Dyes and Pigments **8** (1987) 211–224

Metal Salt Azo Pigments Derived from 3-Hydroxy-2-Naphthohydroxamic Acid

R. M. Christie and S. Moss

Department of Technology, Scottish College of Textiles,
Netherdale, Galashiels TD1 3HF, Scotland, Great Britain

(Received 13 August 1986; accepted 5 September 1986)

SUMMARY

A series of metal salt azo pigments have been prepared from the coupling component 3-hydroxy-2-naphthohydroxamic acid. A comparison of the structure, thermal behaviour and application properties of the hydroxamate salts with those of the related commercially important carboxylate salt pigments is described.

1 INTRODUCTION

Azo pigments, both numerically and in terms of tonnage produced, dominate the yellow, orange and red shade areas in the range of commercial organic pigments. Amongst the most important of these, particularly in the red shade area, are a range of metal salt pigments which are prepared from water-soluble acid azo dyestuffs containing $SO_3^-Na^+$ groups by replacement of the sodium ions with divalent metal cations.[1-4] These products have evolved from a number of 'lake' pigments which were introduced towards the end of the last century but are now largely obsolete, and which consisted of anionic azo dyestuffs precipitated on to inorganic substrates such as alumina or barium sulphate. The metal salt pigments currently in use, commonly referred to as 'toners', no longer contain the inorganic substrate as an essential integral constituent.

In particular, metal salt pigments derived from the products of azo coupling with the coupling component 3-hydroxy-2-naphthoic acid (**2**) (Scheme 1) are products of significant commercial importance. The

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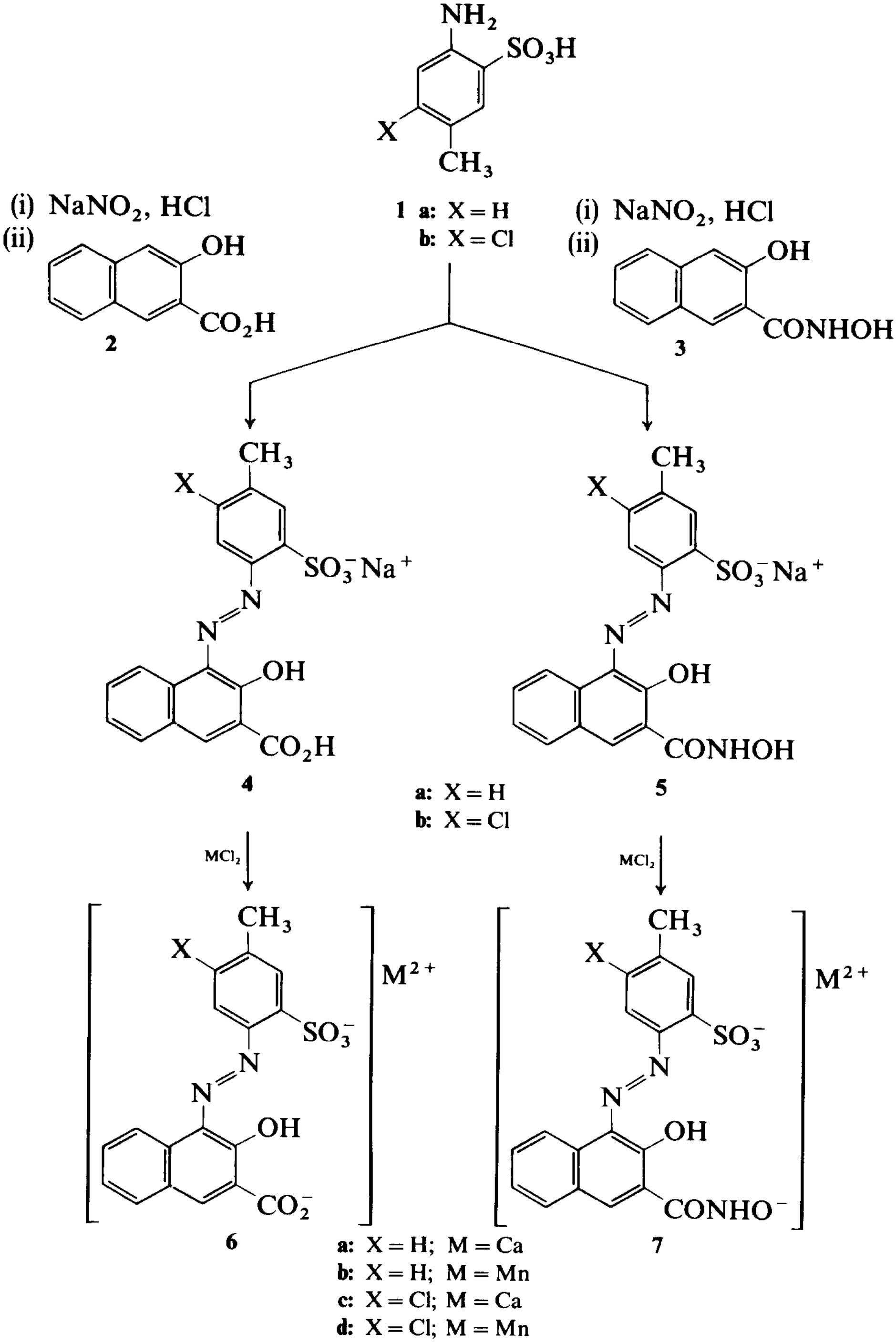

NH2
SO3H
X
CH3
1 a: X = H
b: X = Cl
(i) NaNO2, HCl
(ii)
OH
CO2H
2
(i) NaNO2, HCl
(ii)
OH
CONHOH
3
CH3
X
SO3⁻Na⁺
N
N
OH
CO2H
4
CH3
X
SO3⁻Na⁺
N
N
OH
CONHOH
5
a: X = H
b: X = Cl
MCl2
MCl2
CH3
X
SO3⁻
N
N
OH
CO2⁻
M2+
6
CH3
X
SO3⁻
N
N
OH
CONHO⁻
M2+
7
a: X = H; M = Ca
b: X = H; M = Mn
c: X = Cl; M = Ca
d: X = Cl; M = Mn

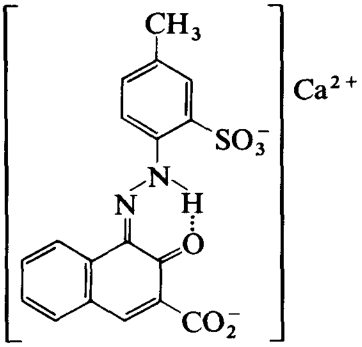
Scheme 1

divalent metals which are most frequently used are the alkaline earths, calcium, strontium and barium and the transition metal manganese. The calcium salts **6a** (C.I. Pigment Red 57: 1) and **6c** (C.I. Pigment Red 48: 2), for example, products of high colour strength and brightness, high transparency and excellent solvent resistance, are especially important for printing ink applications.[5] They do, however, suffer from poor stability to acids and alkalis and inadequate lightfastness, particularly in reduced shades, for most exterior applications. An interesting observation in this series of products is that the manganese(II) salts show significantly better lightfastness than the alkaline earth derivatives. For example, compound **6d** (C.I. Pigment Red 48: 4) finds broader application in industrial coatings as it has sufficient lightfastness in dark shades to be used in longer term exterior applications. One explanation for this observation is that the manganese derivatives ought to be regarded as transition metal complexes since it is well known that transition metal complexes frequently exhibit lightfastness which is superior to that of the free ligand. Among the variety of explanations which have been offered for this effect are a lowering of the electron density at a chromophore when coordinated with a transition metal which leads to improved resistance to photochemical oxidation,[6] and the ability of transition metal ions to quench excited states.[7] Unfortunately the enhancement of fastness properties which results from complex formation is almost inevitably accompanied by a dulling of the colour. The broadening of the absorption band which is responsible for this is probably to an extent attributable to overlap of the ligand π–π^* absorption band with that due to transition metal *d*–*d* transitions and possibly with bands due to ligand–metal charge-transfer transitions.

It is likely that manganese(II) is the preferred transition metal in this series of products since its d^5 configuration gives rise to very weak *d*–*d* absorptions when coordinated octahedrally,[8] but nevertheless the manganese salts are slightly duller in colour than the corresponding calcium derivatives.

There are few reports in the literature of structural investigations on metal salt azo pigments. However, it has recently been demonstrated by solid state ^{13}C-NMR spectroscopy, a technique which appears to offer considerable potential for the study of organic pigment structures, that C.I. Pigment Red 57: 1 (**6a**) exists in the ketohydrazone tautomeric form **8**.[9] The position and nature of the bonding of the metal ions and the location of the water of crystallisation in the crystal lattice, features which play an important role in the properties of pigments of this type, remain to be clarified.

Whilst there is much information on the preparation and properties of a wide range of metal salt azo pigments in the patent literature, there have



8

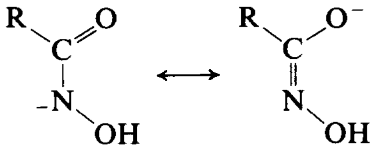
been no reports of structures containing a metal-coordinating functionality other than the sulphonate and carboxylate groups. In this present study, we investigate a number of derivatives containing the hydroxamic acid group. The ability of the hydroxamic acid group to coordinate strongly to metals is well known and the resulting complexes have found extensive analytical and biological application[10,11] so that it is rather surprising that there has been little attempt to exploit hydroxamic acid metal complexes as colourants. A literature survey indicated only one recent reference to the preparation of azo dyes containing hydroxamic acid groups, in that case for evaluation as colorimetric analytical reagents.[12] An additional potentially attractive feature of the hydroxamic acid group for the present study is that it contains the amide (CONH) functionality, probably the most commonly encountered structural feature in organic pigments because its presence generally leads to an enhancement of fastness properties as a result of its ability to form strong hydrogen bonds, both intra- and inter-molecular, in the crystal lattice.[1,4] We now report the preparation of the hydroxamate metal salt pigments **7a**–**7d** together with their carboxylate salt analogues **6a**–**6d** and a comparative study of their structural and application properties.

2 DISCUSSION

2.1 Preparation and structure of the metal salt pigments

The coupling component required for the synthesis of the hydroxamate metal salt pigments, 3-hydroxy-2-naphthohydroxamic acid (**3**), was a known compound previously prepared for evaluation as an inhibitor of nucleic acid biosynthesis.[13] Compound **3** is a potentially inexpensive intermediate readily prepared by conversion of the carboxylic acid **2** to its methyl ester which is then treated with hydroxylamine under alkaline conditions to form the hydroxamic acid. Compound **3** was found to undergo smooth azo coupling with the diazonium salts formed from 4B acid (**1a**) and 2B acid (**1b**) using the conditions normally used for coupling with carboxylic acid **2**. After appropriate adjustment of the pH at the end of the coupling, the monosodium salts **5a** and **5b** were isolated and purified by recrystallisation from water. The intermediates were then smoothly converted to the hydroxamate metal salt pigments **7a**–**7d** by treatment, as appropriate, with soluble calcium or manganese salts in boiling water at a slightly alkaline pH. Parallel preparations of the analogous carboxylate metal salts **6a**–**6d** were also carried out as shown in Scheme 1. Satisfactory yields and analytical data were obtained for all the products (Table 1).

The principal infrared absorption bands of the products are shown in Table 2. The shift in the carbonyl stretching frequency from *ca* 1690 cm^{-1} in the spectra of the carboxylic acids **4a** and **4b** to 1612–1624 cm^{-1} in the spectra of derivatives **6a**–**6d** is as expected for metal salt formation. Similarly, the hydroxamate salts **7a**–**7d** show carbonyl stretching frequencies in the range 1620–1625 cm^{-1}, somewhat lower than those of the hydroxamic acids **5a** and **5b** (1635 and 1652 cm^{-1}, respectively), values which are consistent with literature precedent.[11] The structure of the anion derived from hydroxamic acids remains the subject of some controversy. Whilst recent evidence is strongly in favour of the resonance-stabilised *N*-deprotonated form (**9**) in solution,[14,15] the nature of the anion in the solid state is less well established. In transition metal complexes, the hydroxamate anion is generally believed to behave as a bidentate ligand coordinated as in structure **10**,[11] so that it is probable that the manganese derivatives **7b** and **7d** contain bonding of this type. Accordingly, the pronounced sharp absorptions which are observed at *ca* 3240 cm^{-1} in the infrared spectra of those derivatives are assigned to the N—H group.



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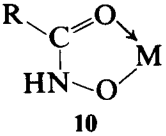

10

To provide further structural characterisation, the thermal behaviour of each of the metal salts **6a**–**6d** and **7a**–**7d** was investigated by differential scanning calorimetry and thermogravimetry. The results are shown in

TABLE 1
Yields and Analytical Data

Metal salt	Yield (%)	Molecular formula	Analysis (%)							
			C		H		N		M (Ca or Mn)	
			Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
6a	88	$C_{18}H_{12}N_2O_6SCa.3H_2O$	44·8	45·2	3·1	3·8	5·8	5·9	8·6	8·4
6b	85	$C_{18}H_{12}N_2O_6SMn.2{\cdot}5H_2O$	44·3	44·6	3·2	3·5	5·7	5·8	11·0	11·4
6c	87	$C_{18}H_{11}N_2O_6SClCa.3H_2O$	42·2	42·1	3·0	3·3	5·3	5·5	7·8	7·8
6d	95	$C_{18}H_{11}N_2O_6SClMn.3{\cdot}5H_2O$	40·0	40·3	2·7	3·3	5·2	5·2	9·6	10·2
7a	81	$C_{18}H_{13}N_3O_6SCa.3H_2O$	43·7	43·8	3·4	3·9	8·7	8·5	7·9	8·0
7b	78	$C_{18}H_{13}N_3O_6SMn.3{\cdot}5H_2O$	41·3	41·8	3·6	3·9	7·9	8·1	10·7	10·6
7c	90	$C_{18}H_{12}N_3O_6SClCa.3H_2O$	40·5	40·9	3·2	3·4	7·3	8·0	8·3	7·6
7d	83	$C_{18}H_{12}N_3O_6SClMn.3H_2O$	40·1	39·8	3·2	3·3	8·1	7·7	9·5	10·1

TABLE 2
Main Infrared Absorption bands (cm^{-1})

Compound	*OH*	*NH*	*C=O*
4a	3 440br	—	1 698
4b	3 380br	—	1 690
6a	3 460br	—	1 624
6b	3 390br	—	1 612
6c	3 450br	—	1 622
6d	3 380br	—	1 619
5a	3 370br	3 240br	1 635
5b	3 440br	3 220br	1 652
7a	3 420br	3 250br	1 622
7b	3 450br	3 242	1 623
7c	3 420br	3 260br	1 625
7d	3 400br	3 245	1 621

Table 3. The course of the thermal decomposition of each of the salts was found to follow a similar pattern. At lower temperatures, endothermic loss of water of crystallisation, often occurring in a number of discrete stages, was observed. The thermogravimetric analysis allowed this water loss to be quantified in each case and provided confirmation of the degree of hydration suggested by the analytical data (Table 1). It should be noted that the metal salts prepared in this study were air-dried to constant weight at room temperature. In industrial practice where the pigments are dried at temperatures above that required for the initial water loss, it is likely that a less hydrated product will result. For example, C.I. Pigment Red 57:1 (**6a**)[9] and C.I. Pigment Red 48:2 (**6c**)[16] are both reported as monohydrates. This is consistent with the DSC and TG results obtained for those salts (Table 3) which show initial water loss below 100°C, leaving in each case a monohydrate. DSC demonstrates that at higher temperatures the salts undergo exothermic decomposition. It is clear from the DSC curves that the hydroxamate salts **7a**–**7d** are somewhat less stable thermally than the carboxylate analogues **6a**–**6d**. This comparison may be seen from Figs 1 and 2, the DSC curves obtained for the manganese salts **6b** and **7b** respectively. The carboxylate salt **6b** shows endothermic loss of water in three discrete stages (peak temperatures 43·0°C, 168·4°C and 248·6°C) and the onset of exothermic decomposition at *ca* 315°C, while the hydroxamate derivative **7b** loses water in a single unresolved step (peak temperature 165·7°C) with the onset of exothermic decomposition at a significantly lower temperature (*ca* 206°C), presumably due to the reduced thermal stability of the hydroxamate group.

TABLE 3
DSC and TG Results

Metal salt	*Endotherms due to loss of water*				*Onset of exothermic decomposition (DSC) (°C)*
	Peak temperature DSC (°C)	*No. of water molecules lost*	*Mass loss (TG) (%)*		
			Found	*Calc.*	
6a	82·6	2	6·8	7·5	315
	214·9	1	3·2	3·7	
6b	43·0	0·5	1·8	1·9	320
	168·4	1	3·7	3·7	
	248·6	1	3·4	3·7	
6c	90·4	2	6·8	7·0	315
	207·3	1	3·4	3·5	
6d	89·3				330
	110·2				
	156·7	3·5[a]	11·8[a]	12·1[a]	
	195·6				
	234·5				
7a	88·5	3	11·8	11·0	158
7b	165·7	3·5	12·0	12·2	206
7c	80·1	3	10·1	10·2	178
7d	83·1	3[a]	11·5[a,b]	9·8[a]	182
	153·0				

[a] DSC resolved the water loss into more than one step, but TG did not allow characterisation of the individual steps due to a degree of overlap. The figures quoted are for total water loss.

[b] The high observed value is probably due to slight overlap of the peak due to endothermic water loss with that due to the exothermic decomposition.

2.2 Application properties

For the purposes of evaluation of the properties of pigments, an industrial paint formulation based on an alkyd/melamine–formaldehyde resin system requiring drying by stoving at 140°C was chosen. Such an application is fairly demanding, particularly with respect to fastness to light, solvents and heat. In common with most organic pigments, commercial metal salt azo pigments are almost invariably prepared in the presence of substantial quantities of additives, e.g. resins and surface-active agents, which assist in providing control of the particle size distribution and surface properties of the pigments in order to optimise their colouristic and dispersion properties. However, for the present comparative study it was felt that such treatments were an unnecessary complication and the properties of the pure metal salts were assessed.

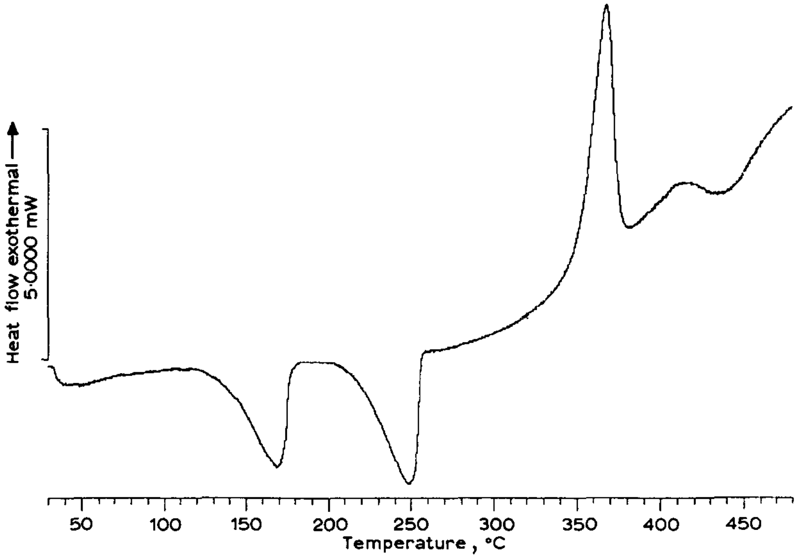

Fig. 1. DSC trace for carboxylate salt **6b**.

The results of the evaluation are contained in Table 4. The hydroxamate salts **7a–7d** were red pigments colouristically very similar to the carboxylate analogues **6a–6d**. Colour measurement carried out on the paint panels did not show any pattern in colour differences which could be attributed to differences in chemical structure. The pigments showed excellent solvent resistance, assessed as overpaint fastness (Section 4.6.2), while the heat

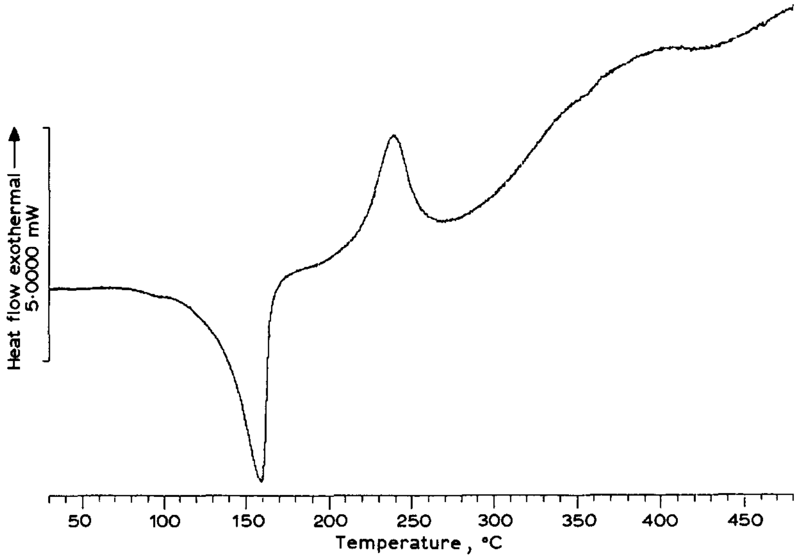

Fig. 2. DSC trace for hydroxamate salt **7b**.

TABLE 4
Pigment Properties in Industrial Paint Application

Compound	*Overpaint fastness*	*Heat stability*	*Lightfastness*		
			Full strength paint	*1:3 reduction with TiO_2*	*1:25 reduction with TiO_2*
6a	5	5	6	6	4–5
6b	5	5	6–7	6	5
6c	5	5	6	6	5
6d	5	5	7	6–7	6
7a	5	5	6	2–3	2
7b	5	5	6	5	3–4
7c	5	5	5	2–3	1–2
7d	5	5	6	4–5	3–4

fastness test (Section 4.6.4) showed good stability of colour at 140°C. The deficiency in the fastness of the metal salt pigments **6a**–**6d** to acids and alkalis,[3] which is illustrated by the discolouration of paint films containing those pigments when treated with aqueous hydrochloric acid and sodium hydroxide respectively and which is generally attributed to acid/base reactions, was equally apparent in paint films containing pigments **7a**–**7d**. The hydroxamate metal salts were found to have somewhat poorer lightfastness than the carboxylate derivatives, the effect being especially pronounced in white reductions containing the calcium salts **7a** and **7c**. The manganese salts **7b** and **7d**, however, showed significantly better lightfastness than the corresponding calcium salts, indicating that the chromophore is in those cases afforded some protection against photochemical degradation by the transition metal, presumably as a result of complexation.

3 CONCLUSIONS

Metal salt azo pigments may be readily prepared from the coupling component 3-hydroxy-2-naphthohydroxamic acid (**3**). The hydroxamate salts **7** which result are similar structurally to the well-known related carboxylate salts **6**, and show typical metal salt azo pigment properties in an industrial stoving paint application. The replacement of the carboxylate group by the hydroxamate group, however, leads to somewhat reduced thermal and photochemical stability.

4 EXPERIMENTAL

Infrared spectra were recorded as KBr discs with a Perkin–Elmer 599B spectrophotometer. ^{1}H-NMR spectra were recorded on a Perkin–Elmer R32 spectrometer for solutions in $(CD_3)_2SO$ using tetramethylsilane as internal reference. Calcium and manganese contents were determined by sample digestion in concentrated nitric and sulphuric acids and analysis using an Instrumentation Laboratories 257 atomic absorption spectrophotometer with correction for matrix effects. C, H and N analyses were performed by the Department of Applied Chemical Sciences, Napier College, Edinburgh. Differential scanning calorimetry was carried out using a Mettler DSC 30 instrument with a heating rate of 5 K min^{-1} and a flowing nitrogen atmosphere. Thermogravimetric analysis was carried out using a Stanton Redcroft TR-01 thermobalance with a heating rate of 10 K min^{-1} and a static air atmosphere.

4.1 Preparation of monosodium salt 5a

2-Amino-5-methylbenzene-1-sulphonic acid (4B acid) (0·08 mol) was diazotised according to literature procedures.[17] The diazonium salt suspension was added dropwise over 45 min to a stirred solution of 3-hydroxy-2-naphthohydroxamic acid (**3**)[13] (16·24 g, 0·08 mol) in 1M aqueous sodium hydroxide (160 cm^3). The resulting red suspension was stirred for a further 30 min and acidified with concentrated hydrochloric acid to pH 2·5. The monosodium salt **5a** (21·0 g, 83%) was obtained as a red powder by filtration, thorough washing with water and drying at 60°C. An analytical sample was obtained by recrystallisation from water. Found: C, 51·6; H, 3·4; N, 9·5; $C_{18}H_{14}N_3O_6SNa$ requires C, 51·1; H, 3·3; N, 9·9%). δ_H 2·77 (3H, s, CH_3), 7·70–8·90 (7H, m, ArH), 9·05 (1H, s, 1-naphthyl-H), 3·77 (1H, br s, NHOH), 9·88 (1H, br s, NHOH), 11·73 (1H, br s, OH).

4.2 Preparation of monosodium salt 5b

2-Amino-4-chloro-5-methylbenzene-1-sulphonic acid (2B acid) (0·08 mol) was diazotised according to literature procedures.[18] A coupling procedure as in Section 4.1 gave the monosodium salt **5b** (19·3g, 53%) as a red powder. (Found: C, 44·2; H, 3·2; N, 8·6; $C_{18}H_{13}N_3O_6SClNa.2H_2O$ requires C, 43·8; H, 3·5; N, 8·5%). δ_H 2·78 (3H, s, CH_3), 7·60–7·85 (6H, m, ArH), 9·03 (1H, 1-naphthyl-H), 3·88 (1H, br s, NHOH), 9·95 (1H, br s, NHOH), 11·67 (1H, br s, OH).

4.3 Preparation of monosodium salts 4a and 4b

These previously reported compounds[18] were prepared by methods similar to those used in Sections 4·1 and 4·2, but using 3-hydroxy-2-naphthoic acid (**2**) as the coupling component.

4.4 Preparation of the metal salts 6a–6d and 7a–7d

The appropriate monosodium salt, i.e. either **4a**, **4b**, **5a** or **5b**, (0·01 mol) was suspended in water (500 cm^3) and the suspension adjusted to pH 8·5 by the addition of dilute aqueous ammonia. Either calcium chloride (0·012 mol) or manganese(II) sulphate monohydrate (0·012 mol) dissolved in water (50 cm^3) was then added and the mixture refluxed with stirring for 30 min. The resulting deep red precipitate of the metal salt was collected by hot filtration, washed thoroughly with water, and air-dried to constant weight over several days at room temperature. Yields and analytical data are contained in Table 1.

4.5 Preparation of industrial stoving paints

A 1 lb honey jar containing a mixture of the pigment (5·0 g), Beetle BA595 (10·0 g), a non-drying alkyd resin based on coconut oil (B.I.P. Chemicals Ltd, Warley, West Midlands, England), xylene–butan-1-ol (4:1) (25·0 g) and 10 mm steatite balls (250 g) was rotated at 120 rpm on rollers for 16 h. A further quantity of Beetle BA595 resin (32·0 g) was then added and milling continued for 20 min. Finally, Dynomin MB-12 (13·0 g), an unmodified isobutylated melamine–formaldehyde resin (Charles Tennant and Co. (London) Ltd, London, England) was added and the paint preparation completed by milling for a further 10 min.

A standard white paint was prepared by a similar process using Tioxide R-CR2 (75·0 g), xylene–butan-1-ol (4:1, 63·0 g), Beetle BA595 resin (30·0 g and 93·9 g) and Dynomin MB-12 resin (38·1 g). Then 1:3 white reductions were prepared by mixing full-strength colour stainer (8·5 g) with white paint (6·0 g) and 1:25 reductions by mixing stainer (3·4 g) with white paint (20·0 g).

4.6 Assessment of pigment properties

4.6.1 Colouristic properties

For colouristic assessment, drawdowns of the full-strength stainer and the 1:3 and 1:25 white reductions on Astralux card were obtained using a 150 μm K-bar. The drawdowns were placed in a fume cupboard for 10 min to allow solvent evaporation and then stoved at 140°C for 60 min.

4.6.2 Overpaint fastness

A full-strength stainer drawdown prepared as in Section 4.6.1 and stoved at 140°C for 15 min was overpainted with the standard white paint using a 150 μm K-bar. After 10 min in a fume cupboard, the card was stoved at 140°C for 45 min. The degree of bleed was assessed against the ISO Grey Scale.

4.6.3 Lightfastness

Strips of drawdowns prepared as in Section 4.6.1 were exposed on a Xenotest 150 instrument for 350 h. Lightfastness was assessed against the British Blue Wool Standards.

4.6.4 Heat stability

A drawdown of the 1:3 white reduction, prepared as in Section 4.6.1, was stoved for 15 min and compared with the drawdown stoved for 60 min.

4.6.5 Fastness to acid and alkali

Acid fastness was assessed as the discolouration caused by contacting the 1:3 reduction, prepared as in Section 4.6.1, with a drop of 5% aqueous hydrochloric acid for 24 h. Fastness to alkali was tested in a similar way using 5% aqueous sodium hydroxide. Each of the paints tested showed a pronounced colour change on exposure both to acid and to alkali.

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