4–5	4–5	5	5	5
	6	Black	4–5	4	3–4	2–3	4–5	4–5	4–5	4–5	4–5	4	5	5

[a] A: staining wool; B: staining nylon.

TABLE 3
Lightfastness of Some Experimental and Commercial Black Dyes

Dye	*Depth of shade (%)*	*Lightfastness*			
		Wool		*Nylon*	
		225·6 kJ m^{-2}	*451·2 kJ m^{-2}*	*225·6 kJ m^{-2}*	*451·2 kJ m^{-2}*
4b	2	3	2	1–2	1
	6	5	4–5	4–5	3
13	2	3–4	2	1	1
	6	4–5	4	4–5	3–4
20	2	1–2	<1	<1	<1
	6	4	3	2–3	1
21	2	1–2	<1	<1	1
	6	5	4	2	1
CI Acid Black 52	2	3–4	2–3	4	2
	6	4–5	3–4	4	2
CI Acid Black 172	2	2	1	1–2	1–2
	6	4	4	<1	<1

at 2% and 6% depth of shade, and the dyeings were evaluated for lightfastness, washfastness and crockfastness according to established procedures.[41] Unlike 1:2 Fe azo dyes which are usually olive-brown, brown or black, the synthesized 1:2 Fe complexed formazan dyes produce violet and blue shades, along with blacks and browns. The dyeings obtained have very good fastness properties (cf. Table 2), and contrary to our



	X
20	H
21	NHAc

previously reported[1,2] 1:2 Fe complexed azo dyes (**20–21**), they show very good lightfastness on nylon. The lightfastness of some of the black dyeings was also evaluated according to GM conditions[42] for automotives and compared with commercial CI Acid Black 172. These results are given in Table 3. It is worthwhile mentioning that the formazan dyes containing sulfonic groups have low exhaustion from the dyebath, a property that could influence their utility.

EXPERIMENTAL

The chemicals used in the synthesis of all dyes were obtained from Aldrich Chemical Company (Milwaukee, WI) or Mobay Chemical Company (Pittsburgh, PA), and were used without further purification. The purity of the synthesized dyes was checked by TLC (BuOH:Pyridine:H_2O 2:2:1), using glass-backed silica gel 60 plates from Bodman Chemical Company (Doraville, GA). The structure of all dyes was confirmed using ^1H NMR (unmetallized dyes) or negative ion FAB spectrometry (unmetallized and metallized dyes). ^1H NMR spectra were recorded on a GE Omega 500 MHz spectrometer, FAB mass spectra were recorded on a JEOL (Tokyo, Japan) HX 110 HF double-focusing mass spectrometer equipped with a FAB ionization source, and visible spectra were recorded using a Perkin-Elmer R-24A spectrophotometer in 50% EtOH/H_2O. Lightfastness, washfastness and crockfastness were evaluated according to AATCC Test Methods 16–1990, 61–1986 and 8–1985, respectively.[41] In every case the rating scale employed ranged from a low of 1 to a high of 5.

Preparation of benzaldehyde phenylhydrazone-4-sulfonamide

4-Aminobenzenesulfonamide (52 g, 0·3 mol) was dissolved in 200 ml H_2O containing 30 ml 30% NaOH and added to 75 ml 4N $NaNO_2$. The resulting solution was poured over 100 g crushed ice containing 100 ml 30% HCl at a rate needed to maintain a reaction temperature of 5°C. The diazotization step was carried out for 40 min and the resultant diazonium salt was then added slowly to a stirred solution of 99·95 g Na_2SO_3 in 250 ml water at 10°C, and the reaction was continued for 1 h. At this point, the reaction temperature was raised to 70°C and 300 ml 30% HCl was added over 30 min. The precipitated product was stirred overnight, collected by filtration, washed with cold water and dried. The phenylhydrazine-4-sulfonamide obtained (47 g) was dissolved in 600 ml H_2O containing 40 ml 30% NaOH, and to this solution 27·5 g (0·26 mol) of benzaldehyde was added at 50–55°C. After stirring for 1 h, the temperature was reduced to 30°C and 24 ml 30%

HCl was added. The precipitated product was collected by filtration, washed with cold water and dried, to give 47·2 g of benzaldehyde phenylhydrazone-4-sulfonamide (m.p. 199°C; lit[43] m.p. 199°C).

^{1}H NMR (DMSO-d$_6$, 500 MHz): δ 7·08, s, (2H), δ 7·13, d, (2H, J = 7·50), δ 7·32, t, (1H, J = 7·50), δ 7·40, t, (2H, J = 7·00), δ 7·65, d, (2H, J = 8·50); δ 7·68, d, (2H, J = 7·50), δ 7·93, s, (1H), δ 10·80, s, (1H).

Preparation of benzaldehyde phenylhydrazone-4-sulfonic acid

Sulfanilic acid (52 g, 0·3 mol) was dissolved in 200 ml H_2O containing 16·5 g Na_2CO_3. The resulting solution was cooled to 10°C and 35 g of conc. H_2SO_4 was then added dropwise, followed by the addition of 75 ml 4N $NaNO_2$. The diazotization step was carried out for 15 min at 10–12°C. The diazonium salt was collected by filtration, washed with a small amount of cold water and added, at 5°C, to a stirred solution of 85 g of Na_2SO_3 in 250 ml H_2O. After stirring the reaction mixture for 1 h, the temperature was raised to 95°C and 240 ml of concentrated H_2SO_4 was added over a period of 30 min. The reaction mixture was left overnight and the precipitated product was collected, washed with cold water and dried. The phenylhydrazine-4-sulfonic acid obtained (52 g) was dissolved in 500 ml H_2O containing 60 ml 30% NaOH, and 30 g (0·28 mol) of benzaldehyde was added at 50–55°C. Stirring was continued for 1 h, the temperature was reduced to 30°C, and the product was precipitated by acidification with 36 ml 30% HCl. The product was collected, washed with a small amount of cold water and dried, to give 50 g of benzaldehyde phenylhydrazone-4-sulfonic acid.

^{1}H NMR (DMSO-d$_6$, 500 MHz): δ 6·98, d, (2H, J = 8·83), δ 7·30, t, (1H, J = 7·35), δ 7·39, t, (2H, J = 7·35), δ 7·45, d, (2H, J = 7·35), δ 7·65, d, (2H, J = 7·35), δ 7·87, s, (1H), δ 10·44, s, (1H).

Preparation of dyes 2a and 2b

A solution of 9·90 g (0·05 mol) 1-hydroxy-2-aminobenzene-4-sulfonamide in 100 ml H_2O containing 6·25 ml 30% NaOH was poured over a mixture of 75 g crushed ice and 14·5 ml 30% HCl. To the resulting suspension, 12·5 ml 4N $NaNO_2$ was added at a rate such that the reaction temperature was kept at 0–5°C. Diazotization was carried out for 1 h, and the solution of the diazonium salt was added dropwise at 0–5°C to 10·59 g (0·054 mol) benzaldehyde phenylhydrazone dissolved in 125 ml H_2O containing 75 ml pyridine and 25 ml 30% NaOH. The coupling reaction was stirred overnight and the intermediate unmetallized dye (**2a**) was salted out of solution, using 15% NaCl, to give 11 g of violet product.

^{1}H NMR (DMSO-d_6, 500 MHz): δ 7·08, d, (1H, J = 8·82), δ 7·30–7·33, m, (3H), δ 7·40, t, (1H, J = 7·35), δ 7·50, m, (3H), δ 7·60, t, (2H, J = 7·35), δ 7·88, d, (2H, J = 8·82), δ 8·13, d, (2H, 7·35), δ 8·27, m, (1H), δ 11·48, s, (1H), δ 15·68, s, (1H). Visible spectrum: λ_{max} = 496 nm, ε = 8,600.

The unmetallized formazan dye was dissolved in 140 ml H_2O containing 2·2 ml 30% NaOH and warmed to 50°C. Then, 3·86 g (0·0139 mol) $FeSO_4 \cdot 7H_2O$ dissolved in 20 ml H_2O was added and the reaction was stirred for 2 h at 60–70°C, monitoring by TLC, using BuOH:pyridine:H_2O 2:2:1 as the eluent. At this point, dye **2a** (R_f = 0·96) was fully converted to the desired 1:2 complex **2b** (R_f = 0·84). Visible spectrum: λ_{max} = 512 nm, ε = 14,200.

Preparation of dyes 3a and 3b

2-Amino-4-chlorophenol (7·175 g, 0·05 mol) was dissolved in 80 ml H_2O containing 10 ml 30% HCl, and after cooling the solution to 0–5°C, diazotization was accomplished with the aid of 12·5 ml 4 N $NaNO_2$. After stirring for 30 min, the diazonium salt obtained was added, at 0–5°C, to a solution of 14·75 g (0·054 mol) of benzaldehyde phenylhydrazone-4-sulfonamide, 25 ml 30% NaOH, and 30 ml pyridine in 350 ml H_2O. The coupling reaction was stirred overnight, and the unmetallized dye (**3a**) was salted out of solution, using 15% NaCl, giving 24 g of a reddish-blue product.

^{1}H NMR (DMSO-d_6, 500 MHz): δ 7·08–7·16, m, (2H), δ 7·34–7·41, m, (2H), δ 7·47, t, (1H, J = 7·50), δ 7·56, s, (2H), δ 7·70–7·89, m, (4H), δ 8·05, m, (1H), δ 8·15, d, (2H, J = 8·82), δ 10·30, bs, (1H), δ 15·14, s, (1H). Visible spectrum: λ_{max} = 503 nm, ε = 6,700.

The unmetallized formazan dye was dissolved in 280 ml H_2O containing 4·4 ml 30% NaOH, and metallized using 6·95 g (0·025 mol) $FeSO_4 \cdot 7H_2O$ dissolved in 40 ml H_2O. The reaction was stirred for 2 h at 60–70°C. At this point, dye **3a** (R_f = 0·82) was fully converted to its 1:2 Fe complex **3b**; (R_f = 0·67). The target 1:2 Fe complex was salted out of solution, using 5% NaCl, to give 18·4 g of the dye. Visible spectrum: λ_{max} = 553 nm, ε = 13,850.

Preparation of dyes 4a and 4b

2-Amino-4-nitrophenol (7·70 g, 0·05 mol) was dissolved in 75 ml H_2O containing 10 ml 30% HCl and, after cooling to 0–5°C, was diazotized with 12·5 ml 4N $NaNO_2$. Diazotization was carried out for 45 min and the diazonium salt obtained was added, at 0–5°C, to a solution of 14·75 g (0·054 mol) benzaldehyde phenylhydrazone-4-sulfonamide and 25 ml 30% NaOH in 350 ml H_2O and 30 ml pyridine. The coupling reaction was stirred overnight. The unmetallized dye (**4a**) was salted out of solution using 15% NaCl to give 21·4 g of reddish-blue product.

^{1}H NMR (DMSO-d_6, 500 MHz): δ 7·22, d, (1H, J = 9·13), δ 7·40–7·45, m, (3H), δ 7·52, t, (2H, J = 7·99), δ 7·84, d, (2H, J = 7·99), δ 7·96, d, (2H, J = 9·13), δ 8·08, d, (2H, J = 7·99), δ 8·15, dd, (1H, J = 3·42, J = 9·13), δ 8·57, d, (1H, J = 3·42), δ 12·30, bs, (1H), δ 15·19, s, (1H). Visible spectrum: λ_{max} = 553 nm, ε = 10,200.

Dye **4a** was dissolved in 280 ml H_2O containing 4·4 ml 30% NaOH, at 50°C, and metallized using 6·95 g (0·025 mol) $FeSO_4 \cdot 7H_2O$ dissolved in 40 ml H_2O. The reaction was stirred for 2 h at 60–70°C. At that point, dye **4a** (R_f = 0·85) was fully converted to 1:2 Fe complexed dye **4b** (R_f = 0·79). The target 1:2 Fe formazan complex was salted out of solution, using 5% NaCl, to give 22·5 g dye. Visible spectrum: λ_{max} = 494 nm, ε = 17,535; 500 nm (sh).

Preparation of dyes 5a and 5b

A solution of 5·45 g (0·05 mol) of 2-aminophenol in 350 ml H_2O containing 5 ml 30% NaOH and 12·5 ml 4 N $NaNO_2$ was poured over 16 g of crushed ice containing 16·6 ml 30% HCl. Diazotization was carried out for 30 min at 0–5°C. The resulting diazonium salt was added dropwise, at 0–5°C, to a solution of 14·75 g (0·054 mol) of benzaldehyde phenylhydrazone-4-sulfonamide and 25 ml 30% NaOH in 350 ml H_2O and 30 ml pyridine. The coupling reaction was stirred overnight. The unmetallized dye **5a** (R_f = 0·83) was salted out of solution, using 15% NaCl to give 15·4 g of red product.

^{1}H NMR (DMSO-d_6, 500 MHz): δ 7·20, t, (1H, J = 7·81), δ 7·45, t, (1H, J = 7·81), δ 7·51, t, (2H, J = 7·81), δ 7·58, bs, (2H), δ 7·71, t, (2H, J = 7·81), δ 8·00–8·03, m, (3H), δ 8·12, d, (2H, J = 7·81), δ 8·25, d, (1H, J = 7·81), δ 8·32, d, (1H, J = 7·81), δ 13·70, bs, (1H), δ 15·34, s, (1H). Visible spectrum: λ_{max} = 474 nm, ε = 11,670; 570 nm (sh).

Preparation of dyes 6a and 6b

Anthranilic acid (6·85 g, 0·05 mol) was dissolved in 75 ml H_2O containing 3 g Na_2CO_3, at 40°C, and 15 ml 30% HCl was added. The reaction mixture was cooled to 0°C and diazotized with 12·5 ml 4 N $NaNO_2$. Diazotization was carried out for 3 min at 0–2°C. The diazonium salt obtained was added, at 0–5°C, to a solution of 14·75 g (0·054 mol) of benzaldehyde phenylhydrazone-4-sulfonamide and 25 ml 30% NaOH in 350 ml H_2O and 30 ml pyridine. The reaction mixture was stirred overnight, and the unmetallized dye (**6a**; R_f = 0·7) was isolated by acidification with 40 ml 30% HCl, to give 21·2 g of reddish-orange product.

^{1}H NMR (DMSO-d_6, 500 MHz): δ 7·19, t, (1H, J = 7·81), δ 7·43, t, (1H, J = 7·81), δ 7·51, t, (2H, J = 7·81), δ 7·59, bs, (2H), δ 7·72, t, (1H, J = 7·81), δ 8·00–8·15, m, (5H), δ 8·23–8·33, m, (3H), δ 13·67, bs, (1H), δ 15·34, s, (1H). Visible spectrum: λ_{max} = 474 nm, ε = 11,285.

The unmetallized formazan dye was dissolved at 50°C in 280 ml H_2O containing 4·4 ml 30% NaOH and metallized with 6·95 g (0·025 mol) $FeSO_4 \cdot 7H_2O$ dissolved in 40 ml H_2O. The reaction was stirred for 2 h at 60–70°C. The target 1:2 Fe complex **6b** (R_f = 0·6) was salted out of solution, using 5% NaCl, to give 22·5 g dye. Visible spectrum: λ_{max} = 551 nm, ε = 7,200, λ'_{max} = 586 nm, ε' = 7,500.

Preparation of dyes 7a and 7b

Diazotization was carried out as described above for the synthesis of dye **3a**, and the resulting diazonium salt was coupled with benzaldehyde phenylhydrazone-4-sulfonic acid dissolved in 300 ml H_2O containing 25 ml 30% NaOH and 30 ml pyridine, under the conditions employed with the synthesis of **4a**. The unmetallized dye **7a** (R_f = 0·69) was salted out of solution with 15% NaCl to give 19·8 g product.

^{1}H NMR (DMSO-d_6, 500 MHz): δ 7·13, d, (1H, J = 9·00), δ 7·72, dd, (1H, J = 3·00, J = 9·00), δ 7·77, t, (2H, J = 7·50), δ 7·82, t, (1H, J = 7·50), δ 7·85–7·92, m, (4H); δ 8·01, s, (1H), δ 8·32, d, (2H, J = 7·50), δ 12·15, s, (1H), δ 15·34, s, (1H). Visible spectrum: λ_{max} = 506 nm, ε = 7,000.

The target unmetallized dye **7b** (Rf = 0·52) was synthesized and isolated in the manner described for **6b**, giving 17·5 g product. Visible spectrum: λ_{max} = 550 nm, ε = 12,700.

Preparation of dye 8b

Using the procedure described above for the synthesis of dyes **4b** and **7b**, 20 g of dye **8b** was obtained.

^{1}H NMR of **8a** (DMSO-d_6, 500 MHz): δ 7·05, d, (1H, J = 8·82), δ 7·42, t, (1H, J = 7·36), δ 7·52, t, (2H, J = 7·36), δ 7·85, d, (2H, J = 7·36), δ 8·12, d, (2H, J = 8·82), δ 8·32, d, (2H, J = 7·36), δ 8·38, dd, (1H, J = 2·94, J = 8·82), δ 8·55, d, (1H, J = 2·94), δ 12·99, bs, (1H), δ 15·48, s, (1H). Visible spectrum of **8a**: λ_{max} = 550 nm, ε = 9,800. Visible spectrum of **8b**: λ_{max} = 502 nm, ε = 17,800; 510 nm (sh). R_f **8a** = 0·67 (BuOH:pyridine:H_2O/2:2:1). R_f **8b** = 0·52.

Preparation of dye 9b

Using the procedure employed in the synthesis of dyes **6b** and **7b**, 22·5 g dye **9b** was obtained.

^{1}H NMR of **9a** (DMSO-d_6, 500 MHz): δ 7·12, t, (1H, J = 7·35), δ 7·43, t, (1H, J = 7·35), δ 7·51, t, (2H, J = 7·35), δ 7·68, t, (1H, J = 7·35), δ 7·80, d, (2H, J = 7·82), δ 7·99, d, (1H, J = 7·35), δ 8·10, d, (2H, J = 7·35), δ 8·17–8·22, m, (3H), δ 13·50, bs, (1H) δ 15·12, s, (1H). Visible spectrum of **9a**: λ_{max} = 465 nm, ε = 13,200. Visible spectrum of **9b**: λ_{max} = 556 nm, ε = 7,100; λ'_{max} = 583 nm, ε = 7,200. R_f **9a** = 0·68 (BuOH:pyridine:H_2O/ 2:2:1). R_f **9b** = 0·61.

Preparation of dye 10

A mixture of 10 g (0·025 mol) dye **2a** and 9·85 g (0·025 mol) dye **5a** was dissolved at 50°C in 275 ml H_2O containing 4·4 ml 30% NaOH and metallized with 6·95 g (0·025 mol) $FeSO_4{\cdot}7H_2O$ dissolved in 40 ml H_2O over 2 h at 60–70°C. The target 1:2 Fe complex was salted out of solution using 5% NaCl to give 18·65 g product, which was a statistical mixture of dyes **10**, **2b**, and **5b**.

R_f of the major dye (**10**) = 0·52.

Preparation of dye 11

A mixture of 10 g (0·025 mol) dye **2a** and 10·75 g (0·025 mol) dye **3a** in 275 ml H_2O containing 4·4 ml NaOH was metallized with 6·95 g (0·025 mol) $FeSO_4{\cdot}7H_2O$ dissolved in 40 ml H_2O over 2 h at 60–70°C. The 1:2 Fe complex was salted out of solution with 5% NaCl to give a statistical mixture of dyes **11**, **2b**, and **3b**.

R_f of the major dye (**11**) = 0·72.

Preparation of dye 12

A solution of 10·75 g (0·025 mol) dye **3a** and 9·85 g (0·025 mol) dye **5a** in 275 ml H_2O containing 4·4 ml NaOH was metallized in the way described previously for **5b**. The 1:2 Fe complex was isolated by salting it out of solution with 5% NaCl, giving 20 g of product which was a statistical mixture of dyes **12**, **3b**, and **5b**.

R_f of the major dye (**12**) = 0·75.

Preparation of dye 13

A solution of 11 g (0·025 mol) dye **4a** and 10·75 g (0·025 mol) dye **3a** in 275 ml H_2O with 4·4 ml 30% NaOH at 50°C was metallized in the way described previously for **4b**. The 1:2 Fe complex containing **13**, **3b**, and **4b** was salted out of solution with 5% NaCl, giving 15·6 g of product.

R_f of the major dye (**13**) = 0·63.

Preparation of dye 14

The synthesis was similar to those described for dyes **13** and **7b**. This afforded 16·5 g of a statistical mixture of dyes **14**, **7b** and **8b**.

R_f of the major dye (**14**) = 0·53.

CONCLUSIONS

The results of this investigation demonstrate that it is possible to prepare 1:2 Fe complexed formazan dyes having good affinity for protein and polyamide fibers. It is worthwhile noting that such dyes expand the spectrum of colors traditionally reported as arising from Fe complexes to include examples of violet and blue colors. The above results also demonstrate that it is possible to synthesize acid black dyes based on the formazan system whose fastness properties compare favorably with those of currently used commercial acid black dyes. Moreover, it is also suggested that the results of this study provide further evidence for the idea that the use of Fe salts as metallizing agents provides a potential solution to the environmental problems associated with the synthesis and application of Cr- and Co-based metallized acid dyes.

ACKNOWLEDGEMENT

The authors wish to thank the National Textile Center for providing the financial support for this investigation.

REFERENCES

1. Sokolowska-Gajda, J., Freeman, H. S. & Reife, A., *Text. Res. J.*, **64**(7), (1994) 388.
2. Freeman, H. S., Sokolowska-Gajda, J. & Reife, A., *Text. Chem. Color.*, **27**(2), (1995) 13.
3. Pabianickie Zaklady Farmaceutyczne 'Polfa', *Polish Patent* 55361 (1968).
4. Instytut Przemyslu Organicznego, *Polish Patent* 55362 (1968).
5. Instytut Przemyslu Organicznego, *Polish Patent* 55636 (1968).
6. Pabianickie Zaklady Farmaceutyczne 'Polfa', *Polish Patent* 116084, Politchnika Lodzka (1983).
7. Osrodek Badawczo-Rozwojowy Przemyslu Barwnikow 'Organika', *Polish Patent* 124566 (1985).
8. Pabianickie Zaklady Farmaceutyczne 'Polfa', *Polish Patent* 146991 (1989).
9. Mitsubishi Kasei Corp., *Japanese Patent* 01161063 (1987).
10. Nippon Kayaku Co., *Japanese Patent* 6090264 (1985).

11. Nippon Kayaku Co., *Japanese Patent* 60226559 (1985).
12. Nippon Kayaku Co., *Japanese Patent* 60258266 (1985).
13. BASF, *German Patent* 3840653 (1990).
14. BASF, *European Patent* 315045 (1989).
15. BASF, *European Patent* 315046 (1989).
16. Ciba-Geigy, *European Patent* 228348 (1987).
17. Bayer, *German Patent* 3743236 (1989).
18. Bayer, *German Patent* 3239364 (1984).
19. Bayer, *German Patent* 3406232 (1985).
20. Bayer, *German Patent* 4005122 (1991).
21. Bayer, *European Patent* 338310 (1989).
22. Hoechst, *German Patent* 3326638 (1985).
23. Hoechst, *German Patent* 3153413 (1985).
24. Hoechst, *German Patent* 3440265 (1986).
25. Hoechst, *German Patent* 3843135 (1990).
26. Hoechst, *US Patent* 4607098 (1986).
27. Ciba-Geigy, *European Patent* 410930 (1991).
28. Ciba-Geigy, *European Patent* 410931 (1991).
29. E. I. du Pont de Nemours & Company, *US Patent* 3592584 (1971).
30. E. I. du Pont de Nemours & Company, *US Patent* 3663525 (1972).
31. Toms River Chemical Corp., *US Patent* 1275877 (1972).
32. Toms River Chemical Corp., *US Patent* 3655637 (1972).
33. Durand & Huguenin, A. G., *US Patent* 3497493 (1970).
34. Fierz-David, H. E. & Blangey, L., *Fundamental Processes of Dye Chemistry*. Interscience Publishers, New York, London, 1949, pp. 128–9.
35. Barber, M. N., Bordoli, R. S., Sedgwick, R. D. & Tyler, A. N., *J. Chem. Soc. Chem. Commun.*, **7** (1981) 325.
36. Freeman, H. S., Hao, Z., Sokolowska-Gajda, J., van Breemen, R. B. & Le, J., *Dyes and Pigments*, **16** (1991) 317.
37. Shimanskas, C., Ng, K. & Karlinger, J., *J. Rap. Commun. Mass Spectrom.*, **3**(9) (1988) 300.
38. Meili, J. & Seibl, J., *Org. Mass Spectrom.*, **19** (1984) 581.
39. Sweetman, B. J. & Blair, T. A., *Biomed. and Environ. Mass Spectrom.*, **17** (1988) 337.
40. Freeman, H. S., van Breeman, R. B., Esancy, J. F., Ukponmwan, D. O., Hao, Z. & Hsu, W.-N., *Text. Chem. Color.*, **22**(5) (1990) 23.
41. *Technical Manual of the American Association of Textile Chemists and Colorists*, Vol. 67, 1992.
42. Bulluck, J. E. & Garrett, D. L., *J. Ind. Fabrics*, **4**(2) (1985) 23.
43. Willstaed, H., *Svensk Kem. Tidskr.*, **55** (1943) 214, 219.