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Macromolecular Azo Pigments

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SUMMARY

Bis-amino azo colours have been polymerised to high molecular weight pigments by condensation with cyanuric chloride, or by conversion to acryloylamido derivatives followed by free-radical induced polymerisation. The products are of high colour value and have low solubility in solvents used in surface coatings.

1. INTRODUCTION

The fastness properties of a pigment are generally dependent on its chemical constitution, and the size of the molecule is of great importance. Amongst other considerations, a sufficiently high molecular weight is necessary to ensure resistance to sublimation and an acceptable degree of insolubility in dispersion media. Simple azo pigments are generally more susceptible to degrading influences such as sunlight and chemical attack, and to bleeding in commercial vehicles, than azo condensation[1] and benzidine pigments.

An attempt to improve the properties of simple azo pigments by Nejatpour[2] produced pigments of the general formula **I** for conversion into macromolecular structures. The functionality of products was a reference to the number of amino groups, which were used to react in various ways to increase the molecular weight of the pigment finally produced, e.g. by polymerisation. The mono-functionality of these

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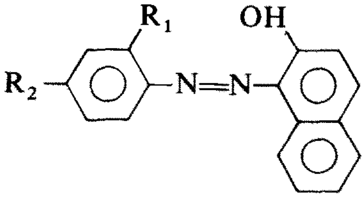


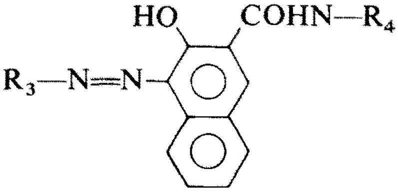
I: $R_1 = NH_2$, $R_2 = H$ or CH_3

compounds imposed limitations on the maximum molecular weight obtainable. Thus condensation with compounds which readily take part in substitution reactions are limited by the functionality of the molecular taking part in the reactions and consequently the highest molecule weight product obtainable with cyanuric chloride was limited to tri-substitution products.

Introduction of reactive polymerisable acryloylamido groups into the amino azo compounds produced monomers which would readily take part in polymerisation. However, if the reacting acryloylamido group was in the *ortho* position to the azo linkage, strong steric effects opposed the production of high molecular weight products. Copolymerisation with low molecular weight colourless compounds gave products of higher molecular weights but of low colour value, e.g. Nejatpour obtained products of the order, ratio of coloured pigment:colourless monomer (acrylonitrile), 1:43.

The compounds described in the present work are bis-functional, with at least one amino or reactive group positioned on a pendant part of the molecular structure. This is not subject to such stringent spatial restrictions as those encountered with monofunctional compounds where the amino (or reactive) group is part of the chromophore. At least one amino or reactive group is not rigidly fixed to the planar *trans*-azo section of the pigment as in Nejatpour's work. The compounds of this present study can be represented by the general formula **II**.

Naphthol Reds, which form the basis of this work, possess good durability, good chemical resistance (including soap resistance) and better light fastness compared with simple azo pigments. This is



II

attributed to the presence of the amide group, which gives the molecule more flexibility and increased intercrystalline bonding.

The bis-functional compounds described are capable of readily reacting with cyanuric chloride to give, in addition to the tri-substitution products obtainable with monofunctional compounds, products which may be linear polymers of high molecular weight. The tri-functionality of cyanuric chloride should make possible crosslinking to give thermosetting polymers, which are highly insoluble in organic media. Furthermore, because the colourless cyanuric chloride structure forms a relatively small proportion in the structure of such a highly crosslinked compound, a polymer is produced with high colour value.

Bis-functional amino-azo compounds with addition-reactive polymerisable groups such as acryloylamido are capable of polymerising to very high molecular weights, with possible crosslinking taking place. This produces pigments which will not dissolve in most of the common solvents encountered in surface coatings. The solvent resistance of such pigments is very high, and there is an increase in all-round fastness properties. The colour value is at least as high as that of any conventional pigment.[3]

2. EXPERIMENTAL

2.1. Coupling components

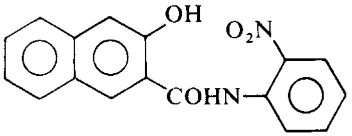
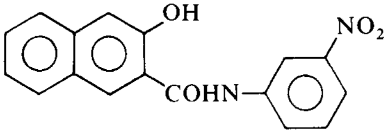
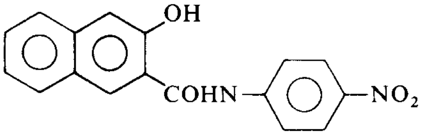
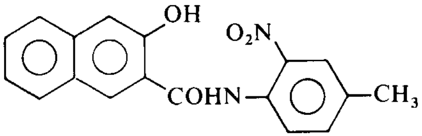
Nitroarylamides of 2-hydroxy-3-naphthoic acid (BONA) were prepared as couplers by modifying the method first reported by Chemische Fabrik Griesheim–Elektron[4] to give good yields and products which were easy to purify. A mixture of equimolar proportions of 2-hydroxy-3-naphthoic acid and a primary aromatic nitroamine (or amide such as *p*-aminobenzamide) were condensed in the presence of 2 moles of a condensing agent. The reaction took place in a boiling solvent such as chlorobenzene, *o*-dichlorobenzene, toluene or xylene. The principal condensing agent was phosphorus trichloride; thionyl chloride and phosphorus pentachloride were also employed (see Table 1).

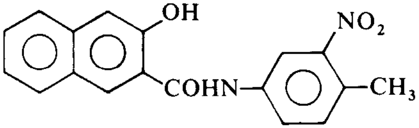
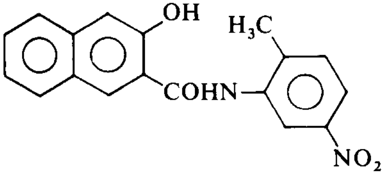
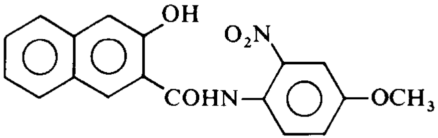
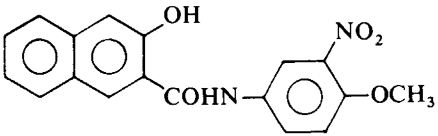
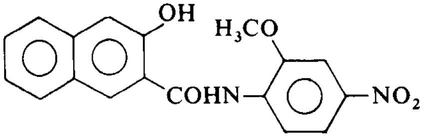
2.2. Nitro-azo pigments

The nitro-azo pigments were obtained by standard diazotisation and coupling methods. The diazo compounds were nitroarylamines with not

TABLE 1

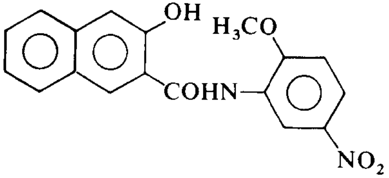
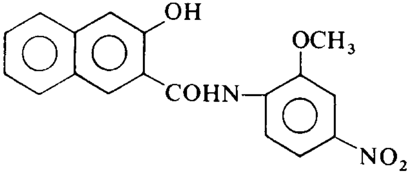
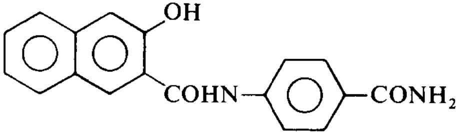
2,3-Hydroxynaphtharylides Prepared as Intermediates or Coupling Components for Further Reaction

Nitroarylamide of BONA	*Solvent/condensing agent*	*Yield (%)*	*Crystallised from*	*Colour*	*Melting point (°C)*
	Toluene/$SOCl_2$	81	Xylene	Intense yellow	192–193
	Toluene/PCl_3	82	Acetic acid	Pale yellow	247
	Toluene/PCl_5	49	Dichlorobenzene	Greenish yellow	258
	Chlorobenzene/PCl_3	68	Dichlorobenzene	Greenish yellow	217–219

	Chlorobenzene/PCl_3	73	Dichlorobenzene	Pale yellow	222–223
	Xylene/$SOCl_2$	65	Chlorobenzene	Yellow	236–237
	Dichlorobenzene/PCl_3	63	Chlorobenzene	Pale yellow	241
	Toluene/PCl_5	79	Acetic acid	Yellow	225
	Toluene/$SOCl_2$	58	Chlorobenzene	Pale yellow	229

(contd)

TABLE 1—*contd.*

Nitroarylamide of BONA	*Solvent/condensing agent*	*Yield (%)*	*Crystallised from*	*Colour*	*Melting point (°C)*
	Xylene/PCl_5	67	Chlorobenzene	Pale yellow	225–226
	Toluene/PCl_3	66	Chlorobenzene	Yellow	233–234
	Toluene/PCl_3	65	Acetic acid	Grey	203

more than one methyl or methoxy group as an additional substituent on the phenyl structure.

Because of the very low solubility of the products, the process of producing bis-nitro pigments is not always straightforward. A finely divided stable suspension of the coupler was used, prepared by acidifying an alkaline solution in the presence of a reaction product of 20 moles of ethylene oxide and 1 mole of octadecyl alcohol.[5]

This was coupled with the diazo-nitro products selected and the end-point of coupling was assessed by spotting the reaction charge onto a filter paper and testing with a solution of R-acid (7-amino-1-naphthol-3,6-disulphonic acid). The nitro-azo pigments were recrystallised to constant melting point from *o*-dichlorobenzene, monochlorobenzene or glacial acetic acid.

2.3. Reduction of nitro groups

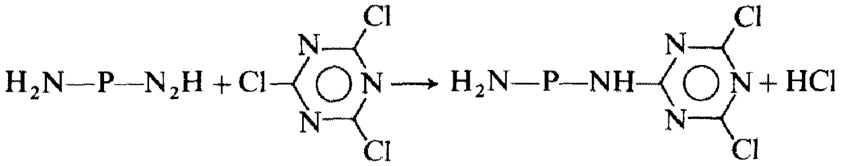
In the 'partial' reduction of nitro groups in the presence of azo groups, sulphides are often used as reducing agents. They must be used with care, particularly in the control of temperature and concentration, to avoid simultaneous reduction of the azo link and hydrolysis of the amide linkages in the compounds. Preliminary work using sodium hydrogen sulphide, sodium polysulphide and sodium sulphide showed that the last of these was the most effective reducing agent. 2-Ethoxyethanol was used to aid reduction of the bis-nitro-azo compounds. The reaction was accomplished in aqueous alcoholic solution by slow addition of approximately 3 moles of sodium sulphide per mole of pigment at 75–95 °C. Heating was continued for 2 h.

Completion of reduction was confirmed by thin layer chromatography. The products were filtered and recrystallised from ethanol to constant melting point.

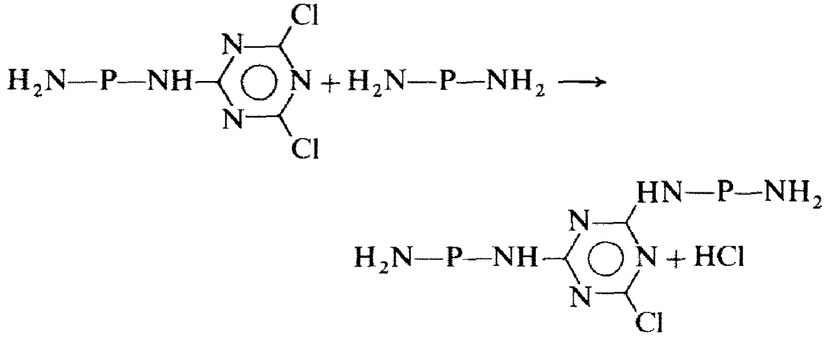
2.4. Condensation of amino-azo compounds with cyanuric chloride

A mixture of freshly distilled and desiccated 2-ethoxyethanol (75 ml), 85 mg of cyanuric chloride and 2·5 ml of redistilled *N*,*N*-dimethylformamide was thermostatted at 25 °C. A finely divided suspension of 2 g of the amino-azo compound in 125 ml of distilled 2-ethoxyethanol was added dropwise over 30 min with stirring. The temperature was gradually raised to 65–70 °C during addition of the amino-azo compound, then it was raised to 125–130 °C and the reaction liquor allowed to reflux for 16 h. The absence of unchanged amino-azo compound was determined using thin layer chromatography. The residue was filtered, washed with 2-ethoxyethanol and dried at 60 °C.

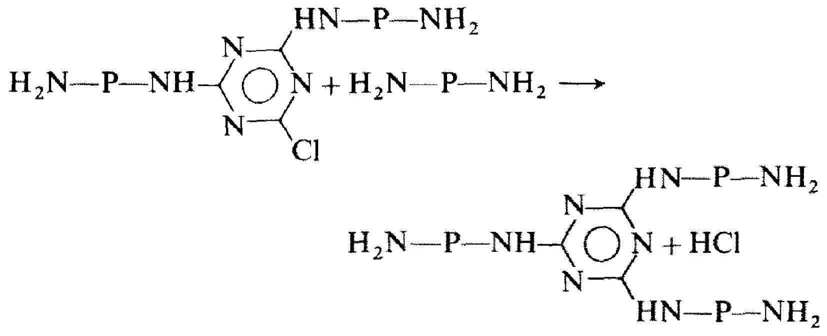
The condensation of bis-amino-azo compounds with cyanuric chloride takes place in a stepwise fashion:



(1)

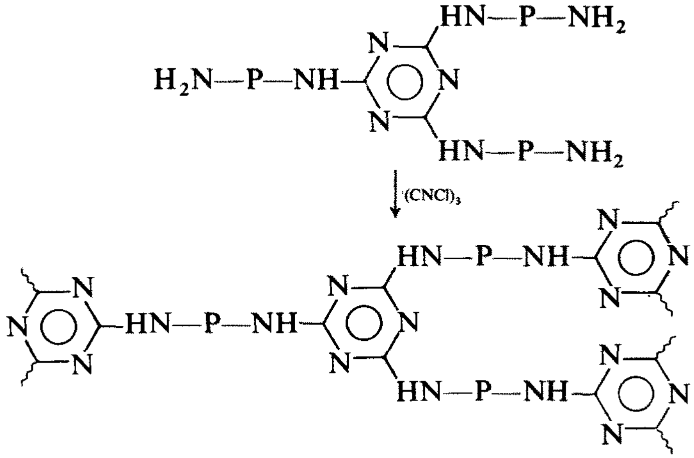


(2)

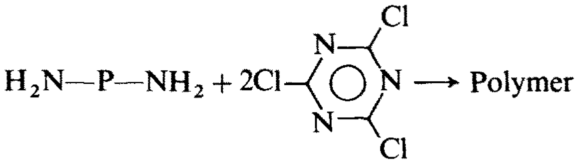


(3)

Further reaction of the tri-substitution product of eqn (3) with cyanuric chloride produces linear and (possibly) crosslinked polymers (eqns (4) and (5)).



(4)



(5)

2.5. Preparation of acryloylamido monomers

The condensation of acryloyl chloride with the amino groups of the amino-azo compounds produced addition-polymerisable monomers. Acryloyl chloride was itself prepared by the reaction between benzoyl chloride (b.p. 197 °C) and acrylic acid (b.p. 142 °C) in molar ratio 3:2. The large difference in the boiling points of the reactants and acryloyl chloride (b.p. 72–76 °C) enhanced the ease of recovery of the product (78 % yield). Hydroquinone was added as a polymerisation inhibitor.

An excess of acryloyl chloride was diluted with redistilled acetone and reacted with the amino-azo compounds. Acryloyl chloride reacts more readily with amino groups than with hydroxyl groups also present in these compounds. The yield of the required acryloylamido products was generally high.

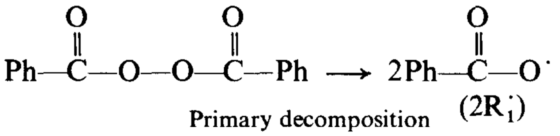
2.6. Polymerisation of acryloylamido monomers

Bulk addition polymerisation was used because of its simplicity and the ease with which the final products could be purified. Two initiators were used, namely benzoyl peroxide (BPO) and azobisisobutyronitrile (AIBN), in order to study the effect of different initiators.

2.6.1. Benzoyl peroxide (BPO) initiation

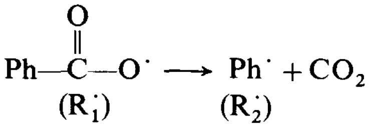
In connection with bulk polymerisation, two types of reactions are distinguished with BPO: those mainly connected with the monomer, and others connected with the initiator. Under conventional conditions, as in the case of this work, propagation is the main reaction. Furthermore, the resulting benzoyl radical undergoes partial secondary decomposition to phenyl radicals which are themselves capable not only of starting kinetic chains but also of terminating the growing chains. Different steps of radical formation have to be considered:

Decomposition:



$$\mathrm{Ph{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Ph} \xrightarrow{} \underset{(2R_1^{\cdot})}{\mathrm{2Ph{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O^{\cdot}}} \qquad (6)$$

Primary decomposition



$$\underset{(R_1^{\cdot})}{\mathrm{Ph{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O^{\cdot}}} \longrightarrow \underset{(R_2^{\cdot})}{\mathrm{Ph^{\cdot}}} + \mathrm{CO_2} \qquad (7)$$

Initiation:

$$R_1^{\cdot} + M \longrightarrow R_1{-}M \qquad (8a)$$

$$R_2^{\cdot} + M \longrightarrow R_2{-}M \qquad (8b)$$

Termination:

Chain termination occurs by one of these conditions:

$$P_n^{\cdot} + P_m \rightarrow P_n + P_m \text{ or } P_{n+m} \qquad (9)$$

Polymer radical termination

$$R_1^{\cdot} + P^{\cdot} \longrightarrow R_1{-}P \qquad (10)$$

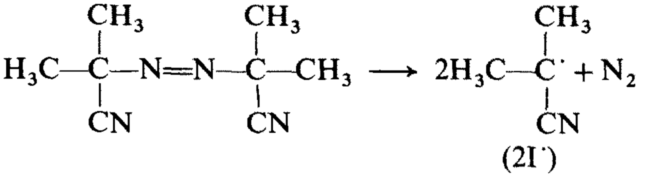
Primary radical termination

The polymers had very high molecular weights (see Table 3) and therefore the ratio of polymerisation to termination was high.

Polymerisation was achieved under anaerobic conditions by bubbling nitrogen through the reaction vessel which was immersed in an oil bath. A mixture of 2 g of the monomer, 20 ml of a 0·2 % stock solution of benzoyl peroxide in chloroform and 100 ml of dioxane was added to the vessel and the contents stirred at 90 °C for 12 h. The polymer was collected from an excess of petroleum ether, filtered off, washed with ethanol and dried at 40 °C.

2.6.2. *Azobisisobutyronitrile (AIBN) initiation*

The initiation of polymerisation is a two-step sequence. The first step is dissociation of the initiator,



$$H_3C-\underset{CN}{\overset{CH_3}{C}}-N{=}N-\underset{CN}{\overset{CH_3}{C}}-CH_3 \longrightarrow 2H_3C-\underset{CN}{\overset{CH_3}{C^{\cdot}}}+N_2 \qquad (11)$$

$(2I^{\cdot})$

The second step is the addition of the initiator fragment radical ($I^{\cdot}$) to the monomer molecule ($CH_2{=}CHCOHNR$) to give a radical:

$$I^{\cdot}+CH_2{=}CHCOHNR \longrightarrow I{-}CH_2{-}{}^{\cdot}CHCOHNR \qquad (12)$$

This new radical then adds further monomer molecules in rapid succession to form a polymer chain. In this propagation the active centre remains, being continuously relocated at the end of the chain:

$$I{-}CH_2{-}{}^{\cdot}CHCOHNR \xrightarrow{CH_2{=}CHCOHNR} I{-}CH_2{-}{}^{\cdot}CHCOHNR{-}CH_2{-}CHCOHNR \qquad (13)$$

Propagation continues until the growing chain radical becomes deactivated. Since the monomer contains two acryloylamido groups, reaction of both will necessarily lead to crosslinking. Such crosslinking renders the polymer thermosetting and gives greatly enhanced resistance to dissolution, etc.

Pure AIBN (75 mg), obtained by recrystallising twice from petroleum ether, was dissolved in 5 ml of *N,N*-dimethylformamide and added to 100 ml of freshly redistilled chlorobenzene contained in a reaction vessel which was fitted with a nitrogen inlet, a dropping funnel and a reflux condenser and was thermostatted in a water bath at 65–70 °C. A solution of 2 g of the monomer dissolved in 100 ml of chlorobenzene was added over 30 min to the reaction vessel. The temperature was then raised to 90–95 °C and the reaction proceeded at this temperature to an end-point, checked by thin layer chromatography (see Table 3). The reaction product was filtered cold and washed with ethanol.

2.7. Assessment of molecular weights by Rast's camphor method

If a compound has a definite melting point, this indicates lack of crosslinking and relatively low molecular weight. Such products were examined by Rast's camphor method to determine molecular weight.

The high freezing point depression of camphor[6] permits the use of ordinary melting point apparatus to determine the molecular weight of an additive. A mixture of the sample under investigation and re-sublimed camphor was placed into a small loosely stoppered tube and the mixture melted by carefully heating for 30 s; the mixture was stirred with a platinum wire and care was taken to avoid sublimation of the camphor.

The melting point of the mixture was determined using a Mettler FPI melting and boiling point instrument. The difference between the melting point of camphor and that of the mixture gave the depression of the melting point of the camphor caused by the addition of the compound. The experiment was repeated until reproducible results were obtained.

The molecular weight M was calculated from eqn (14)

$$M = \frac{1000kw}{\Delta TW} \tag{14}$$

where k is the molecular weight depression constant of camphor (49·7), w is the weight of the compound added, W is the weight of the camphor (generally 5–10 times the value of w) and ΔT is the depression of the melting point of camphor.

2.8. Molecular weights of acryloylamido-azo polymers from viscometry

The viscosity of even dilute polymer solutions are appreciably greater than those of the pure solvent and this difference is related to a number of factors, principally the size, shape and number of polymer chains in solution.

The relationship advanced by Staudinger[7] between viscosities of dilute solutions of linear polymers and their molecular weights (eqn (15)) was used with modifications (16) to account for crosslinking in the polymers examined in this work:

$$\eta_{sp}/c = K\bar{M} \tag{15}$$

$$\eta_{sp}/c = K\bar{M}^a \tag{16}$$

where the specific viscosity η_{sp} equals $\eta_R - 1$ (η_R is the relative viscosity), c

is the concentration in moles of recurring unit per litre, $\bar{M}$ is the average molecular weight, and a is a constant. K and a values were $2{\cdot}43 \times 10^{-2}$ mol litre^{-1} and 0·75 respectively, as determined by Cleland and Stockmeyer[8] for calculating the molecular weights of polyacrylonitrile in dimethylformamide at 25 °C.

An Ubbelohde viscometer[9] was used to measure the viscosities and intrinsic viscosities of the polymers.

3. RESULTS AND DISCUSSION

Macromolecular azo pigments have been produced by the condensation of bis-functional amino-azo compounds with cyanuric chloride, and also by free-radical addition polymerisation of bis-functional acryloylamido-azo monomers.

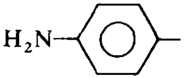
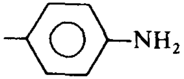
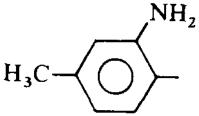
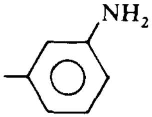
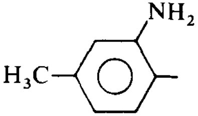
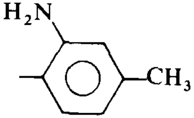
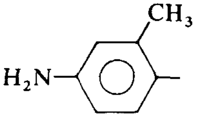
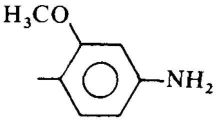
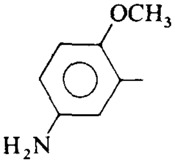
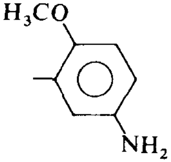
The products resulting from the condensation of amino-azo compounds with cyanuric chloride are given in Table 2. They were examined by elemental analysis (C, H, N, Cl), infrared spectroscopy and molecular weight assessment using the freezing point depression of camphor and viscosity techniques. The reactions gave products with molecular weights higher than those for the tri-substitution products, thus confirming that polymeric compounds were produced. Being polymeric, some degree of crosslinking is present. Examination of the spectra in the region of free amino (NH_2) groups confirmed that total reaction of the amino compounds had occurred. Chlorine analysis showed the extent to which cyanuric chloride had reacted.

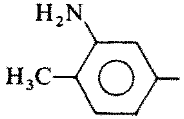
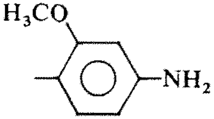
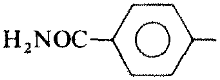
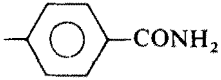
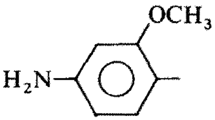
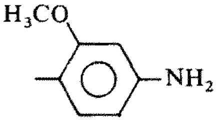
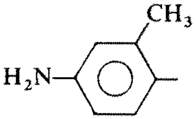
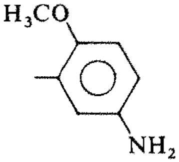
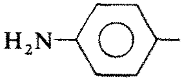
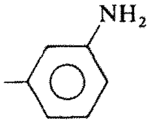
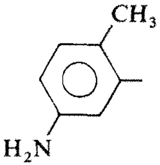
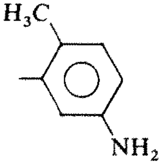
The products of the addition polymerisation of acryloylamido compounds are listed in Table 3. The results showed that the bis-functionality of the monomers enhanced the production of very high molecular weights. This confirms that polymerisation readily took place, leading to highly crosslinked polymers. The molecular weights were much higher than for products of cyanuric chloride condensation with amino-azo compounds.

Preliminary experiments showed that BPO-initiated polymerisations proceeded best in dioxane, although halogenated solvents gave moderate yields. The main problem with BPO-initiated polymerisation reactions was the separation of unreacted and low molecular weight components from the final products. The polymers produced had molecular weights in the region 18 000–42 000.

TABLE 2

Compounds **II** Obtained by Condensation of Cyanuric Chloride with Bis-amino-azo Products

R_3	R_4	*Colour*	*Yield* (%)	*Molecular weight*
		Violet	88·75	3 438
		Purple	67·35	2 142
		Purple	69·11	1 985
		Violet	76·25	2 533
		Purple	75·16	2 528

		Purple	77·33	2 378
		Red	85·5	2 655
		Violet	84·11	2 500
		Violet	87·4	1 535
		Violet	83·4	2 484
		Violet	79·6	2 348

(contd)

TABLE 2—*contd.*

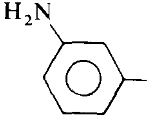
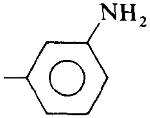
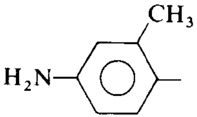
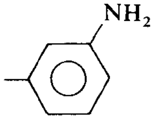
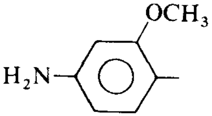
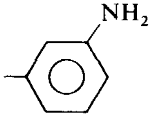
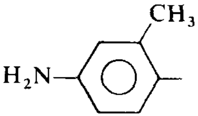
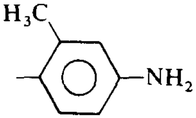
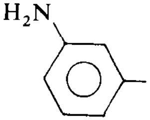
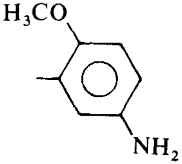
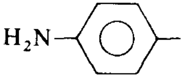
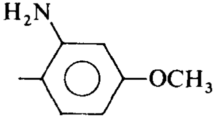
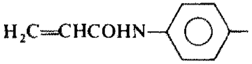
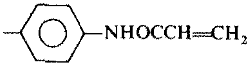
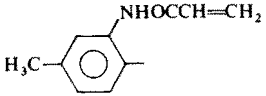
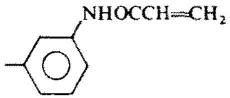
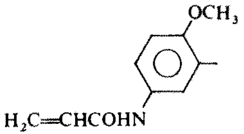
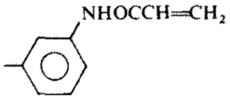
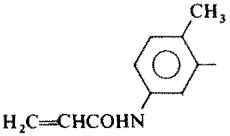
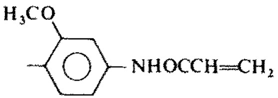
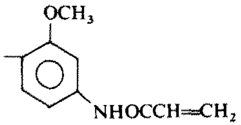
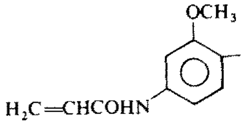
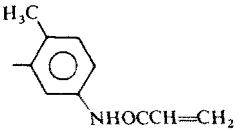
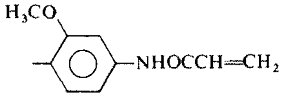
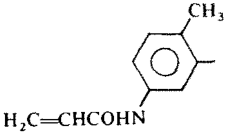
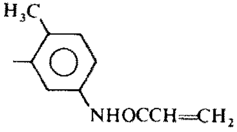
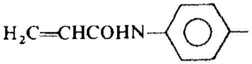
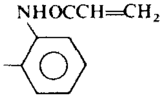
R_3	R_4	*Colour*	*Yield (%)*	*Molecular weight*
		Purple	68·25	1 617
		Violet	71·21	1 984
		Purple	67·8	1 236
		Brown	84·3	1 852
		Violet	75·01	1 794
		Purple	76·15	2 815

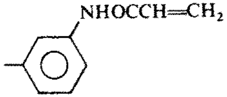
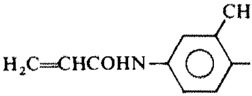
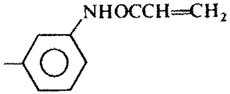
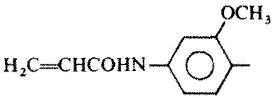
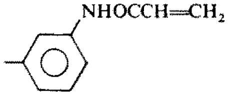
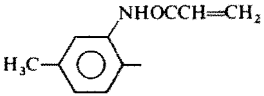
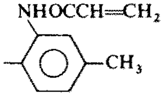
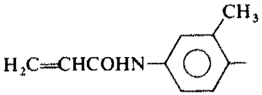
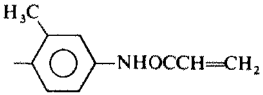
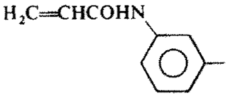
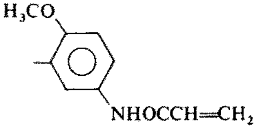
TABLE 3
Conditions and Products of the Polymerisation of Acryloylamido Monomers

R$_3$	*R*$_4$	*Wt of monomer (g)*	*Initiator/ amount*	*Solvent/amount (ml)*	*Reaction time (h)*	*Yield (%)*	*Colour*	*Av. Mol. weight*
		2	AIBN/0·75 g	Chlorobenzene/100	10	92·5	Purple	47 350
		2	BPO/25 ml	Dioxane/100	10	72·7	Purple	29 173
		2	AIBN/0·087 g	Chlorobenzene/100	10	78·4	Violet	25 475
		2	BPO/35 ml	Dioxane/100	16	79·0	Purple	29 967
		2	BPO/35 ml	Chlorobenzene/100	15	66·8	Violet	32 546

(*contd*)

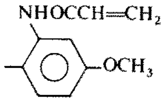
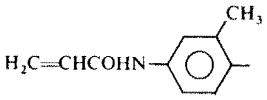
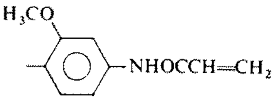
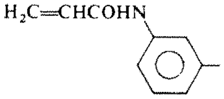
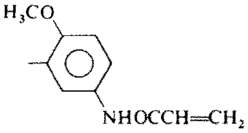
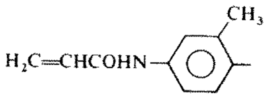
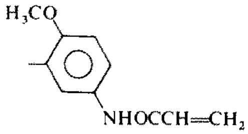
TABLE 3—*contd.*

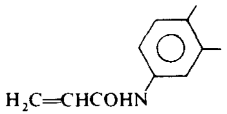
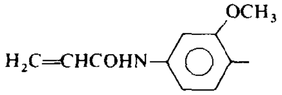
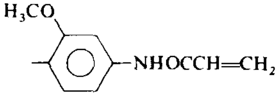
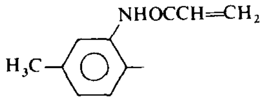
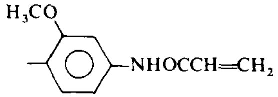
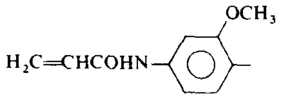
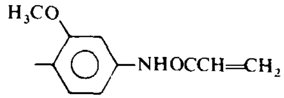
R$_3$	*R*$_4$	*Wt of monomer*	*Initiator/ amount*	*Solvent/amount (ml)*	*Reaction time (h)*	*Yield (%)*	*Colour*	*Av. Mol. weight*
		2	AIBN/0 093 g	Chlorobenzene/100	12	89 6	Violet	23 069
		2	AIBN/0·075 g	Chlorobenzene/100		10	Red	34 864
		2	AIBN/0 093 g	Chlorobenzene/100		14	Violet	31 560
		2	BPO/30 ml	Dioxane/100	12	69·0	Purple	30 957
		2	AIBN/0 075 g	Chlorobenzene/100	10	75 2	Red	34 116

		2	AIBN/0·075 g	Chlorobenzene/100	10	75·6	Purple	38 437
		2	BPO/20 ml	Dioxane/100	16	74·8	Violet	36 751
		2	AIBN/0·087 g	Chlorobenzene/100	10	71 4	Violet	32 576
		2	BPO/30 ml	Dioxane/100	15	76·3	Violet	17 784
		2	AIBN/0·087 g	2-Ethoxyethanol/100	12	85·8	Violet	51 440
		2	AIBN/0·087 g	Chlorobenzene/100	10	72·5	Violet	12 045

(contd)

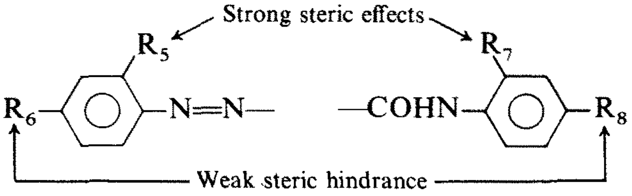
TABLE 3—*contd.*

R₃	*R₄*	*Wt of monomer (g)*	*Initiator/ amount*	*Solvent/amount (ml)*	*Reaction time (h).*	*Yield (%)*	*Colour*	*Av. Mol. weight*
		2	AIBN/0·087 g	Chlorobenzene/100	10	74 4	Violet	40 754
		2	AIBN/0 087 g	Chlorobenzene/100	10	78 4	Violet	54 771
		2	AIBN/0·087 g	Chlorobenzene/100	11	72 7	Violet	29 000
		2	AIBN/0·087 g	Chlorobenzene/100	10	79·1	Brown	39 689

		2	BPO/35 ml	Dioxane/100	16	72·3	Purple	42 289
		2	BPO/35 ml	Dioxane/100	16	78·5	Violet	20 005
		2	AIBN/0 093 g	Chlorobenzene/100	12	73·6	Violet	37 505
		2	BPO/25 ml	Dioxane/100	15	68·5	Purple	33 225

AIBN-initiated polymerisation reactions gave better yields than BPO-initiated polymerisations for similar reaction times. Halogenated solvents gave the best results, although 2-ethoxyethanol was also employed. The products had molecular weights in the region of 12 000–55 000. Thus BPO-initiated polymerisation reactions gave products with a small spread of molecular weights, but AIBN initiation gave products with relatively higher molecular weights spread over a wider range.

Steric effects, although not very noticeable in the polymerisation reactions (since the polymers produced were generally of very high molecular weights), did have some effects, as is seen from Table 3. Steric effects would normally be expected to be most deleterious for groups *ortho* to the azo linkage or pendant amide group:



where R_5, R_6, R_7 and R_8 are reactive groups.

The methods investigated appear to be universally applicable in the production of high molecular weight pigments with high colour values. They are particularly applicable in the colouration of surface coatings, especially by such processes as block insertion polymerisation.

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