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Investigation of vat dyes as potential high performance pigments

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Abstract

A number of vat dyes and anthraquinone intermediates (**4–8c**, **15**) have been synthesised and then pigmented using high energy bead milling. These potential pigments have been tested alongside an isoindolinone Pigment Yellow 110 in a thermosetting acrylic/melamine formaldehyde resin paint system. Light fastness, durability and contact bleed properties were obtained for these pigments in full, reduced and metallic shades. Results have shown that these converted vat dyes and intermediates can give pigments with excellent tinctorial properties as well as good lightfastness, durability and overspray fastness properties. However, none of the vat dyes or intermediates have all of the necessary properties required of an automotive quality pigment.

Keywords: Vat dyes; Pigments; Synthesis; Paint; Light fastness; Durability

1. Introduction

Yellow is one of the most popular colours in plastics with demand historically met by cadmiums, lead chromes and more recently by condensed azos and benzimidazolones. Environmental pressures and legislation have gradually seen the decline in use of lead chrome (Pigment Yellow 34) and cadmium pigments (Pigment Yellow 37 and 44) in the plastics and automotive paint industry [1]. This has left a gap in the palette of stylists because the excellent properties and shades obtained from these pigments cannot be achieved by the use of the organic pigments alone, presently on the market. Yellow organic pigments are used in many industrial paint and ink applications but only to a certain extent in the automotive industry, and mainly in niche markets [2].

A short review of the properties and uses of yellow organic pigments puts this situation into context [2,3]. For instance, monoazo pigments based on acetoacetanilides such as Pigment Yellow 74 are all yellow, have good weatherfastness, chemical resistance properties and high tinctorial strength in full shades but suffer poor lightfastness properties in reduced shade, have poor heat and solvent fastness and are therefore limited to use in air drying paints such as decorative house paints. However, monoazo pigments containing the benzimidazolone moiety such as Pigment Yellow 151

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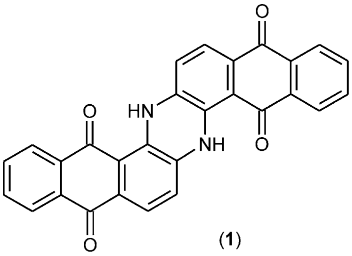
have improved solvent resistance, lightfastness and heat stability. They are suitable for use in high quality stoving industrial finishes and certain automotive finishes. Diazo pigments based on diarylide (benzidine) yellows such as Pigment Yellow 12, in general, have better tinctorial strength, solvent resistance and heat stability than the simple monoazo acetoacetanilide pigments but they have poor lightfastness properties and are therefore more commonly used in inks and to a lesser extent in plastics and paints. The diazo pigments more commonly referred to as condensed azos such as Pigment Yellow 93, based on a central diaminobenzene rather than a benzidine moiety and containing an additional arylamide group appended to the end of the molecule, have greater heat stability and consequently are used in plastic applications. The monoazo pyrazolone lakes such as Pigment Yellow 183 have exceedingly good heat fastness properties and are used in plastics but they have no use in paints because of their alkaline solubility. The copper azo-methine yellows such as Pigment Yellow 117 are dull greenish yellow and have excellent solvent resistance and weather fastness properties. They are highly transparent and so their main use is in automotive metallic paints, and because of their cost, mainly on sports cars. Isoindolinone yellow pigments such as Pigment Yellow 109 (azine types) and Pigment Yellow 139 (methine types) have excellent chemical and solvent resistance combined with good heat stability and lightfastness properties. Some of these pigments are used in automotive and industrial paints including metallic finishes where their intermediate transparency is an advantage but they do suffer from poor weatherfastness becoming more intense (darkening) on weathering, especially in full shade [3]. Anthraquinone yellows such as the flavanthrone Pigment Yellow 24 have very good lightfastness especially in reduced shades but again suffer from darkening in full shades. They are generally used in automotive and refinish metallic paints. Quinophthalone yellows such as Pigment Yellow 138 is a medium performance pigment used in plastics and industrial paints.

A new high performance organic pigment must have excellent lightfastness (6–7 minimum) and durability (weatherfastness) properties (4–5 minimum over 9 weeks exposure) in both full and reduced shades. It must also have good overspray fastness properties, i.e. not suffer from contact bleed. It is well established that polycyclic vat dyes have the physical properties required to convert them into high performance pigments, approximately 25 vat dyes have been successfully converted to pigments. Indanthrone (Pigment Blue



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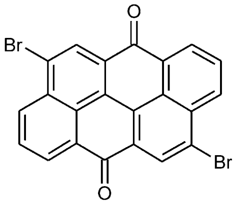

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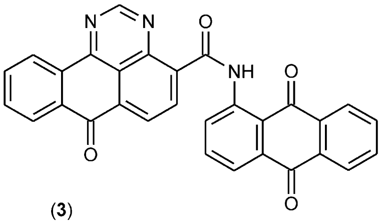


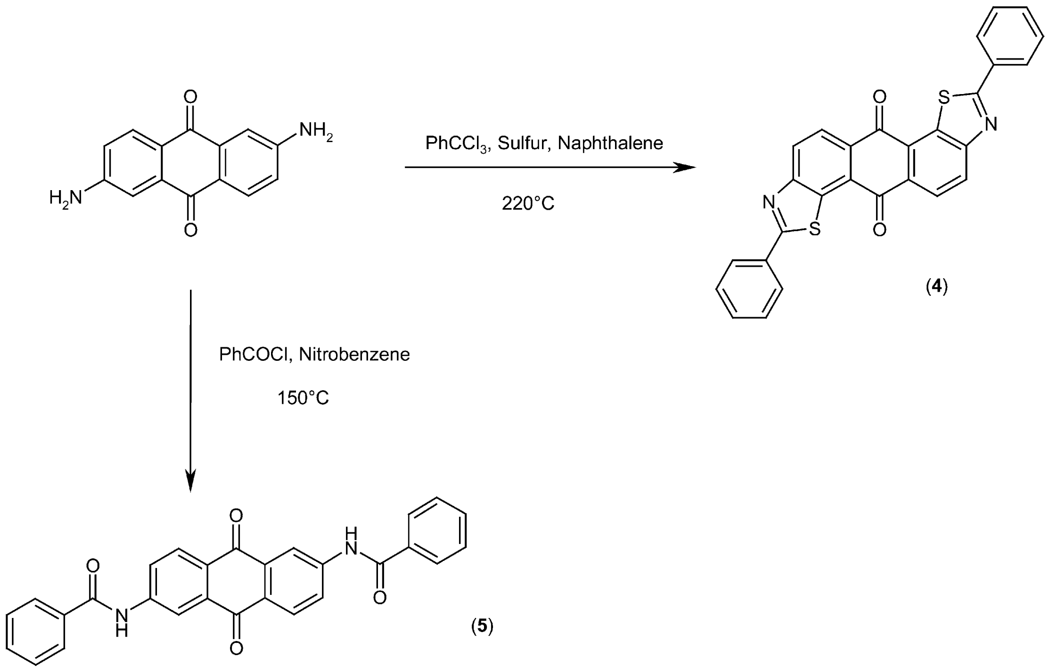
(**3**)

60) (**1**), dibromoanthanthrone (Pigment Red 168) (**2**) and anthrapyrimidine (Pigment Yellow 108) (**3**) to name but a few, were all used as vat dyes, being Vat Blue 4, Vat Orange 3 and Vat Yellow 20 respectively, before they were used as pigments. Perylenes and perinonones have also made this transition [3]. The criterion for the selection of new pigments has changed over the last decade, the changing colour fashions and advent of metallic and pearlescent finishes linked with improved pigment technology has made the investigation of vat dyes worthy of reappraisal. As part of our research programme into developing alternative organic yellow and orange pigments for plastics colouration and the automotive paint industry [2,4,5], we have examined the potential of some yellow and orange vat dyes as pigments.

2. Results and discussion

A survey was conducted of the physical properties of all the vat yellows, oranges and vat dye intermediates. From this survey in which properties such as high melting points above 300 °C, no or very low solubility in organic solvents, and strong tinctorial properties were all required in a compound, a shortlist of molecules was chosen to test as pigments. A number of yellow and orange vat dyes and some intermediates (**4–8c**, **15**) were then prepared in good to excellent yields, as shown in Schemes 1–7.

Vat Yellow 2 (**4**) was prepared from the condensation of 2,6-diaminoanthraquinone with α,α,α-trichlorotoluene and sulphur by a modification of the process detailed in the Badische patent [6], see Scheme 1. The anthraquinone (**5**) was prepared simply by benzoylation of 2,6-diaminoanthraquinone using benzoyl chloride, see also Scheme 1. Anthanthrone (**6**) was prepared from methyl 8-bromonaphthoate, by a three stage route using the procedures of Cooke [7] and Ansell [8], see Scheme 2. The dianthraquinone intermediates (**7a** and **b**) were prepared by the acylation of 1-aminoanthraquinone and 1-amino-5-*N*-benzoylaminoanthraquinone (**13**) respectively with terephthaloyl chloride using a modification of the procedure of Hefti [9], see Schemes 3 and 4. The

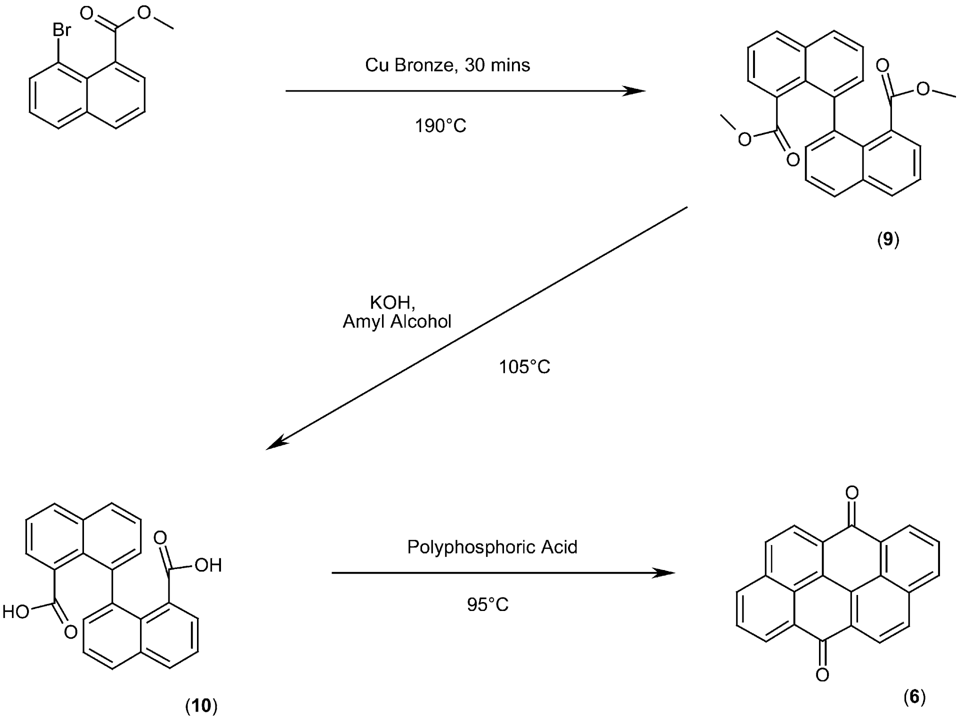


Scheme 1. Synthesis of Vat Yellow 2 (**4**) and anthraquinone (**5**).

anthraquinone intermediates (**8a** and **b**) were prepared by the procedure of Moergeli [10] from 1,5-dichloroanthraquinone and the corresponding substituted benzamides, see Scheme 5, and the anthraquinone (**8c**) was prepared from 1,5-diaminoanthraquinone and 2,4-dichlorobenzoyl chloride, see Scheme 6. Vat Orange 15 (**15**) was prepared by a five stage, synthetic route, see Schemes 3 and 7.

The synthesis of carbazole (**15**) was problematic in that the formation of intermediates such as 1-amino-5-chloroanthraquinone and its *N*-benzoyl derivative in a pure form could only be achieved with difficulty and in very poor yields. Usually, mixtures of monoaminoanthraquinones, diaminoanthraquinones and the starting material dichloroanthraquinones was isolated from the reaction of a dichloroanthraquinone with ammonia. This procedure could be improved slightly by doing the reaction in an autoclave [11], and by employing the variation in solubilities of each product, the intermediates can be isolated in approximately 80–90% purity. This was not ideal for our investigation since impurities could affect the tinctorial properties of a pigment in a deleterious manner and have been known to seriously affect overspray fastness properties so the carbazole (**15**) was prepared from a high purity source of 1-amino-5-chloroanthraquinone.

Benzoylation of 1-amino-5-chloroanthraquinone to give the intermediate (**11**) in good purity and yield was done in the usual manner by using benzoyl chloride. The synthesis of 1-amino-5-*N*-benzoylaminoanthraquinone (**13**) by treatment of the *N*-benzoyl derivative (**11**) with ammonia was not used since formation of unwanted dianthrimide would be a serious problem. Instead, anthraquinone (**11**) was converted to 1-benzoylamino-5-tosylaminoanthraquinone (**12**) in very good yield by treatment with toluenesulfonamide and base in white spirit. The use of white spirit rather than *o*-dichlorobenzene or nitrobenzene in this reaction was to simplify the removal of solvent and cheapen the route. Acid hydrolysis of (**12**) to give 1-amino-5-*N*-benzoylaminoanthraquinone (**13**) was achieved in excellent yield using



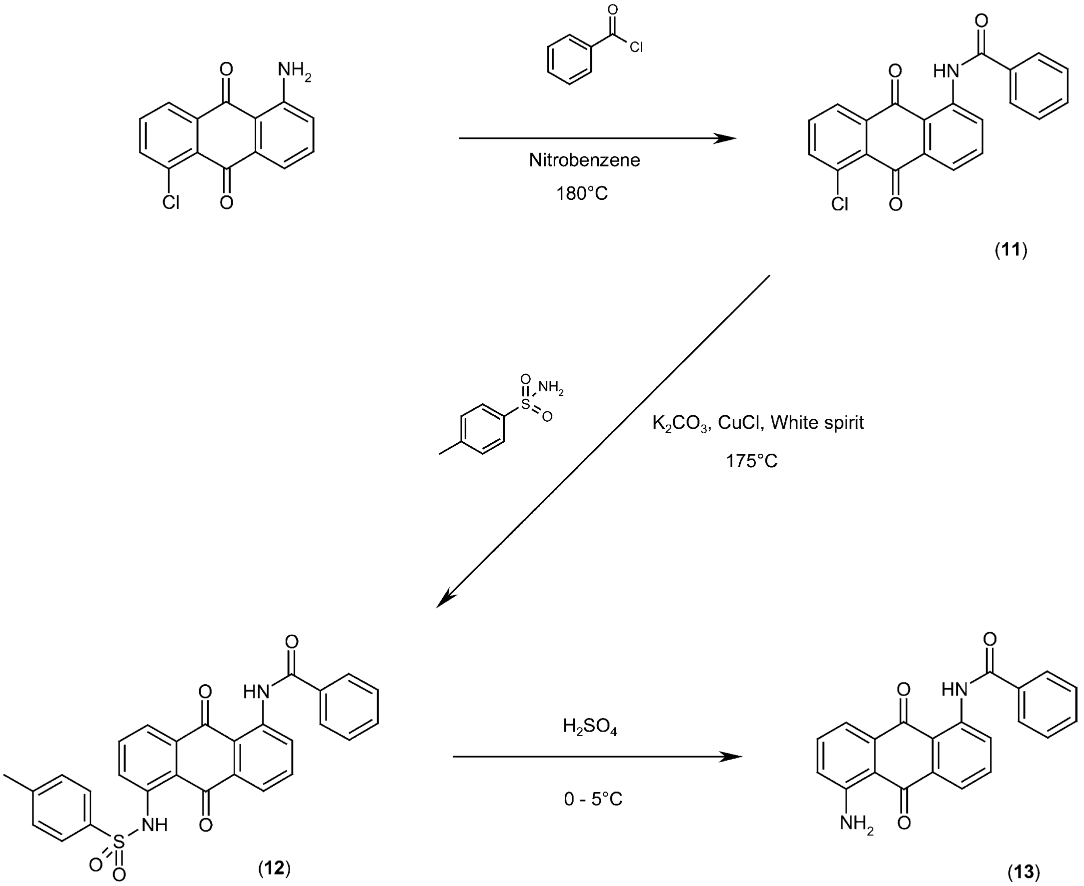
Scheme 2. Synthesis of anthanthrone (**6**).

sulphuric acid. This intermediate was used in the synthesis of the dye (**7b**) by condensation with terephthaloyl chloride (see Scheme 4) and in the synthesis of the vat dye (**15**), indirectly via the dianthrimide (**14**), by condensation with 5-*N*-benzoylamino-1-chloroanthraquinone (**11**), see Scheme 7.

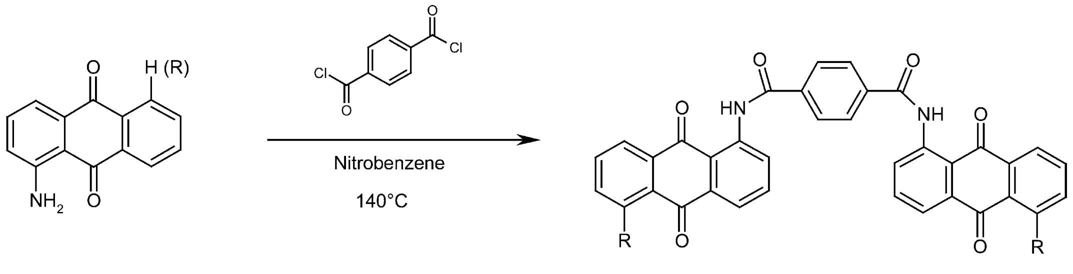
All of the chosen dyes and intermediates (**4–8c**, **15**) in this examination were pigmented using a batchwise high energy bead milling process. To obtain the maximum colour value from a pigment, it is essential that the pigment has the correct particle size. Pigments are usually synthesised in a non-pigmentary crude form of relatively large particle size, sometimes up to 100 μm. They are subsequently reduced to pigmentary size (0.05–0.5 μm) either by attrition (milling) or by a reprecipitation process.

In the milling method, breakdown of the pigment particles, aggregates and agglomerates was effected by movement of a large number of beads. The axis of rotation was vertical and the grinding medium used was glass beads. The speed of rotation was such that the beads continually rise with the rotation and then cascade down crushing and shearing the pigments. The pigments were then subjected to a final purification process. In this technique, a sulphuric acid slurry of the pigment was heated to boil for 8 h and then on cooling, the pH was adjusted from 1.5 to 4. The pigment was then filtered off, dried and finally ground to a fine powder.

This general procedure was used for the pigmentation of all the vat dyes and intermediates (**4–8c**, **15**). Analytical results for these pigments are presented in Table 1. These pigments were then



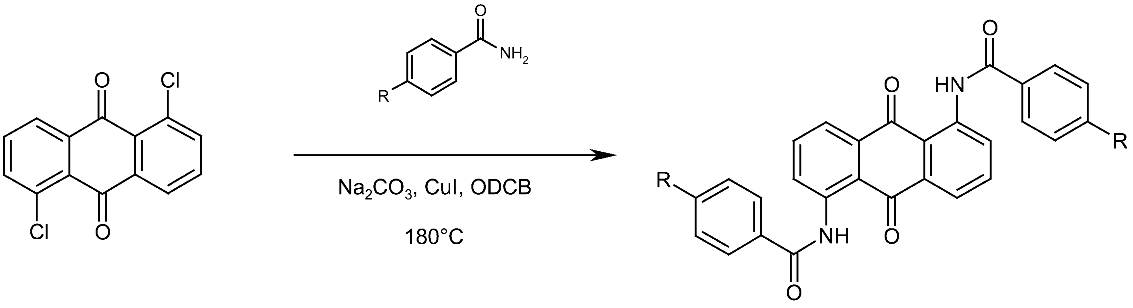
Scheme 3. Synthetic route to the intermediates for the anthraquinone, Vat Yellow 13 (**7b**) and the carbazole, Vat Orange 15 (**14**).



R = NHCOPh (**13**)

R = H (**7a**)
R = NHCOPh (**7b**)

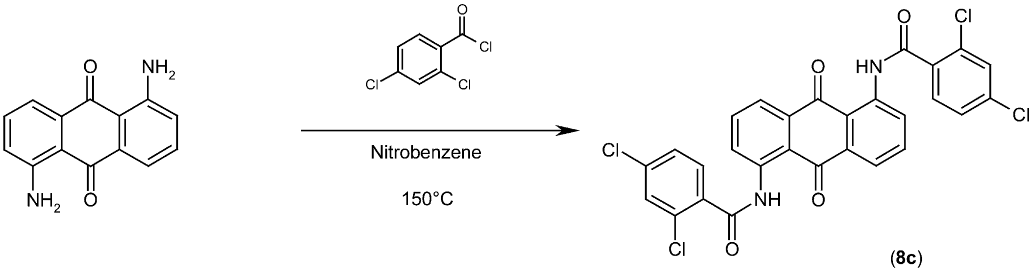
Scheme 4. Synthesis of anthraquinones, Vat Yellow 26 (**7a**) and Vat Yellow 13 (**7b**).



R = H (**8a**)

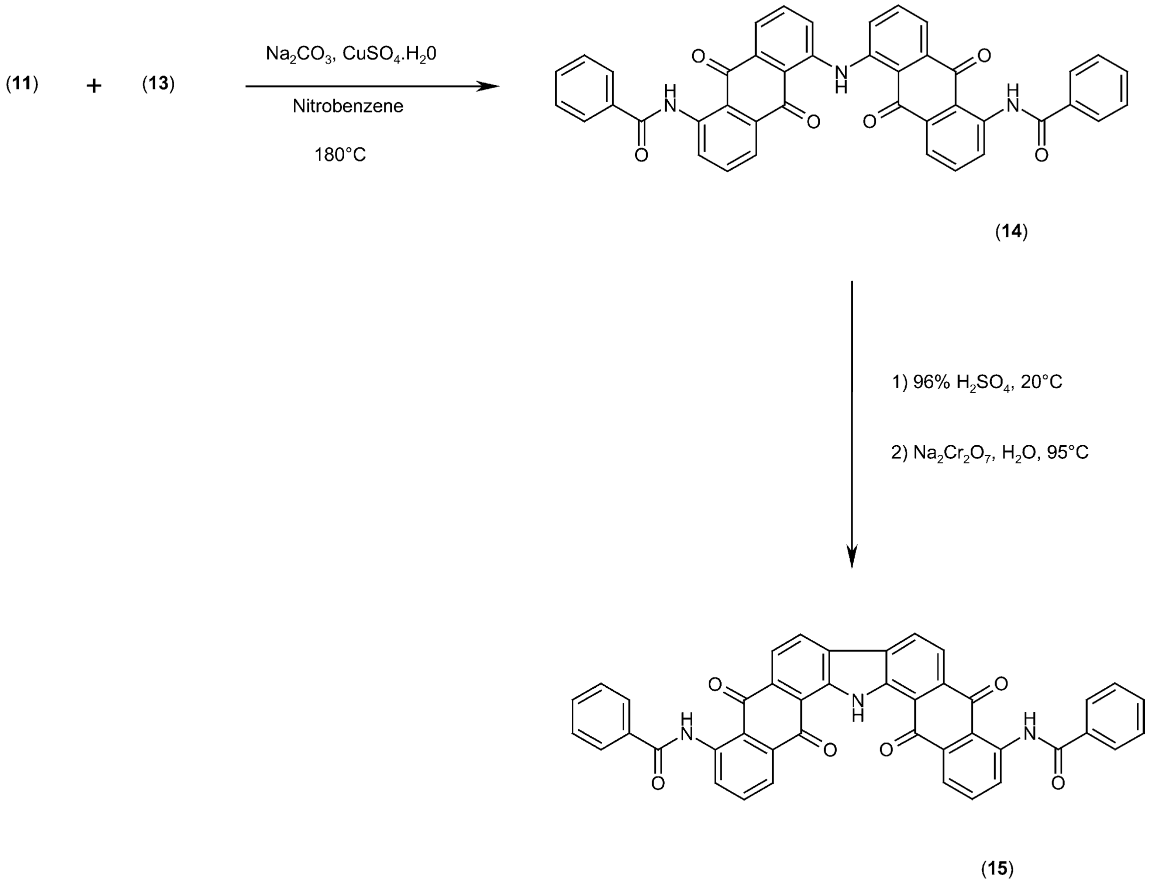
R = OCH_3 (**8b**)

Scheme 5. Synthesis of the anthraquinones (**8a** and **b**).



(**8c**)

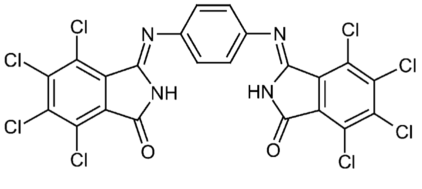
Scheme 6. Synthesis of anthraquinone (**8c**).



Scheme 7. Synthesis of carbazole, Vat Orange 15 (**15**).

dispersed into a thermosetting acrylic/melamine formaldehyde resin paint system and coated or sprayed on various substrates to ascertain their tinctorial properties, light fastness, weather fastness and overspray fastness in full, reduced and metallic shades. The results of these paint tests are shown in Tables 2, 3 and 4 respectively and are compared against a control of the isoindolinone Pigment Yellow 110 (**16**).

A brief summary of the results of the tinctorial properties for each vat dye and intermediate follows. The indanthrone (**4**) was a bright, strong and intense mid-shade yellow with an attractive green flip when observed from an acute angle. It was overspray fast (good contact bleed), but in pale metallics and reduced shade patterns, it had poor durability and lightfastness respectively. The anthraquinone (**5**) was a greenish yellow of moderate brightness and excellent contact bleed but had poor lightfastness properties. The anthanthrone (**6**) was an intense, strong, red-shade orange pigment with good lightfastness and durability properties at all depths of shade/colour, aluminium ratios but had a marked contact bleed problem. The dianthraquinone (**7a**) was a dull orange with poor lightfastness in reduced shades but good overall contact bleed. The dianthraquinone



(16)

Table 1
Analytical data for pigments (**4–8c**, **15**)

Pigment	Formula	Found			Required			Mass
		%C	%H	%N	%C	%H	%N	spec
4	$C_{28}H_{14}N_2O_2S_2$	70.80	3.20	5.10	70.85	3.00	5.90	
5	$C_{28}H_{18}N_2O_4$	76.10	4.40	6.00	75.35	4.05	6.30	446 (M^+–H, 30%)
6	$C_{22}H_{10}O_2$	86.50	3.20	0	86.30	3.30	0	
7a	$C_{36}H_{20}N_2O_6$	74.40	3.60	4.80	75.00	3.50	4.85	576 (M^+, 20%)
7b	$C_{50}H_{30}N_4O_8$	73.40	3.50	6.50	73.70	3.70	6.85	814 (M^+, 10%)
8a	$C_{28}H_{18}N_2O_4$	75.30	3.80	6.20	75.35	4.05	6.30	446 (M^+–H, 35%)
8b	$C_{30}H_{22}N_2O_6$	71.00	4.20	5.30	71.15	4.40	5.50	506 (M^+, 55%)
8c	$C_{28}H_{14}Cl_4N_2O_4$	56.60	2.50	4.70	57.55	2.40	4.80	
15	$C_{42}H_{23}N_3O_6$	75.70	3.60	6.50	75.80	3.50	6.30	665 (M^+, 100%)

Table 2
Tinctorial properties of pigments (**4–8c**, **15**) in full shade paint patterns

Pigment	Hue[a]	Brightness[a]	Intensity[a]	Transparency[a]	QUV durability	Light fastness	Overspray fastness
4	12	−2	−2	4	4–5	7	4–5
5	−16	−16	−4	1	2–3	4–5	5
6	−8	−2	0	6	4–5	6–7	2
7a	8	−12	1	4	4–5	6–7	4–5
7b	4	−4	−4	12	3–4	6	3–4
8a	0	−16	0	2	4–5	5	3–4
8b	8	−12	1	3	4–5	6–7	4
8c	6	−2	1	2	3–4	5	3
15	−6	0	2	8	4–5	7	3–4
Control	0	0	0	0	4–5	7	5

[a] Hue + = redder − = greener. Brightness + = brighter − = duller. Intensity + = more intense − = less intense. Transparency + = more transparent − = less transparent.

Table 3
Tinctorial properties of pigments (**4–8c**, **15**) in reduced shade paint patterns

Pigment	Hue[a]	Brightness[a]	Strength[b]	QUV durability	Light fastness	Overspray fastness
4	16	4	80:100	3–4	3	4–5
5	−16	0	130:100	3–4	3	5
6	−12	0	80:100	4	6–7	2
7a	−2	−8	115:100	4	5	5
7b	8	1	90:100	4	6–7	3–4
8a	4	−16	130:100	3–4	5	3–4
8b	2	−8	110:100	4	6–7	5
8c	4	0	120:100	2–3	1	3–4
15	−4	0	90:100	4	6–7	3–4
Control	0	0	100:100	4	7	5

[a] Refer to Table 2.

[b] Strength <100 = stronger >100 = weaker.

Table 4
Tinctorial properties of pigments (**4–8c**, **15**) in metallic shade paint patterns

Pigment	Hue[a,b]	Brightness[a,b]	Intensity[a,b]	Flip/flop[b]	QUV durability[b]	QUV durability[c]	Light fastness[b]
4	16	8	2	Green	5	2	7
6	−12	4	12	Neutral	4–5	4–5	6–7
7	8	6	4	Neutral	4	3	5
8c	12	0	4	More yellow	3	4	3–4
15	−6	4	4	Neutral	4–5	5	7
Control	0	0	0	Neutral	4–5	4–5	7

[a] Refer to Table 2.
[b] For 70/30 colour/aluminium metallic patterns.
[c] For 30/70 colour/aluminium metallic patterns.

(**7b**) was a bright red-shade yellow which was very transparent. Its lightfastness was marginally down for use as a high performance, automotive pigment as was its durability and overspray fastness. The anthraquinone (**8a**) was tinctorially a bright greenish yellow but unfortunately, it had poor overspray fastness and lightfastness. The anthraquinone (**8b**) was a very dull orange with modest lightfastness and contact bleed. The anthraquinone (**8c**) was a red-shade yellow with good opacity and millbase rheology. Unfortunately, it suffered from poor lightfastness in reduced shades and had suspect durability and poor overspray fastness. The carbazole (**15**) was an orange pigment which had a very poor millbase rheology. It had excellent lightfastness and durability but suffered from poor contact bleed.

3. Experimental

3.1. General

Unless otherwise stated, all reactants were purchased from Aldrich Chemical Co. (Milwaukee, WI) and were used without further purification. 1-Amino-5-chloroanthraquinone and 1,5-diaminoanthraquinone were purchased from Avocado Research Chemicals Ltd. (Heysham, UK) without further purification. All solvents were purchased as GPR grade from Fisher Scientific UK Ltd. (Loughborough, UK) and were used without further purification or drying. Non aqueous reactions were performed in a nitrogen atmosphere. Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. Proton Nmr spectra, mass spectra and microanalytical determinations were performed by Avecia Analytical Sciences Group on a Bruker DPX 300 MHz spectrometer, a Micromass Platform II or a Finnigan MAT 900XLT instrument and a Leco 932 C H N S analyser respectively. Proton NMR spectra were recorded in deuterated D6-dimethylsulphoxide solvent unless otherwise stated and chemical shifts are quoted in p.p.m. relative to tetramethylsilane as an internal reference. Lightfastness results were obtained using an air cooled Xenon Arc Fading Tester 150.

3.2. Synthesis of intermediates (*9–14*)

Dimethyl-1,1′-binaphthyl-8,8′-dicarboxylate (**9**) was prepared from methyl 8-bromo-1-naphthoate using Cooke's modification [7] of the method of Hall [12]. Methyl 8-bromo-1-naphthoate [13] was obtained from naphthalic anhydride in a four stage synthesis via 8-bromonaphthoic acid [14].

1,1′-Binaphthyl-8,8′-dicarboxylic acid (**10**) was prepared from the diester (**9**) using the method of Stanley [15].

3.2.1. 1-N-Benzoylamino-5-chloroanthraquinone (*11*)

1-Amino-5-chloroanthraquinone (25 g 97 mmol) was stirred in nitrobenzene (150 ml) at 150 °C. A solution of benzoyl chloride (18.2 g 129 mmol) in nitrobenzene (20 ml) at 100 °C was added dropwise over 10 min. The whole mixture was stirred at

180 °C for 1 h, allowed to cool to 120 °C and sodium carbonate (2 g) was added. The mixture was stirred at 120 °C for 30 min and then filtered hot. The isolated solid was washed with more nitrobenzene (50 ml) and then slurried into hot water (200 ml). The hot mixture was steam distilled to remove trace amounts of nitrobenzene and then filtered. The solid was washed with hot water (3 × 100 ml) until alkali free and finally dried in an oven at 90 °C. A yellow solid was obtained (33.5 g 95%), m.p. 218–221 °C; δ ($CDCl_3$) 7.55–7.65 (3H, m, aromatic $H_{3', 4' \text{ and } 5'}$), 7.7 (1H, t, *J* 7.8 Hz, aromatic H_3), 7.82 (1H, dd, *J* 7.8, 1 Hz, aromatic H_2), 7.86 (1H, t, *J* 7.7 Hz, aromatic H_7), 8.08 (1H, dd, *J* 7.8, 1 Hz, aromatic H_6), 8.16 (2H, m aromatic $H_{2' \text{ and } 6'}$), 8.38 (1H, dd, *J* 7.7, 1 Hz, aromatic H_4), 9.35 (1H, dd, *J* 7.7, 1 Hz, aromatic H_8), 13.1 (1H, bs, NH). *m*/*z* 361 (M^+, 100%). Elemental analysis, calculated for $C_{21}H_{12}ClNO_3$; C, 69.7; H, 3.35; N, 3.85; Cl, 9.8. Found: C, 69.3; H, 3.3; N, 3.9; Cl, 9.3.

3.2.2. 1-N-Benzoylamino-5-N-tosylaminoanthraquinone (12)

1-*N*-Benzoylamino-5-chloroanthraquinone (11) (33 g 91 mmol) was added to a stirred slurry of 4-toluenesulfonamide (23.8 g 139 mmol), potassium carbonate (15.5 g 112 mmol) and cuprous chloride (0.94 g 9.5 mmol) in white spirit (200 ml). The whole mixture was stirred at 175 °C for 8 h under a nitrogen atmosphere and then allowed to cool. The mixture was poured into stirring water (300 ml) and the whole mixture was stirred at 90 °C for 1 h. The aqueous phase was separated and sodium bicarbonate (6 g) was added. The mixture was stirred at 100 °C for 30 min. The hot mixture was steam distilled to remove trace amounts of white spirit and then filtered. The isolated solid was washed with hot water (3 × 100 ml) until alkali free and finally dried. A mustard yellow solid was obtained (41.6 g 92%), m.p. 258–260 °C (dec.); δ 2.32 (3H, s, CH_3), 7.35 (2H, d, *J* 7.8 Hz, aromatic $H_{3' \text{ and } 5'}$), 7.6–7.7 (3H, m, aromatic H), 7.75–8.1 (8H, m, aromatic H), 9.12 (2H, d, *J* 7.8 Hz, aromatic $H_{2' \text{ and } 4'}$), 11.8 (1H, bs, NH), 12.75 (1H, bs, NH). *m*/*z* 496 (M^+, 52%). Elemental analysis, calculated for $C_{28}H_{20}N_2O_5S$; C, 67.75; H, 4.05; N, 5.65; S, 6.45. Found: C, 67.4; H, 4.0; N, 5.5; S, 6.2.

3.2.3. 1-Amino-5-N-benzoylaminoanthraquinone (13)

1-*N*-Benzoylamino-5-*N*-tosylaminoanthraquinone (**12**) (41 g 83 mmol) was added over 30 min to stirred 96% sulphuric acid (200 ml) at 0 °C. The whole mixture was stirred at 0–5 °C for 3 h and then added to a stirred mixture of ice/water (1100 ml) keeping the temperature below 25 °C. The mixture was filtered and the isolated solid was washed with hot water (200 ml) at 50 °C. The solid was slurried in a mixture of concentrated ammonia solution (10 ml) and water (500 ml) to neutralise the product, stirred at room temperature for 1 h and then filtered off. The solid was washed with water (2 × 100 ml) and dried. A red solid was obtained (27.73 g 98%), m.p. 254–256 °C; δ 7.25 (1H, dd, *J* 7.7, 1 Hz, aromatic H_6), 7.42 (1H, dd, *J* 7.7, 1 Hz, aromatic H_2), 7.52 (1H, t, *J* 7.7 Hz, aromatic H_7), 7.58–7.7 (3H, m, aromatic $H_{3',4' \text{ and } 5'}$), 7.83 (1H, t, *J* 7.7 Hz, aromatic H_3), 7.88 (2H, bs, NH_2), 7.93 (1H, dd, *J* 7.7, 1 Hz, aromatic H_8), 8.09 (2H, dd, *J* 7.7, 1 Hz, aromatic $H_{2' \text{ and } 6'}$), 9.15 (1H, dd, *J* 7.7, 1 Hz, aromatic H_4), (1H, bs, NHCO). *m*/*z* 342 (M^+, 53%). Elemental analysis, calculated for $C_{21}H_{14}N_2O_3$; C, 73.65; H, 4.1; N, 8.2. Found: C, 73.0; H, 4.1; N, 7.7.

3.2.4. 5,5′-Bis(N-benzoylamino)-1,1′-dianthrimide (14)

1-Amino-5-*N*-benzoylaminoanthraquinone (**13**) (10 g 29 mmol) was added over 15 min to a stirred solution of 1-*N*-benzoylamino-5-chloroanthraquinone (**11**) (11.6 g 32 mmol), cupric sulphate monohydrate (0.54 g 3 mmol) and sodium carbonate (10 g 9.5 mmol) in nitrobenzene (150 ml) at 120 °C. The whole mixture was stirred at 180 °C for 16 h and then allowed to cool to 80 °C. The mixture was poured into stirring water (150 ml) and then was stirred at 80 °C for 1 h. The aqueous phase was separated, steam distilled to remove trace amounts of nitrobenzene and then filtered. The isolated solid was washed with hot water (3 × 100 ml) until alkali free, slurried in methanol (2 × 100 ml), filtered off and finally dried. A red solid was obtained (15.8 g 82%), m.p. > 300 °C; *m*/*z* 667 (M^+, 32%). Elemental analysis, calculated for $C_{42}H_{25}N_3O_6$; C, 75.55; H, 3.75; N, 6.3. Found: C, 74.7; H, 3.6; N, 6.5.

3.3. Synthesis of vat dyes (**4**, **7*b***, **15**) and intermediates (**5**–**8*c***)

3.3.1. 2,8-Diphenylanthraquinone-1′(S),2′,5′(S),6′-dithiazole (Vat Yellow 2) (**4**)

A mixture of α,α,α-trichlorotoluene (45.5 g 233 mmol), sulfur (7.65 g 240 mmol) and naphthalene crystals (55 g) was heated to 90 °C. After 30 min, the mixture was now mobile and 2,6-diaminoanthraquinone (17.1 g 72 mmol) and cuprous chloride (0.18 g 1.8 mmol) were added evenly over 20 min to the stirred mixture. The temperature was raised to 180 °C over 1 h and the whole mixture was stirred at this temperature for 8 h and then at 220 °C for 8 h. The mixture was allowed to cool to 180 °C and then added to stirred 1,2-dichlorobenzene (120 ml) heated at 100 °C. Sodium carbonate (7.5 g) was added over 10 min to the stirred mixture until the solution was alkaline. The whole mixture was stirred at 160 °C for 3 h and then filtered hot. The isolated solid was slurried repeatedly in more 1,2-dichlorobenzene (3 × 80 ml), kept at 160 °C for 15 min and filtered. The damp solid was slurried in water (200 ml) containing sodium sulphide (10 g) to remove excess sulphur and then the mixture was steam distilled to remove 1,2-dichlorobenzene. The mixture was filtered and the solid was washed with more hot water (3 × 100 ml) until free from alkali. The yellow solid was air dried (22.4 g 66%), m.p. >300 °C.

3.3.2. 2,6-Dibenzoylanthraquinone (**5**)

2,6-Diaminoanthraquinone (15 g 63 mmol) was stirred in nitrobenzene (150 ml) at 150 °C. A solution of benzoyl chloride (17.9 g 127 mmol) in nitrobenzene (30 ml) at 100 °C was added dropwise over 10 min. The whole mixture was stirred at 150 °C for 1 h, allowed to cool to 120 °C and sodium carbonate (2 g) was added. The mixture was stirred at 120 °C for 30 min and then filtered hot. The isolated solid was washed with more nitrobenzene (50 ml) and then slurried into hot water (200 ml). The hot mixture was steam distilled to remove trace amounts of nitrobenzene and then filtered. The solid was washed with hot water (3 × 100 ml) until alkali free and finally dried in an oven at 90 °C. A yellow solid was isolated (23.9 g 85%), m.p.>300 °C.

3.3.3. Anthanthrone (**6**)

1,1′-Binaphthyl-8,8′-dicarboxylic acid (**10**) (40 g 117 mmol) was added evenly over 2 h to stirred polyphosphoric acid (200 ml) at 90 °C. The dark brown mixture was stirred at 100 °C for 2 h and then poured into an ice water mixture (1500 g) containing sodium chloride (100 g). The precipitated, red solid was filtered off, washed with more water (300 ml), slurried in an aqueous sodium carbonate solution (300 ml) and then filtered off. The reddish orange solid was slurried in water (500 ml), filtered off and then washed with methanol (2 × 250 ml). The solid was then oven dried (30.5 g 85%), m.p. > 350 °C.

3.3.4. N,N′-Di-1-anthraquinonyl terephthalimide (Vat Yellow 26/Pigment Yellow 123) (**7*a***)

1-Aminoanthraquinone (20 g 90 mmol) was added over 1 h to terephthaloyl chloride (9.15 g 45 mmol) stirred in nitrobenzene (70 ml) at 90 °C and then the whole mixture was stirred at 140 °C for 3 h. The mixture was allowed to cool to 120 °C and sodium carbonate (2 g) was added. The mixture was stirred at 120 °C for 30 min and then filtered hot. The isolated solid was washed with more nitrobenzene (30 ml) and then slurried into hot water (200 ml). The hot mixture was steam distilled to remove trace amounts of nitrobenzene and then filtered. The solid was washed with hot water (3 × 100 ml) until alkali free. The reddish orange solid was air dried (21.8 g 84%), m.p. >300 °C.

3.3.5. 5,5′-Di-benzoylamino-N,N′-di-1anthraquinonyl terephthalimide (Vat Yellow 13) (**7*b***)

This was prepared similarly as for (**7a**) above except 1-amino-5-*N*-benzoylaminoanthraquinone (**13**) (17.1 g 50 mmol) was used in place of 1-aminoanthraquinone and the amount of terephthaloyl chloride (5.10 g 25 mmol) used, was adjusted. A dull, reddish yellow solid was obtained (16.3 g 80%), m.p. >300 °C.

3.3.6. 1,5-Dibenzoylaminoanthraquinone (**8*a***)

1,5-Dichloroanthraquinone (15 g 54 mmol), benzamide (13.5 g 111 mmol) and sodium carbonate (15 g 142 mmol) were stirred in 1,2-dichlorobenzene (200 ml). A warm solution of cuprous iodide (1.5 g 8 mmol) in quinoline (10 g) was added to the stirred mixture and the whole was stirred at reflux (180 °C) for 8 h. The hot mixture was filtered to give an orange solid which was washed with more hot 1,2-dichlorobenzene (2 × 50 ml), then ethanol 74OP (3 × 50 ml) until the filtrate was colour free to give a yellow solid. The solid was washed with distilled water until alkali free (3 × 50 ml) and finally with ethanol 74OP (50 ml). The yellow solid was then air dried (18.1 g 75%), mp >350 °C.

3.3.7. *1,5-Di-(4-methoxybenzoylamino)anthraquinone (**8b**)*

This was prepared similarly as for (**8a**) above but 4-methoxybenzamide (16.8 g 111 mmol) was used in place of benzamide. An orange solid was isolated (22.4 g 82%), m.p. >300 °C.

3.3.8. *1,5-Di-(2,4-dichlorobenzoylamino)anthraquinone (**8c**)*

1,5-Diaminoanthraquinone (20 g 84 mmol) was stirred in nitrobenzene (200 ml) at 150 °C. A solution of 2,4-dichlorobenzoyl chloride (35.6 g 170 mmol) in nitrobenzene (30 ml) at 100 °C was added dropwise over 10 min. The whole mixture was stirred at 150 °C for 1 h, allowed to cool to 120 °C and sodium carbonate (2 g) was added. The mixture was stirred at 120 °C for 30 min and then filtered hot. The isolated solid was washed with more nitrobenzene (50 ml) and then slurried into hot water (200 ml). The hot mixture was steam distilled to remove trace amounts of nitrobenzene and then filtered. The solid was washed with hot water (3 × 100 ml) until alkali free and finally dried in an oven at 90 °C. A reddish yellow solid was isolated (38.7 g 79%), m.p.>300 °C.

3.3.9. *5,5′-Bis(N-benzoylamino)-1,1′-dianthrimidecarbazole (Vat Orange 15) (**15**)*

The dianthrimide (**14**) (38.2 g 57 mmol) was added evenly over 2 h to stirred 96% sulphuric acid (180 ml) keeping the temperature at 15–20 °C. The mixture was stirred at this temperature for 6 h until the solution was clear of unreacted starting material. The solution was carefully added over 15 min to stirred water (920 ml) with cooling. Then sodium dichromate (50 g 168 mmol) was added slowly to the stirred solution to prevent frothing. The mixture was stirred at 95 °C for 6 h and then allowed to cool to 50 °C, filtered and the isolated solid was washed acid free with more water (2 × 500 ml). The paste was slurried in water (600 ml) and sodium carbonate (5 g) was added followed by sodium bicarbonate (15 g) and sodium hypochlorite (50 g). The mixture was stirred at 80 °C for 4 h and then diluted with water (400 ml). The mixture was filtered and the isolated solid was washed alkali free with water (2 × 500 ml), and dried in an oven at 90 °C to give a dull orange powder (33 g 87%), m.p. >300 °C.

3.4. *General milling procedure*

The vat dye/intermediate (15 g) and sodium dodecyl sulphate (5.5 g) were stirred in water (54 ml). This mixture was milled in a Dispermat SL mixer using 3 mm glass beads for 2 h. After milling, the dispersion was filtered off from the beads. The pH of the dispersion was adjusted to 1.5 using 20% sulphuric acid. The mixture was heated to boil and the reflux was maintained for 8 h, allowed to cool and the pH adjusted to 4 using aqueous 5M sodium hydroxide solution. The pigment was filtered off and washed acid free with distilled water. The pigment was dried in an oven at 90 °C and ground to a fine powder with a coffee grinder.

3.5. *Method of paint manufacture*

The pigments were dispersed into a thermosetting acrylic melamine formaldehyde resin system using a red devil stainer milling. The control was an isoindolinone, Pigment Yellow 110, available from Ciba Geigy under the tradename Irgazin® Yellow 3RLTN.

3.5.1. *Millbase*

Glass beads (3 mm) (125 g) were weighed into a 140 ml screw cap bottle. Into this, 50% thermosetting acrylic resin H190-315 (ex PPG autocolor supplied in xylene) (10 g) in 4:1 xylene:butanol (15 g) and the pigment (5.3 g) were added. The bottle was shaken by hand until homogeneous and then shaken on a Red Devil shaker for 30 mins. The seed/bit level was noted and found to be off-guage. The millbase was allowed to cool to room temperature.

3.5.2. Letdown

Into the tared 140 ml glass bottle containing the millbase was added 50% thermosetting acrylic resin H190-315 (43.4 g) in xylene carefully as follows: 2, 4, 8, 16 g etc. After each addition the bottle was shaken vigorously. Then, approximately half of the millbase contents were transferred to a 280 ml bottle without the beads and the letdown was continued with addition of 60% Cymel® 615 resin (ex Cytec supplied in white spirit) (26.6 g) and xylene (5.8 g) into the 140 ml bottle. The 140 ml bottle was shaken by hand and then all the contents including the beads were poured into the 280 ml bottle which was shaken to ensure homogeneity. The paint was checked visually to make sure shock seeding had not occurred. The total paint weight is 106 g and the pigment content is 5% with a Pigment/Binder ratio of 0.12/1 and a pigment /resin solution ratio of 17.5/82.5.

3.5.3. Full shade

Full shade patterns were obtained by drawdown on black/white card by means of a 250 μm bar. The paint was allowed to air dry for 15 min and then stoved at 120 °C for 30 min. Tinctorial and lightfastness/overspray fastness properties were assessed from these patterns.

3.5.4. Reduced shade

Into a 70 ml screw cap bottle, the coloured paint (4.0 g) and a white thermosetting acrylic/MF stoving enamel (ex Avecia) (TiO_2 content 25%) (20 g) was added. The contents were mixed thoroughly by rolling on a mill until the mixture is visually homogeneous. The reduced shade paints were sprayed (Spray booth/gun AGG-500 series ex De Vilbiss co) on white card (for tinctorial and lightfastness assessments) and Q-panels (for durability assessments), allowed to dry for 15 min and then stoved in an oven at 120 °C for 30 min.

3.6. Method of metallic paint manufacture

3.6.1. Aluminium stainer

Into a tared 1 l paint can, aluminium paste SSP 504AR (ex Silberline Ltd) (30 g) was weighed and then a mixture of 50% thermosetting acrylic resin H190-315 (40 g), toluene (20 g) and xylene (10 g) was added and the whole was mixed slowly by hand until homogeneous. More 50% thermosetting acrylic resin H190-315 (300 g) was carefully added in aliquots of 10, 20, 20, 50, 100, 100 g mixing by hand throughout. A mixture of Cymel® 615 resin (150 g) and xylene (50 g) is finally added to the stainer mixture and stirred in by hand until homogeneous. The aluminium content of the stainer is 5%.

3.6.2. Letdown solution

Into a tared 1 l paint can, 50% thermosetting acrylic resin H190-315 (225.6 g), Cymel® 615 resin (112.8 g), 1-methoxy-2-propanol acetate (240 g) and toluene (72 g) was weighed and the whole mixture was mixed by hand until homogeneous.

3.6.3. Strong metallic shade (70/30 aluminium/colour stainer)

Into a tared 140 ml bottle, 5% aluminium stainer (6 g), colour stainer (14 g) and letdown solution (30.4 g) were weighed. The contents are mixed by hand until homogeneous and the paint is sprayed on to Q-panels to full hide. The Q-panels are air dried for 15 min and then stoved at 120 °C for 45 min.

3.6.4. Pale metallic shade (30/70 aluminium/colour stainer)

The above method for the 70/30 strong metallic shade was repeated but using 14 g aluminium stainer and 6 g of colour stainer.

3.7. Assessment and measurement of paint patterns

3.7.1. Tinctorial properties

Hue, brightness, intensity and transparency for each shade were assessed in traces of change from the control paint for that shade. It is an internal method used in ICI Colours Division many years ago and still operated in the same laboratories of its successors. A ‘trace’ is the least perceptible difference to the average eye of a trained colourist. In practice, it is generally the lower end of the scale that is important and where there is little disagreement between trained observers as to what constitutes a trace. Large variations are less easily agreed. The scale contains values of 0 (meaning equal), 1, 2, 3, 4, 6, 8, 12 and 16 traces.

3.7.2. *Overspray fastness*

Full and reduced shade patterns were sprayed over with the thermosetting acrylic/melamine formaldehyde white paint system (ex Avecia) until full hide was achieved. These patterns were then stoved in an oven at 180 °C for 10 mins. The bleed into the white overspray patterns were assessed using the 1–5 International Grey Scale based on ISO 105 A03 (1994) for assessing staining by comparison with the corresponding white finish as control, 1 being least fast showing colour migration/staining into the top white coat and 5 being fully overspray fast showing no colour migration.

3.7.3. *Light fastness*

Full/reduced shade paint patterns were exposed to light in a Xenon arc tester until a change in shade (usually a fade in the colour) could be detected using the British Standard BS EN 20105-B02 (1993) Appendix A, blue wool scale (1–8), 1 being least fast, 8 being fully light fast indicating no discernible change.

3.7.4. *QUV durability (weatherfastness)*

The full, reduced and metallic shade pattern Q-panels were exposed on a QUV accelerated weathering tester machine for 1000 h with 8 h cycles of 4 h ultraviolet light followed by 4 h condensation. Each pattern is assessed for a change in colour on the 1–5 International grey scale (ISO 105 A02, 1994), 1 being least durable, 5 being fully durable and less than 4 being unacceptable for a high performance pigment.

4. Conclusions

The conversion of some vat dyes and their intermediates into pigments with good tinctorial properties can be achieved with limited success by a high energy bead milling pigmentation process. Yellow and orange pigments have been prepared with similar lightfastness, QUV durability and contact bleed properties as the commonly used isoindolinone Pigment Yellow 110 (**16**). The pigments with the best overall tinctorial properties are the carbazole, Vat Orange 15 (**15**), and the anthanthrone (**6**), although both suffer from a poor contact bleed problem. This overspray fastness problem may be due to the presence of impurities in the pigment and warrants further investigation into the syntheses of the carbazole (**15**) and anthanthrone (**6**), and alternative pigmentation processes to improve the tinctorial properties still further. Ultimately, none of the vat dyes or the intermediates investigated in this examination had the complete set of required properties of a high performance pigment to be used in the automotive industry. However, some of these vat dyes have attractive shades and lightfastness properties that they could be used in less demanding coating applications.

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