Available online at www.sciencedirect.com

SCIENCE DIRECT®

Dyes and Pigments 62 (2004) 235–248

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

Investigation of 1,1′,5,1″-trianthrimide as a potential high performance pigment

D. Thetford[a,*], A.P. Chorlton[b], J. Mason[a]

[a] Avecia Ltd, Research Department, PO Box 42, Hexagon House, Blackley, Manchester M9 8ZS, UK
[b] Millennium Pharmaceuticals Ltd, Granta Park, Great Abington, Cambridge CB1 6ET, UK

Received 29 September 2003; received in revised form 9 December 2003; accepted 9 December 2003

Abstract

1,1′,5,1″-Trianthrimide (**1**) has been synthesised by two methods utilising different raw materials but the same reaction conditions. The crude products were pigmented by different methods and these potential pigments have been tested alongside an anthraquinone red, Pigment Red 177, and a perylene red, Pigment Red 179, in a thermosetting acrylic/melamine formaldehyde resin paint system. Light fastness, durability and contact bleed properties were obtained for these samples in full, reduced and metallic shades. Results have shown that this pigment does have excellent tinctorial properties as well as good lightfastness, durability and overspray fastness properties depending on the method of synthesis and the method of pigmentation.

© 2003 Elsevier Ltd. All rights reserved.

Keywords: Trianthrimide; Pigments; Synthesis; Paint; Light fastness; Durability

---

1. Introduction

As part of our research programme into developing alternative organic yellow and orange pigments for plastics colouration and the automotive paint industry [1–4], a survey of vat dyes and their intermediates, in which properties such as high melting points above 300 °C, no or very low solubility in organic solvents, and strong tinctorial properties were required, had been conducted. From this survey, a previously used, maroon colourant for viscose, 1,1′,5,1″-trianthrimide (**1**), had come to our attention and warranted further investigation into its use as a high performance pigment [5]. This compound had also been patented as a pigment in a number of applications including pigmentation of plastics [6] and as a dye for PVC [7]. Our initial work which is not reported here in any detail, was targeted at the colouration of plastics with a small amount of testing work done in paints. The results of this work indicated that 1,1′,5,1″-trianthrimide (**1**) had good tinctorial properties but was found to be too dull to be of commercial interest. A new high performance pigment must have excellent lightfastness (6–7 minimum) and durability (weatherfastness) properties (4–5 minimum over 9 weeks exposure) in both full

---

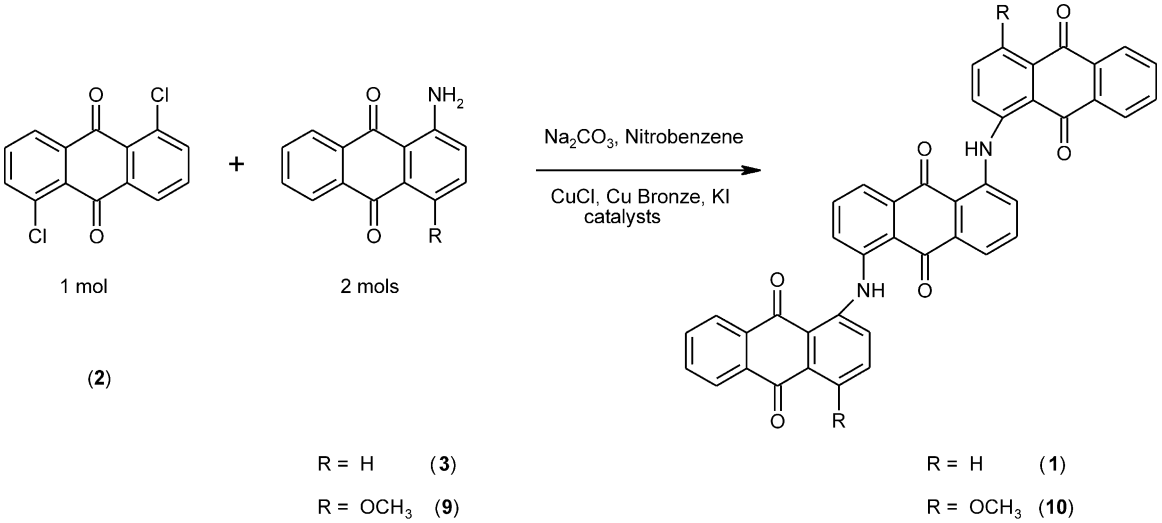
* Corresponding author. Tel.: +44-161-721-1401; fax: +44-161-721-5240.
E-mail address: dean.thetford@avecia.com (D. Thetford).

0143-7208/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2003.12.009

and reduced shades. It must also have good overspray fastness properties, ie. not suffer from contact bleed. 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 trianthrimide chromogen worthy of reappraisal.

2. Results and discussion

1,1′,5,1″-Trianthrimide (**1**) was obtained in excellent yield by reacting 1,5-dichloroanthraquinone (**2**) with 1-aminoanthraquinone (**3**) in nitrobenzene with a copper salt catalyst, see Scheme 1. The crude pigment was pigmented with hot dimethylformamide, then dispersed into a thermosetting acrylic/melamine formaldehyde resin (TSA/MF) paint system and coated or sprayed on various substrates to ascertain its tinctorial properties, light fastness, durability and overspray fastness in full, reduced and metallic shades. The results are shown in Tables 1–3 and compared with those of an anthraquinone red, Pigment Red 177 (**4**), and a perylene maroon, Pigment Red 179 (**5**), as controls. From these results, it was seen that 1,1′,5,1″-trianthrimide (**1**) was a dull, blue-shade red with good lightfastness and reasonable durability properties but not acceptable enough for automotive quality. However, when compared with the perylene maroon (**5**), it was shown to be a more attractive pigment in terms of the tinctorial properties, being bluer in



Scheme 1. Synthesis of 1,1′,5,1″-trianthrimide (**1**) and 4′,4″-dimethoxy-1,1′,5,1″-trianthrimide (**10**) by Route 1.

Table 1
Tinctorial properties of trianthrimide (**1**) in full shade, prepared by route 1

Pigment	Hue[a]	Brightness[a]	Intensity[a]	Opacity[a]	QUV durability	Light fastness	Overspray fastness
1	−4	−4	8	6	4	7	3
4	0	4	−8	−10	4–5	6–7	5
5[b]	0	0	0	0	4–5	6–7	5

[a] Hue + = yellower, − = bluer. Brightness, + = brighter − = duller. Intensity + = more intense, − = less intense. Opacity + = more opaque, − = less opaque.

[b] Pigment Red 179.

Table 2
Tinctorial properties of trianthrimide (**1**) in reduced shade, prepared by route 1

Pigment	Hue[a]	Brightness[a]	Strength[c]	QUV durability	Light fastness	Overspray fastness
1	−8	2	95:100	4	7	4
4	0	6	90:100	4–5	7	5
5[b]	0	0	100:100	4–5	6–7	5

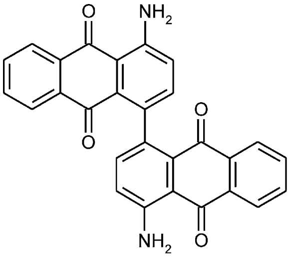
[a] Refer to Table 1.
[b] Refer to Table 1.
[c] Strength <100 = stronger, >100 = weaker.

Table 3
Tinctorial properties of trianthrimide (**1**) in metallic shade, prepared by route 1

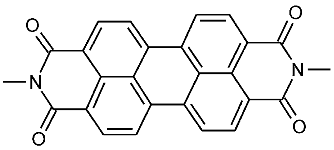
Pigment	Hue[a,d]	Brightness[a,d]	Intensity[a,d]	Flip/Flop[d]	QUV durability[d]	Light fastness[d]
1	−8	4	2	neutral	4	7
4	4	10	2	neutral	4–5	7
5[b]	0	0	0	neutral	4–5	7

[a] Refer to Table 1.
[b] Refer to Table 1.
[d] For 70/30 colour/aluminium metallic patterns.

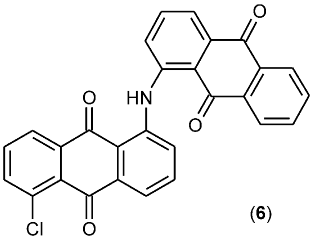
shade, brighter and more intense. Unfortunately, the trianthrimide (**1**) was not overspray fast and this confirmed previous work which indicated that the trianthrimide, prepared by the above route, suffers from poor contact bleed in PVC [8]. This behaviour has been attributed to the presence of trace amounts of 5-chloro-1,1-dianthrimide (**6**).



(**4**)



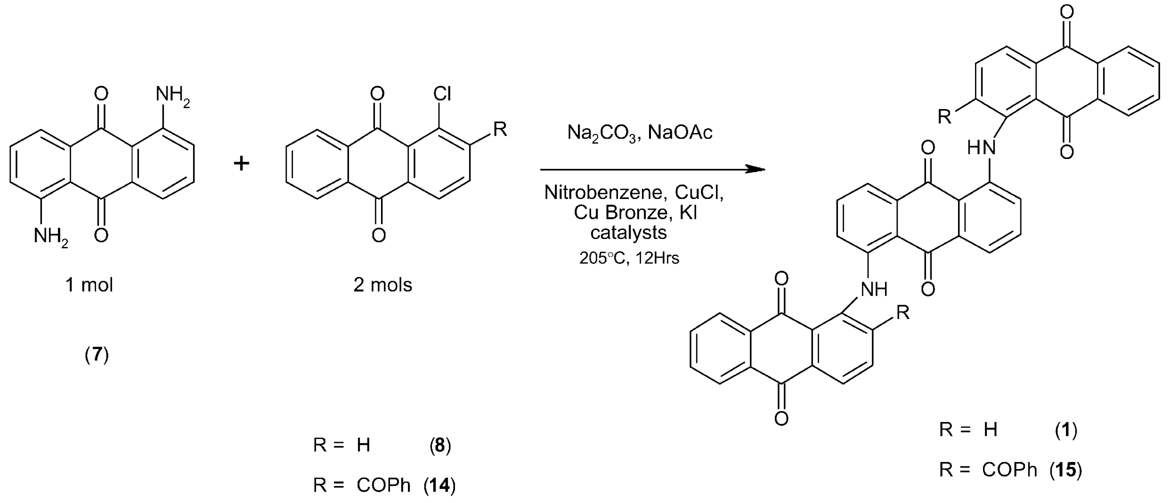
(**5**)



(**6**)

The trianthrimide (**1**) was then prepared in good yield by reacting 1,5-diaminoanthraquinone (7) with 1-chloroanthraquinone (8) in nitrobenzene using the same catalyst and reaction conditions as in the first route, see Scheme 2. Again, the crude pigment from this reaction was pigmented using hot dimethylformamide and similarly tested in the TSA/MF resin paint system. The results of the tinctorial properties of this trianthrimide sample are shown in Tables 4 and 5. In this case, the pigment was found to have excellent contact bleed, durability and lightfastness properties. Thus, the overspray fastness problem had been overcome and the lightfastness and durability properties had been improved by the use of alternative raw materials. However, the negative features of this trianthrimide sample were its weakness and dullness. These properties may be inherent in the trianthrimide chromogen or may be a consequence of particle size. The latter explanation seems to offer the best solution since the trianthrimide made by the first route was significantly stronger and brighter.

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 micron. They are subsequently reduced to pigmentary size (0.05–0.5 micron) either by attrition (milling) or by a reprecipitation process. In our previous work on vat dyes [4], a more detailed description of the batchwise, high energy bead milling was given. For the other pigmentation process employed in this investigation (reprecipitation), a concentrated sulphuric acid solution of the crude pigment was made and then blown through a narrow venturi



Scheme 2. Synthesis of 1,1′,5,1″-trianthrimide (**1**) and 2′,2″-dibenzoyl-1,1′,5,1″-trianthrimide (**15**) by Route 2.

Table 4
Tinctorial properties of trianthrimide (**1**) in full shade, prepared by route 2

Pigment	Hue[a]	Brightness[a]	Intensity[a]	Opacity[a]	Light fastness	Overspray fastness
1	−12	12	4	0	7	5
5[b]	0	0	0	0	6–7	5

[a] Refer to Table 1.
[b] Refer to Table 1.

Table 5
Tinctorial properties of trianthrimide (**1**) in reduced shade, prepared by route 2

Pigment	Hue[a]	Brightness[a]	Strength[c]	Light fastness	Overspray fastness
1	−16	0	160:100	7	5
5[b]	0	0	100:100	6–7	5

[a] Refer to Table 1.
[b] Refer to Table 1.
[c] Refer to Table 2.

into water (turbulent drown-out). This precipitated the pigment into a very fine form. The particle size of the pigment can be controlled to a certain extent by addition of solvents such as nitrobenzene or surfactants to the sulphuric acid solution, additions of larger amounts giving larger particle size.

Each of these techniques are used to give specific grades of pigment. High energy milling generally gives larger particle sizes thus giving opaque pigments whereas turbulent drown-out gives a smaller particle size pigment which are more transparent. Both of these techniques were used to pigment trianthrimide (**1**) prepared by the second route [1,5-diaminoanthraquinone (**7**) with 1-chloroanthraquinone (**8**)]. The pigment samples were dispersed in the TSA/MF resin paint system and coated or sprayed on various substrates to ascertain their tinctorial properties, light fastness, durability and overspray fastness in full, reduced and metallic shades. The results are shown in Tables 6–8 for the milling and drown-out samples.

Table 6
Tinctorial properties of trianthrimide (**1**) in full shade, prepared by route 2

Pigment	Hue[a]	Brightness[a]	Intensity[a]	Opacity[a]	QUV durability	Light fastness	Overspray fastness
1[e]	−60	3	8	6	4–5	7	5
1[f]	−70	6	16	−2	4–5	7	4–5
5[b]	0	0	0	0	4–5	6–7	4–5

[a] Refer to Table 1.
[b] Control.
[e] High energy bead milling sample.
[f] Turbulent drown-out sample.

Table 7
Tinctorial properties of trianthrimide (**1**) in reduced shade, prepared by route 2

Pigment	Hue[a]	Brightness[a]	Strength[c]	Light fastness	Overspray fastness
1[e]	−32	−12	70:100	7	5
1[f]	−31	4	70:100	7	5
5[b]	0	0	100:100	6–7	5

[a] Refer to Table 1.
[b] Refer to Table 1.
[c] Refer to Table 2.
[e] Refer to Table 6.
[f] Refer to Table 6.

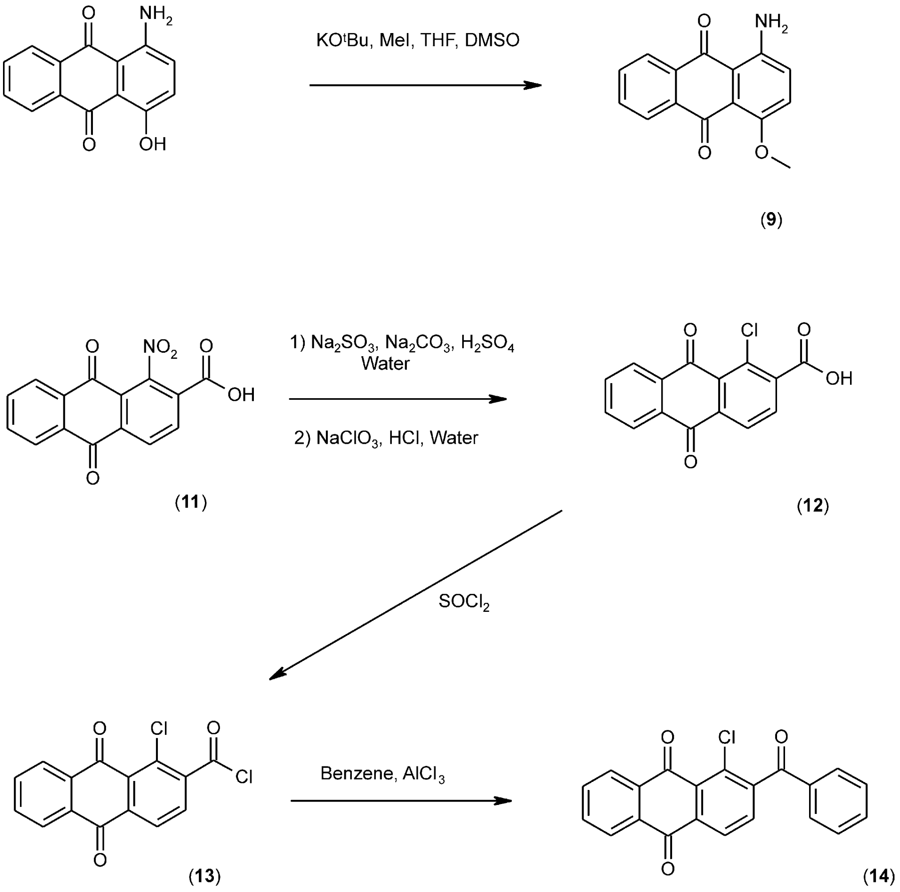
Table 8
Tinctorial properties of trianthrimide (**1**) in metallic shade, prepared by route 2

Pigment	Hue[a,d]	Brightness[a,d]	Intensity[a,d]	Flip/Flop[d]	QUV durability[d]	Light fastness[d]
1[e]	−66	−6	2	redder	4–5	7
1[f]	−60	6	6	redder	4–5	7
5[b]	0	0	0	neutral	4–5	7

[a] Refer to Table 1.
[b] Refer to Table 1.
[d] Refer to Table 3.
[e] Refer to Table 6.
[f] Refer to Table 6.

From these results, it was seen that high energy bead milling gave a much more attractive product in terms of tinctorial properties than the previous DMF pigmentation process. The pigment has altered so much in shade, it could now be classed as a violet and not a maroon and it was not readily comparable with Pigment Red 179 because it was 60–70 traces bluer in full shade. It was also considerably stronger and more intense than earlier samples. The turbulent drown-out pigmentation process has provided a further step improvement in terms of hue, brightness and intensity both in reduced and metallic shades. QUV durability was acceptable in all depths of shade and with incorporation of aluminium. However, the only true guide to assess the weather durability of pigments is Florida (1–2 years) exposure tests. Samples of trianthrimide (**1**) have been sent to Florida and the results are awaited.

The pigmentary properties found in 1,1′,5,1″-trianthrimide (**1**) may be present in other analogues that could give alternative shades. Our investigation has examined several other trianthrimides (**10**,**15**,**18**), prepared in a similar manner to the trianthrimide (**1**), see Schemes 1, 2 and 5, using various substituted anthraquinones. These anthraquinone intermediates were prepared by the following methods, see Schemes 3 and 4. The aminoanthraquinone (**9**) was obtained in good yield using the method of Isobe [9], see Scheme 3, by selective *O*-methylation of 1-amino-4-hydroxyanthraquinone. Reaction of methoxy substituted aminoanthraquinone (**9**) and 1,5-dichloroanthraquinone (**2**) gave the dimethoxytrianthrimide



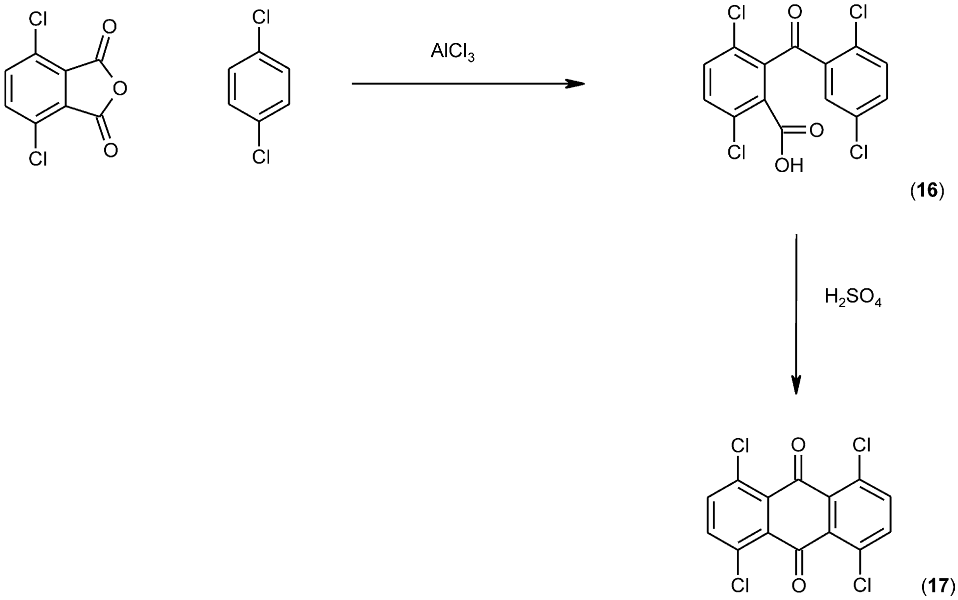
Scheme 3. Synthesis of anthraquinone intermediates (**9**) and (**14**).

(**10**) in good yield using the route 1 procedure, see Scheme 1.

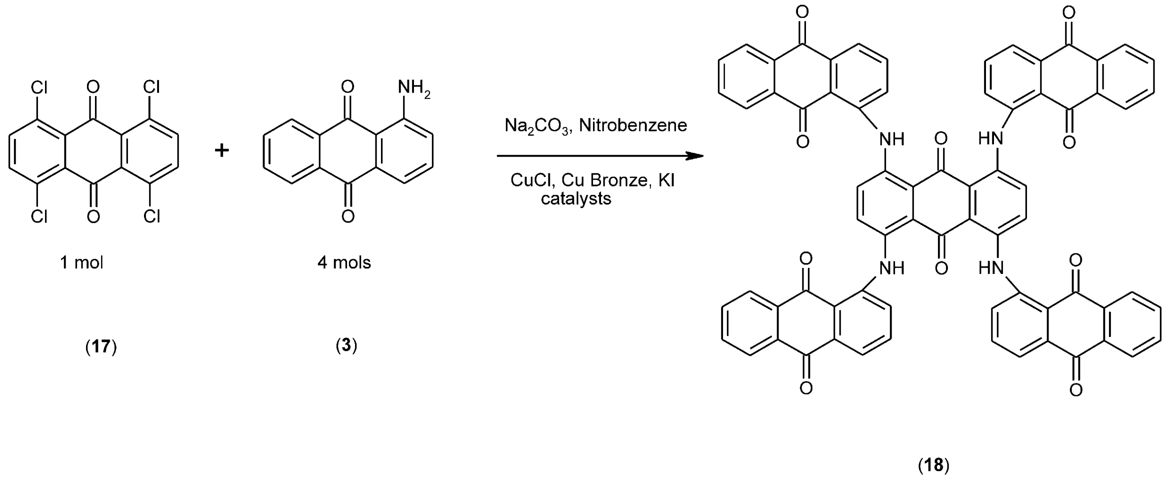
However, the dibenzoyl substituted trianthrimide (**15**) was prepared from the benzoyl substituted anthraquinone (**14**) and 1,5-diaminoanthraquinone (**7**) in good yield by the route 2 procedure, see Scheme 2. The preparation of the benzoylanthraquinone (**14**) was achieved via a 5 stage synthesis from 2-methylanthraquinone in moderate overall yield, see Scheme 3. 2-Methylanthraquinone was converted to the 2-carboxy-1-nitroanthraquinone (**11**) in moderate yield by nitration to 2-methyl-1-nitroanthraquinone using the method of Peters [10] and then subsequent chromate oxidation of the methyl group to the carboxylic acid moiety using the method of Brown [11]. The nitroanthraquinone (**11**) was converted to the 2-carboxy-1-chloroanthraquinone (**12**) in good yield via the sodium salt of the sulfo-carboxy intermediate using the method of Scalera [12] with sodium sulphite and sodium chlorate. Conversion to the acid chloride (**13**) was achieved using thionyl chloride and subsequent Friedel–Crafts acylation of benzene gave the benzoylanthraquinone (**14**) in excellent yield.

The pentanthrimide (**18**) was prepared from 1-aminoanthraquinone (**3**) and the tetrachloro substituted anthraquinone (**17**) using the route 1 procedure, see Scheme 5. The tetrachloroanthraquinone (**17**) was synthesised by the Friedel–Crafts acylation of 1,4-dichlorobenzene by 3,6-dichlorophthalic anhydride to give the benzoyl benzoic acid (**16**) in very good yield and then cyclisation to the anthraquinone (**17**) using sulphuric acid in excellent yield, see Scheme 4.

All the trianthrimide analogues (**10**, **15** and **18**) were pigmented using the DMF pigmentation process and similarly to the trianthrimide (**1**) were dispersed into the TSA/MF resin paint system and then coated or sprayed on various substrates to ascertain their tinctorial properties, light fastness, durability and overspray fastness in full and reduced shades. The influence of a methoxy substituent in the trianthrimide (**10**) exerted a bathochromic shift on the chromogen giving a violet pigment. This compound was tested against two violet pigment controls, a β-quinacridone, Pigment Violet 19 (**19**) and a dioxazine, Pigment Violet 23 (**20**). However, the methoxytrianthrimide (**10**) was tinctorially very difficult to assess because it was so weak and so only lightfastness, durability and contact bleed were measured. The results are given in Table 9. The benzoyl trianthrimide (**15**) and pentanthrimide (**18**) both have similar hues to



Scheme 4. Synthesis of anthraquinone intermediate (**17**).



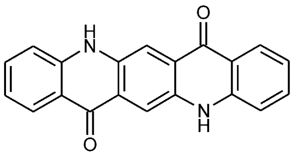
Scheme 5. Synthesis of 1,1′,4,1″,5,1‴,8,1⁗-pentanthrimide (**18**) by Route 1.

Table 9
Paint properties of methoxytrianthrimide (**10**)

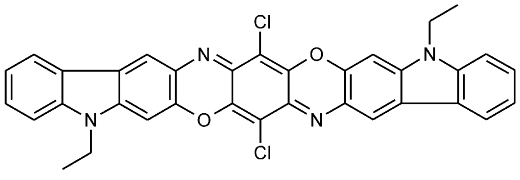
Pigment	QUV durability	Light fastness[a]	Light fastness[b]	Overspray fastness[a]	Overspray fastness[b]
10	4	7	6	5	5
19	5	6–7	7	4–5	4–5
20	5	6	7	5	5

[a] In full shade.
[b] In reduced shade.

the parent trianthrimide (**1**) and were tested against the perylene maroon (**5**). The results for these pigments are shown in Tables 10 and 11.



(**19**)



(**20**)

From the results, it was seen that the methoxytrianthrimide (**10**) had better lightfastness in full paint shade compared to the controls but lower lightfastness in reduced shade and lower durability. The benzoyltrianthrimide (**15**) was weak in reduced shade and had unacceptable durability although lightfastness and overspray fastness were comparable to the controls in both full and reduced shade. The pentanthrimide (**18**) was also weak and dull in reduced shades and it had acceptable light fastness and overspray fastness properties but it had unacceptable durability. These poor results may be due to the pigmentation technique used to isolate these analogues but even so they do not compare well to the samples of the parent trianthrimide (**1**) pigmented by the same technique (see Tables 1–5). Further work in this area was not pursued.

Table 10
Tinctorial properties of benzoyltrianthrimide (**15**) and pentanthrimide (**18**) in full shade

Pigment	Hue[a]	Brightness[a]	Intensity[a]	Opacity[a]	Light fastness	Overspray fastness
15	0	8	−4	4	6–7	5
18	−16	−8	12	−2	6–7	5
4	0	4	−8	−10	6–7	5
5[b]	0	0	0	0	6–7	5

[a] Refer to Table 1.
[b] Refer to Table 1.

Table 11
Tinctorial properties of benzoyltrianthrimide (**15**) and pentanthrimide (**18**) in reduced shade

Pigment	Hue[a]	Brightness[a]	Strength[c]	QUV durability	Light fastness	Overspray fastness
15	−8	4	160:100	2	6	5
18	−8	−4	170:100	3	6–7	5
4	0	6	90:100	4–5	7	5
5[b]	0	0	100:100	4–5	7	5

[a] Refer to Table 1.
[b] Refer to Table 1.
[c] Refer to Table 2.

3. Experimental

3.1. General

Unless otherwise stated, all chemicals were purchased from Aldrich Chemical Co. (Milwaukee, WI, USA) and were used without further purification. 1-Amino-4-hydroxyanthraquinone and 2-methylanthraquinone were purchased from Avocado Research Chemicals Ltd (Heysham, UK). All solvents were purchased as GPR grade from Fisher Scientific UK Ltd (Loughborough, UK) and were used without further purification or drying unless otherwise stated in which case solvents were dried using the methods given by Perrin [13]. Non-aqueous reactions were performed in a nitrogen atmosphere. Silica gel 60 (230–400 mesh) available from Merck was used for chromatography. 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 300M Hz instrument, a Micromass Platform II or 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 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 anthraquinone intermediates (*9,11–14,16,17*)

3.2.1. 1-Amino-4-methoxyanthraquinone (*9*)

1-Amino-4-methoxyanthraquinone (**9**) was prepared in 75% yield from 1-Amino-4-hydroxyanthraquinone by a modification of the method of Isobe [9]. The reactants were stirred at room temperature for 5 h. The isolated reaction product was filtered through a silica pad using dichloromethane as eluant. The anthraquinone (**9**) (R_f 0.06) was isolated as a purple solid, m.p. 182–4 °C; δ 3.85 (3H, s, OCH_3), 7.28 (1H, d, J 9.5 Hz, aromatic H_2), 7.51 (1H, d, J 9.5 Hz, aromatic H_3), 7.85 (2H, m, aromatic $H_{6,7}$), 7.97 (2H, bs, NH_2), 8.06 (1H, m, aromatic H_8), 8.15 (1H, m, aromatic H_5); m/z 254 ($M^+ + H$, 100%). Elemental analysis required for $C_{15}H_{11}NO_3$; C, 71.1; H, 4.4; N, 5.5. Found: C, 71.0; H, 4.4; N, 5.5.

3.2.2. 2-Carboxy-1-nitroanthraquinone (*11*)

2-Carboxy-1-nitroanthraquinone (**11**) was prepared in 40% overall yield from 2-methylanthraquinone via 2-methyl-1-nitroanthraquinone using the methods of Peters [10] and Brown [11] respectively.

3.2.3. 2-Carboxy-1-chloroanthraquinone (*12*)

Sodium sulfite (75 g 595 mmols) was added to a stirred solution of 2-carboxy-1-nitroanthraquinone (59.5 g 200 mmols) and sodium carbonate (11.2 g 106 mmols) in water (800 ml) at 60 °C. The whole mixture was stirred at reflux for 16 h and then concentrated sulphuric acid (54 ml) was added gradually. The mixture was filtered hot and the filtrate was cooled in ice to precipitate the sodium salt of sulphoanthraquinone carboxylic acid. This yellow solid was filtered off and suspended in a mixture of water (800 ml) and concentrated hydrochloric acid (200 ml). The mixture was stirred at reflux and then sodium chlorate (42 g 395 mmols) in water (200 ml) was added over 4 h to the boiling solution. The mixture was stirred at reflux a further 4 h, then cooled to room temperature and filtered to give a pale yellow solid (37.3g 65%), m.p. 268–72 °C, (lit. m.p. 271–2 °C [12]); δ 7.85–7.95 (2H, m, aromatic $H_{6,7}$), 7.98 (1H, d, J 7.8 Hz, aromatic H_3), 8.13–8.2 (2H, m, aromatic $H_{5,8}$), 8.24 (1H, d, J 7.8 Hz, aromatic H_4); m/z 286 (M^+, 100%). Elemental analysis required for $C_{15}H_7ClO_4$; C, 62.85; H, 2.45; Cl, 12.35. Found: C, 62.7; H, 2.5; Cl, 12.7.

3.2.4. 2-Chloroacyl-1-chloroanthraquinone (*13*)

2-Carboxy-1-chloroanthraquinone (**12**) (37 g 129 mmols) was added gradually to stirred thionyl chloride (200 g 1681 mmols) at room temperature over 1 h, some effervescence was observed. The mixture was stirred at reflux for 4 h, cooled to 0 °C and then a solid was filtered off. The yellow solid (**13**) was washed with cold toluene (100 ml) and then dried (29.6 g 75%), m.p. 210–13 °C.

3.2.5. 2-Benzoyl-1-chloroanthraquinone (*14*)

2-Chloroacyl-1-chloroanthraquinone (**13**) (26.6 g 87 mmols) was slurried in dry benzene (100 ml) at room temperature. Powdered aluminium chloride (13.3 g 50 mmols) was added fairly rapidly to the stirred mixture and the temperature was raised to 60 °C and maintained at this temperature for 30 min. More powdered aluminium chloride (13.3 g 50 mmols) was added over 1 hour to the mixture and this was stirred at 60 °C for a further 5 h. The mixture was added to ice water (1000 ml), the excess benzene was removed by steam distillation and a yellow solid was filtered off. The solid was slurried in hot, aqueous 0.5M HCl solution (300 ml), filtered off, then slurried in hot, aqueous 0.5M sodium hydroxide solution (200 ml) and filtered off once again. The solid was washed alkaline free with water (2 × 100 ml) and finally dried to give a yellow solid (27.5g 91%), m.p. 194–96 °C; δ 7.56 (2H, td, J 7.5, 1.5 Hz, aromatic $H_{3',5'}$), 7.71 (1H, tt, J 7.5, 1.5 Hz, aromatic $H_{4'}$), 7.78 (2H, dt, J 7.5,1.5 Hz, aromatic $H_{2',6'}$), 7.88–7.98 (3H, m, aromatic $H_{3,6,7}$), 8.2 (2H, m, aromatic $H_{5,8}$), 8.34 (1H, d, J 8.2 Hz, aromatic H_4); m/z 346 (M^+, 70%). Elemental analysis required for $C_{21}H_{11}ClO_3$, C, 72.75, H, 3.2, Cl, 10.2. Found: C, 72.4, H, 3.3, Cl, 9.9.

3.2.6. 2-(2′5′-Dichlorobenzoyl)-3,6-dichlorobenzoic acid (*16*)

3,6-Dichlorophthalic anhydride (43.4 g 200 mmols) was stirred in 1,4-dichlorobenzene (430 g 2925 mmols) at 180 °C until a solution was evident. Powdered aluminium chloride (87 g 327 mmols) was added portionwise over 1 h (large quantities of HCl was evolved) and then the mixture was stirred at 200 °C for 2 h and then allowed to cool to room temperature. Water (250 ml) was added dropwise to the mixture and then the dichlorobenzene was removed by steam distillation. The aqueous liquors were decanted from a tarry residue and then aqueous 10% sodium carbonate solution (500 ml) was added to the residue. The mixture was steam distilled for 30 min and then filtered. The filtrates were acidified with concentrated HCl to precipitate a cream solid. The solid was filtered off, washed with more water (2×100 ml) and finally dried (61.2 g 84%), m.p. 207–9 °C (lit m.p. 214–15 °C [14]); m/z 362 (M^+, 15%). Elemental analysis, calculated for $C_{14}H_6Cl_4O_3$: C, 46.2; H, 1.65; Cl, 38.95. Found: C, 46.3; H, 1.6; Cl, 38.8.

3.2.7. 1,4,5,8-Tetrachloroanthraquinone (*17*)

2-(2′5′-Dichlorobenzoyl)-3,6-dichlorobenzoic acid (**16**) (61 g 168 mmols) was added over 30 min to stirring 100% sulphuric acid (30 ml) at 100 °C and then the mixture was stirred at 180 °C for 2 h. The mixture was cooled to room temperature and diluted with water (65 ml). The precipitated solid was filtered off, washed successively with water (200 ml), hot, aqueous 2 M sodium carbonate solution (100 ml), water (200 ml) and then finally dried. A lemon yellow solid was isolated (48.8g 84%), m.p. 353–4 °C (lit. m.p. 342–3 °C [14]); *m*/*z* 344 (M^+, 75%). Elemental analysis, calculated for $C_{14}H_4Cl_4O_2$; C, 48.6; H, 1.15; Cl, 41.0. Found: C, 47.9; H, 1.4; Cl, 41.7.

3.3. Synthesis of pigments (*1*,*10*,*15*,*18*)

3.3.1. 1,1′,5,1″-Trianthrimide (*1*)—preparation from 1,5-dichloroanthraquinone (Route 1)

A mixture of 1-aminoanthraquinone (22.53 g 101 mmols), 1,5-dichloroanthraquinone (13.83 g 50 mmols), sodium carbonate (10.6 g 100 mmols), cuprous chloride (0.15 g 2 mmols), copper bronze (0.15 g 2 mmols) and potassium iodide (0.05 g 0.3 mmols) was ground together. This material was then added evenly over 6 h to well stirred nitrobenzene (450 ml) at 205 °C. After the addition, heating was continued for 12 h at reflux and then the suspension was allowed to cool to 40 °C. The mixture was filtered and the isolated solid was washed with more nitrobenzene (50 ml), toluene (100 ml) and finally acetone (100 ml). The resultant solid was stirred in boiling DMF (250 ml), then filtered off hot, washed with cold DMF (100 ml) and finally water (1000 ml). The maroon solid was air dried at 95 °C (30.2g 93%); m.p. > 300 °C; *m*/*z* 651 ($M^+ + H$, 100%), also 463 [M^+, 2% evidence for dianthrimide (**6**)]. Elemental analysis, calculated for $C_{42}H_{22}N_2O_6$: C, 77.5; H, 3.4; N, 4.3. Found: C, 76.7; H, 3.4; N, 4.6.

3.3.2. 1,1′,5,1″-Trianthrimide (*1*)—preparation from 1,5-diaminoanthraquinone (Route 2)

A mixture of 1-chloroanthraquinone (48.5 g 200 mmol), 1,5-diaminoanthraquinone (23.8 g 100 mmol), sodium carbonate (10.6 g 100 mmol), sodium acetate (10.6 g 120 mmol), cuprous chloride (0.3 g 4 mmols), copper bronze (0.3 g 4 mmols) and potassium iodide (0.1 g 0.6 mmols) was ground together. This material was then added evenly over 6 h to well stirred nitrobenzene (900 ml) at 205 °C. After the addition, heating was continued for 12 h at reflux and then the suspension was allowed to cool to 40 °C. The mixture was filtered and the isolated solid was washed with more nitrobenzene (100 ml), toluene (200 ml) and finally acetone (200 ml). The resultant solid was stirred in boiling DMF (550 ml), then filtered off hot, washed with cold DMF (200 ml) and finally water (1000 ml). The red solid was air dried at 95 °C, (50.7g 78%); m.p. > 300 °C; *m*/*z* 651 ($M^+ + H$, 100%). Elemental analysis, calculated for $C_{42}H_{22}N_2O_6$: C, 77.5; H, 3.4; N, 4.3. Found: C, 76.9; H, 3.4; N, 4.6.

3.3.3. 4′,4″-Dimethoxy-1,1′,5,1″-trianthrimide (*10*) using Route 1

A mixture of 1-amino-4-methoxyanthraquinone (**9**) (15.5 g 61 mmols), 1,5-dichloroanthraquinone (8.31 g 30 mmols), sodium carbonate (6.40 g 60 mmols), cuprous chloride (0.15 g 2 mmols), copper bronze (0.15 g 2 mmols) and potassium iodide (0.05 g 0.3 mmols) was ground together. This material was then added evenly over 6 h to well stirred nitrobenzene (250 ml) at 205 °C. After the addition, heating was continued for 12 hours at reflux and then the suspension was allowed to cool to 40 °C. The mixture was filtered and the isolated solid was washed with more nitrobenzene (50 ml), toluene (100 ml) and finally acetone (100 ml). The resultant solid was stirred in boiling DMF (250 ml), then filtered off hot, washed with cold DMF (100 ml) and finally water (1000 ml). The violet solid was air dried at 95 °C, (16.2g 75%); m.p. > 350 °C; *m*/*z* 711 ($M^+ + H$, 100%). Elemental analysis, calculated for $C_{44}H_{26}N_2O_8$: C, 74.35; H, 3.7; N, 3.95. Found: C, 74.4; H, 3.3; N, 4.3.

3.3.4. 2′,2″-Dibenzoyl-1,1′,5,1″-trianthrimide (*15*) using Route 2

A mixture of 2-benzoyl-1-chloroanthraquinone (**14**) (23.5 g 68 mmols), 1,5-diaminoanthraquinone (8 g 34 mmols), sodium carbonate (3.60 g 34 mmols), cuprous chloride (0.15 g 2 mmols), copper bronze (0.15 g 2 mmols) and potassium iodide

(0.1 g 0.6 mmols) was ground together. This material was then added evenly over 2 h to well stirred nitrobenzene (250 ml) at 205 °C. After the addition, heating was continued for 12 h at reflux and then the suspension was allowed to cool to 40 °C. The mixture was filtered and the isolated solid was washed with more nitrobenzene (50 ml), toluene (100 ml) and finally acetone (100 ml). The resultant solid was stirred in boiling DMF (250 ml), then filtered off hot, washed with cold DMF (100 ml) and finally water (1000 ml). The maroon solid was air dried at 95 °C, (21.32 g 73%); m.p. >350 °C; *m/z* 859 (M^+ +H, 100%). Elemental analysis, calculated for $C_{56}H_{30}N_2O_8$: C, 78.3; H, 3.5; N, 3.25. Found: C, 77.9; H, 3.7; N, 2.9.

3.3.5. 1,1′,4,1″,5,1‴,8,1⁗-Pentanthrimide (**18**) using Route 1

A mixture of 1-aminoanthraquinone (27.9 g 125 mmol), 1,4,5,8-tetrachloroanthraquinone (**17**) (10.38 g 30 mmol), sodium carbonate (12.72 g 120 mmol), cuprous chloride (0.3 g 4 mmol), copper bronze (0.3 g 4 mmol) and potassium iodide (0.1 g 0.6 mmol) was ground together. This material was then added evenly over 6 h to well stirred nitrobenzene (500 ml) at 205 °C. After the addition, heating was continued for 12 h at reflux and then the suspension was allowed to cool to 40 °C. The mixture was filtered and the isolated solid was washed with more nitrobenzene (100 ml), toluene (200 ml) and finally acetone (200 ml). The resultant solid was stirred in boiling DMF (400 ml), then filtered off hot, washed with cold DMF (100 ml) and finally water (1000 ml). The maroon solid was air dried at 95 °C, (21.6g 68%), m.p. >350 °C; *m/z* 1093 (M^+ +H, 26%). Elemental analysis, calculated for $C_{70}H_{36}N_4O_{10}$: C, 76.9; H, 3.3; N, 5.1. Found: C, 76.5; H, 3.3; N, 4.6.

3.4. Pigmentation procedures

3.4.1. High energy milling

The trianthrimide sample (15 g), sodium dodecyl sulphate (5.5 g) were stirred in water (100 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.

3.4.2. Turbulent drown-out

The trianthrimide sample (30 g) was dissolved in a solution of 96% sulphuric acid (345 g), (338 g of 98% sulphuric acid + 7g water), with stirring. Solsperse® 24000 (ex Avecia) (0.3 g) was added to the solution and then the whole mixture was screened through a copper sieve (0.5 micron). The solution was then drowned out through a narrow venturi (2 mm jet size) using 10 psi pressure into water (2375 ml). The resultant suspension was filtered and the solid was washed acid free with distilled water. The filter cake was slurried in water (300 ml) containing calsolene oil (6 drops) and a surfactant, Synperonic® NP4 (ex ICI) (1.75 g). The slurry was steam distilled for 3 h and then the pigment was filtered off and dried in an oven at 65 °C.

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 (**5**) was a perylene maroon, Pigment Red 179, available from BASF under the tradename, Paliogen® Maroon L4020. The anthraquinone red (**4**) used in the preliminary tests is a Pigment Red 177 available from Ciba under the tradename, Cromophtal® Red A3B. The β-quinacridone violet and dioxazine violet used as controls for the trianthrimide (**10**) are Pigment Violet 19 and 23 respectively. Both are available from Heubach under the tradenames Monolite® Violet 4R and Monolite® Violet RN respectively.

3.5.1. Millbase

Glass beads (3 mm) (125 g) were weighed into a 140 ml screw cap bottle. Into this, a 50% H190-315 thermosetting acrylic resin (ex PPG autocolor, supplied as 50% solids 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 the mixture was homogeneous and then shaken on a Red Devil shaker for 30 min. 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 was added 50% H190-315 thermosetting acrylic resin (43.4 g) carefully as follows: 2 g, 4 g, 8 g, 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) (29.7 g) and xylene (2.5 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 micron bar. The paint was allowed to air dry for 15 min and then stoved at 120 °C for 30 min.

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) were added. The contents were mixed thoroughly by rolling on a mill until the mixture is visually homogeneous. The reduced shade paints were sprayed on white card (Spray booth/gun AGG-500 series ex De Vilbiss co), 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 litre 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 (167.5 g) and xylene (32.5 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 litre paint can, 50% H190-315 thermosetting acrylic resin (225.6 g), Cymel® 615 resin (126 g), 1-methoxy-2-propanol acetate (230 g) and toluene (69 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 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 min. 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 fade could be detected using the British standard BS EN 20105-B02 (1993) Annex A, blue wool scale (1–8), 1 being least fast, 8 being fully light fast indicating no discernible change.

3.7.4. QUV durability

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

1,1′,5,1″-Trianthrimide (**1**) prepared from 1,5-diaminoanthraquinone (**7**) and 1-chloroanthraquinone (**8**) and pigmented by high energy bead milling or a turbulent drown out procedure gives a very attractive violet-maroon pigment of commercial interest. Pigmented trianthrimide (**1**) looks a very attractive product which occupies a position in colour space not achievable using currently available pigments and has acceptable lightfastness, durability and overspray fastness properties for use in high quality coating and plastics colouration. All of these properties including tinctorials were dependant on two factors, the raw materials employed to prepare the crude pigment and the method of pigmentation used to make the final pigment product. The former ultimately controls the type of impurities generated in the crude pigment whereas both factors control the amount of impurities present and the latter controls the particle size of the pigment. Investigations into alternative trianthrimides as high performance pigments, has proved unsuccessful.

Acknowledgements

The authors are grateful to Peter Livesey of Avecia Ltd for testing in paints and William Allen of Avecia Ltd for helpful discussions.

References

[1] Chorlton AP, Mason J. EP 553 965, 1993, (to Avecia Ltd).
[2] Chorlton AP, Mason J. EP 804 509, 1995, (to Avecia Ltd).
[3] Chorlton AP, Hardman J, Thetford D. Dyes Pigm 2003;59(2):185–91.
[4] Chorlton AP, Thetford D. Dyes Pigm 2004;61(1):49–62.
[5] Ackroyd P, Irving F. GB 867 983, (to ICI), 10/05/61.
[6] Deverell-Smith R. GB 983 381, (to ICI), 28/02/63.
[7] Caliezi A. DE 1 100 943, (to Ciba), 09/10/59.
[8] Avecia Ltd. Internal Report.
[9] Okita T, Isobe M. Tetrahedron 1994;50(38):11143–52.
[10] Wood GD, Peters AT. J Chem Soc 1962:3373–8.
[11] Bennett S, Sharples D, Brown JR. J Med Chem 1982;25(4):369–73.
[12] Scalera M. US 2 499 003, (to American Cyanamid), 02/11/46.
[13] Perrin DD, Armarego WLF, Perrin DR. Purification of laboratory chemicals. Pergamon Press; 1966.
[14] Naiki K. J Soc Org Synthet Chem Japan 1955;13:72–8.