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An Investigation into the Synergism of Monoazoacetoacetanilide Pigments

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ABSTRACT

A series of monoazoacetoacetanilide yellow pigments was synthesized and synergistic relationships between certain pigments were observed. The synergistic effects are discussed and the properties of the synergistic pigments correlated with their crystal structure as determined by X-ray powder diffraction, single-crystal analysis, and transmission electron micrographs. The results indicate that modification of the pigment crystals by the formation of a solid solution is one of the reasons for the synergism of these pigments.

1 INTRODUCTION

In the range of classical organic pigments, by far the most important yellow pigments are the azo pigments derived from acetoacetanilide coupling components.[1] The monoazoacetoacetanilides are traditionally known as Hansa Yellows and the disazoacetoacetanilides as the Benzidine Yellows. Among the most important commercially are C.I. Pigment Yellows 1, 3, 73, 74, 12, 13, 14, 17, and 83. Both types have advantages and disadvantages in their applications. The former are characterized by good light-fastness but relatively poor solvent resistance, and the latter exhibit superior tinctorial strength and transparency but poor light-fastness. In order to improve their application properties, several methods have been used, one of which is the synergism effect, which can extend the range of colour and shade of the

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classical pigments and make the mass tone of the inks and coatings prepared from the synergistic pigments deeper and of higher tinctorial strength than the individual pigments. In this present paper, synergistic species of monoazoacetoacetanilides are synthesized, and the observed synergism effects are discussed. Reasons for the synergism of pigments in relation to their crystal structure were also investigated by X-ray powder diffraction and electron micrography.

2 RESULTS AND DISCUSSION

2.1 Materials studied

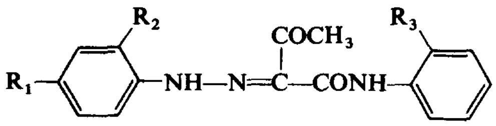
Synergistic pigments can be synthesized from either mixed diazo components or mixed coupling components by using the well-established azo-coupling procedures. Table 1 lists the pigments involved in the present study.

In our experiments, several series of mixed synthetic-pigment species were obtained, and their synergistic effects examined. We discuss here three examples, i.e. A + D, A + E, F + G mixed synthetic-pigment systems, to explain the synergistic effect.

2.2 The colour measurements of the synergistic species

Colour measurements were carried out according to ISO 787/24. The pigments were finely ground and printed onto paper. Colour differences

TABLE 1
Pigments Involved in the Study



No.	*Name*	*R_1*	*R_2*	*R_3*
A	C.I. Pigment Yellow 1	CH_3	NO_2	H
B	C.I. Pigment Yellow 3	Cl	NO_2	Cl
C	C.I. Pigment Yellow 4	NO_2	H	H
D	C.I. Pigment Yellow 5	H	NO_2	H
E	C.I. Pigment Yellow 6	Cl	NO_2	H
F	C.I. Pigment Yellow 65	OCH_3	NO_2	OCH_3
G	C.I. Pigment Yellow 74	NO_2	OCH_3	OCH_3

TABLE 2
The Colour Properties of the A + D Synergistic System

	A	*Molar ratio between the pigments A and D*								*D*
		80:20		*60:40*		*40:60*		*20:80*		
		M	*P*	*M*	*P*	*M*	*P*	*M*	*P*	
K/S	1·727	2·566	1·302	1·541	1·155	2·790	0·623	1·458	0·545	0·971
L	89·63	88·53	88·74	89·01	88·98	89·66	88·86	89·74	89·47	89·46
C	63·65	73·89	65·74	65·47	63·26	73·87	53·50	65·88	50·02	57·41
h	99·77	95·50	95·67	97·05	96·43	69·96	97·82	98·33	99·88	99·90
Δ*E*		8·16		2·33		20·43		15·87		

Note: M, mixed synthetic pigments; P, physical mixture; *K*/*S*, colour strength; *L*, lightness; *C*, chroma; *h*, hue; Δ*E*, colour saturated compared with the corresponding physical mixtures.

between the mixed synthetic pigments and the corresponding physical mixtures were determined. Data reported are the means of several evaluations.

The results indicate that synergistic effects do not exist in all the mixed synthetic-pigment systems but that in some systems there is an improvement. For example, in the A + D system, which is formed by the components C.I. Pigment Yellow 1 and C.I. Pigment Yellow 5, the chroma and colour strength are improved with respect to those of the physical mixtures of the same components, the colour is deeper, and the chroma becomes brighter, although hue becomes slightly reddish compared with that of the two components. The colour properties were measured by using an ACS-1800 Colour Measurement Instrument, and the results are listed in Table 2. Figure 1(a) shows the reflection patterns of the synergistic species and

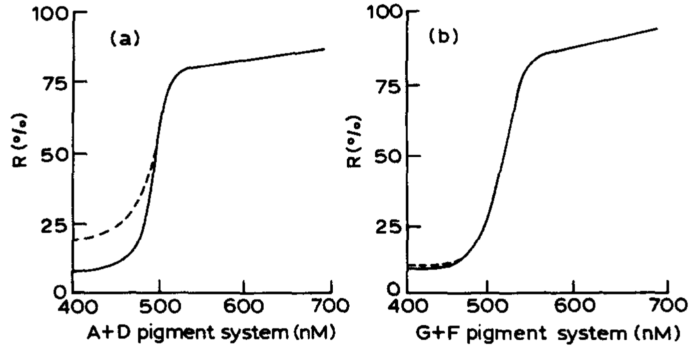


Fig. 1. The light-reflection patterns of pigments: (a) A + D pigment system, (b) G + F pigment system. (– – – –) physical mixture, (————) mixed synthetic pigment.

TABLE 3
The Colour Properties of A + E Mixed Synthetic Pigments

	A	*Molar ratio between the pigments A and E*								*E*
		80:20		*60:40*		*40:60*		*20:80*		
		M	*P*	*M*	*P*	*M*	*P*	*M*	*P*	
K/S	1·727	7·418	6·655	8·321	6·966	6·323	6·302	6·345	5·981	8·132
L	89·63	87·17	87·10	87·33	86·95	87·45	87·05	87·62	87·28	87·10
C	63·65	85·37	85·19	86·54	89·20	85·16	85·07	85·40	84·55	69·97
h	99·77	93·26	93·10	93·23	92·75	93·54	92·66	93·73	92·96	101·89
ΔE		1.81		2·72		1·26		1·24		

physical mixtures and indicates that the absorption of the synergistic species is increased in the range 400–500 nm compared with that of the physical mixtures. Similar results were also obtained with the A + E mixed synthetic-pigment system (Table 3). In these cases, we conclude that a synergistic effect between either C.I. Pigment Yellow 1 and C.I. Pigment Yellow 5 or between C.I. Pigment Yellow 1 and C.I. Pigment Yellow 6 exists. However, in the G + F mixed synthetic-pigment system, no such improvement was apparent. Figure 1(b) shows the light-reflection spectrum of the latter mixed synthetic-pigment system. The results show that the light absorption of the mixed synthetic G + F pigments in the range of 400–500 nm is similar to that of the physical mixture containing the same components. These results imply that their colour properties are similar to that of the physical mixtures and that there is no synergistic effect between C.I. Pigment Yellow 65 and C.I. Pigment Yellow 74.

2.3 Crystal structure of the synergistic pigments

2.3.1 Factors affecting colour

Since pigments are applied in a solid-state-particulate form, the colour observed in the application process will be dependent not only on the molecular structure but also on the nature of the inter-molecular associations in the crystal lattice, e.g. the size and shape of the crystals, the crystal-lattice type, the surface character of the crystals, and the state of aggregation.[2] One important aspect of this study was to establish the reasons for the synergism of the pigments with respect to the properties of the crystals of the synergistic pigments.

2.3.2 X-Ray powder diffraction of synergistic pigments and their components

The powder patterns of C.I. Pigment Yellow 1 and C.I. Pigment Yellow 5

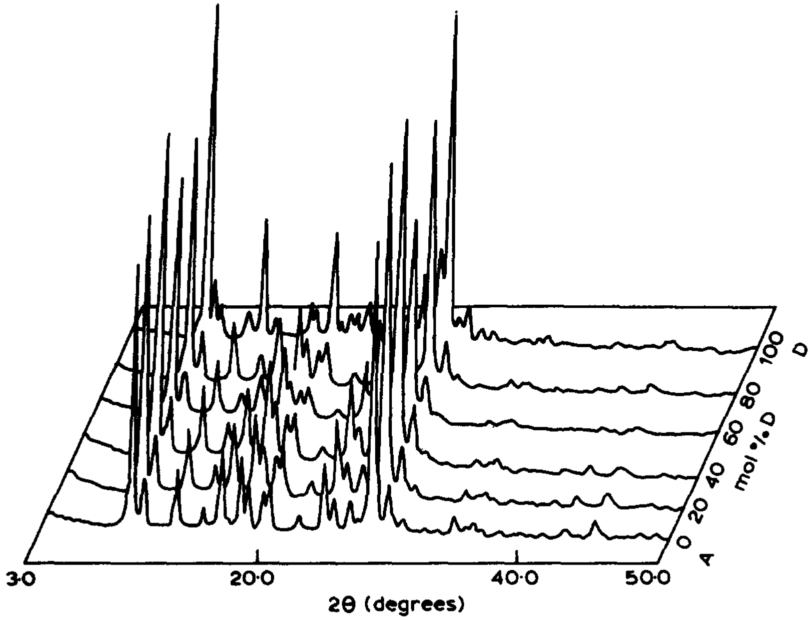


Fig. 2. The X-ray powder-diffraction patterns of the mixed synthetic-pigment system A + D and its components.

and their synergistic species were obtained on a Rigaku D/MAX-RB X-Ray Diffraction Instrument and are shown in Fig. 2. It is apparent that the diffraction patterns of the synergistic pigments are more similar to C.I. Pigment Yellow 1 and different from C.I. Pigment Yellow 5, and that the physical mixture of the same components reverses the crystal patterns of the components. The same observation was obtained in the synergism of C.I. Pigment Yellow 1 and C.I. Pigment Yellow 6 (Fig. 3). The results imply that the synergistic species form a solid solution. As a result, the colour properties of the pigments are improved, since the crystallgraphic modification affects their light-absorption characteristics.

In the G + F mixed synthetic-pigment system (Fig. 4), the main peaks of the two components are reversed, there is only a small change in diffraction angles and strength compared with the physical mixtures (Fig. 5), which are the sum of the patterns of each of the components. Its colour properties, therefore, are only slightly changed with the corresponding physical mixtures.

A series of melting points of the synergistic system A + D and the mixed synthetic-pigment system G + F were measured and are shown in Fig. 6. These additionally confirm that the mixed synthetic-pigment system A + D forms a solid solution over a large range of compositions, while the mixed synthetic-pigment system G + F only exists as a eutectic mixture of the two

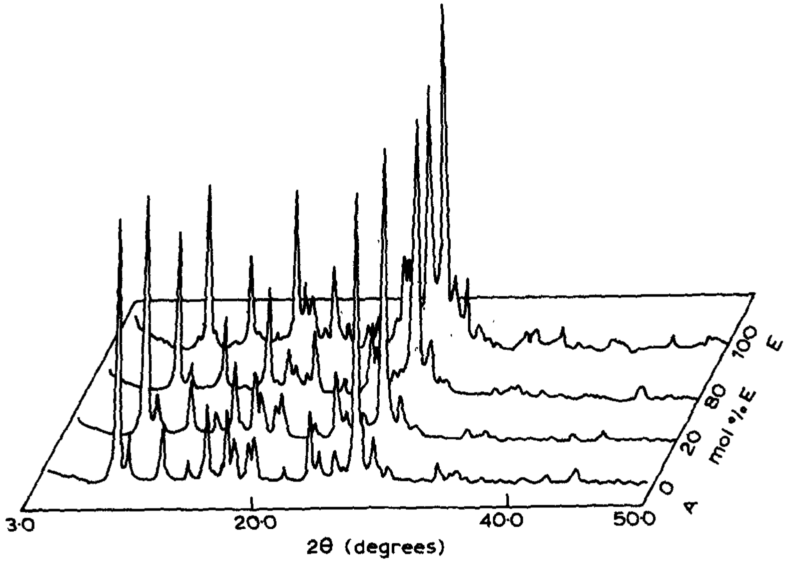


Fig. 3. The X-ray powder-diffraction patterns of the mixed synthetic-pigment system A + E and its components A and E.

components. Concerning the properties of the pigments, this formation of a solid solution to improve the crystals may be one reason for the synergism.

2.3.3 Comparison of single crystals

A single crystal of a synergistic species (40% mol C.I. Pigment Yellow 1 and 60% mol C.I. Pigment Yellow 5) was obtained by slowly cooling a saturated

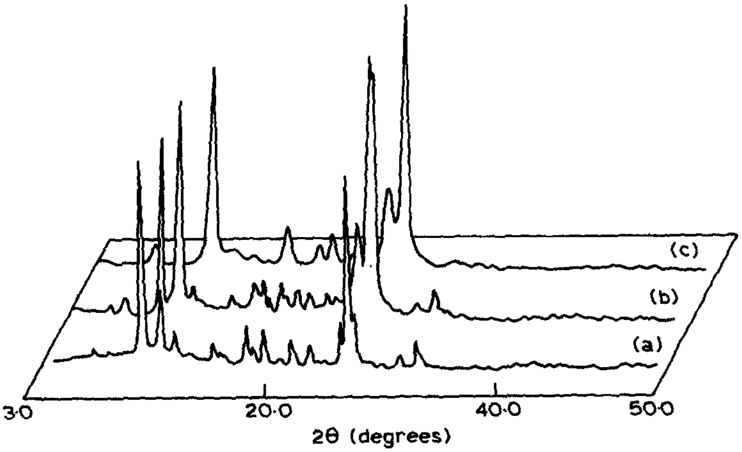


Fig. 4. The X-ray powder-diffraction patterns of (a) component G; (b) 60% pigment G and 40% pigment F, mixed synthetic pigment; (c) component F.

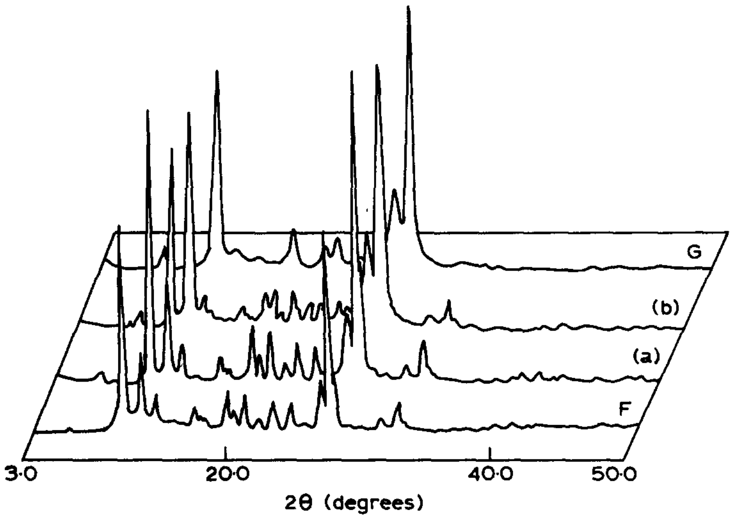


Fig. 5. The X-ray powder-diffraction patterns of the physical mixtures of (a) 80% mol pigment F and 20% mol pigment G and (b) 20% mol F and 80% mol G and their components G and F.

solution of the pigments from 85°C to room temperature for several weeks. The crystal structure was determined via an Enraf-Nonius CAD-4 Automatic Four-circle Diffractometer.

Comparison of cell dimensions and the ratios between them, as well as X-ray diffraction patterns, have been used to confirm isomorphism, e.g. such data for C.I. Pigment Yellows 1 and 6 indicate that the two pigments are not strictly isomorphous.[3] In the present work, we found that the powder patterns of C.I. Pigment Yellow 1, Hansa Yellow 5G, and the mixed synthetic pigments were similar; comparison of the cell dimensions (Table 4) gives further indication that the three pigments are isomorphous.

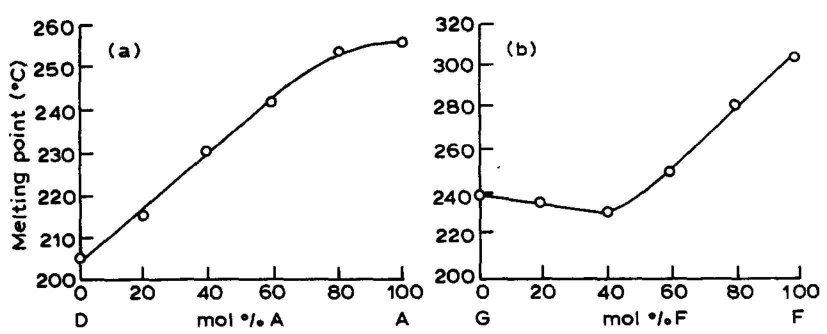


Fig. 6. The relationships between the melting points and the compositions of the mixed synthetic pigments: (a) A + D system, (b) G + F system.

TABLE 4
Single-crystal Data of Related Pigments (Å)

Pigments	*a*	*b*	*c*	*β°*	*Reference*
C.I. Pigment Yellow 1	7·598	20·375	10·440	98·18	[3]
Mixed crystal of 40% A and 60% D	7·581(5)	20·379(2)	10·406(2)	98·30(3)	
Hansa Yellow 5G	7·567	20·420	10·345	99·29	[4]
α-C.I. Pigment Yellow 5	7·593	20·029	10·217	101·87	[5]

The single-crystal data are listed in Table 4 and compared with those for the related pigments. The most noticeable feature is that the cell dimension of the A + D synergistic species is similar to that of C.I. Pigment Yellow 1 and Hansa Yellow 5G; data have also been reported for mixed crystals containing 53% C.I. Pigment Yellow 1 and 47% C.I. Pigment Yellow 5.[4] Thence, it can be concluded that the A + D synergistic species are isomorphous with C.I. Pigment Yellow 1 and Hansa Yellow 5G. Since C.I. Pigment Yellow 5 has two crystal forms, the synergistic species is isomorphous with the α-form, recrystallized from toluene, and different from the other form of the original synthetic pigments.

In terms of molecular packing within the crystal structure, the two types of molecule are stacked at random to form a solid solution. Thus, in the case of the A + D synergistic species, the parent lattice is that of C.I. Pigment Yellow 1, and molecules of C.I. Pigment Yellow 5 replace some of the molecules of C.I. Pigment Yellow 1 in the parent lattice to form a solid solution. As the two pigments formed a solid solution with the crystal packing of C.I. Pigment Yellow 1, the cell dimension approaches that of C.I. Pigment Yellow 1, although the amount of C.I. Pigment Yellow 1 is 20% mol less than that of C.I. Pigment Yellow 5.

As the molecules of C.I. Pigment Yellow 5 are introduced into the lattice of the molecules of C.I. Pigment Yellow 1, the interaction of the molecules will be changed,[6] which will affect the properties of the crystals. As a result, the light-absorption characteristics of the pigments are changed and synergism results.

2.4 Nature of the synergistic pigment particles

Organic pigments are composed of tiny molecular crystals, typically of size 0·1–1 μm. Although the characteristic colour of an organic pigment is determined primarily by its chemical constitution, the effectiveness of a given chemical type of pigment in imparting colour is dependent on its particle size in dispersion.[7] The formation of a solid solution of the

TABLE 5
The Specific Surface Area of Synergistic Pigments (m^2/g)

	Molar ratios between pigments A and D					
	A	*80:20*	*60:40*	*40:60*	*20:80*	*D*
Synergistic species	18·9	22·9	16·9	17·6	13·5	5·9
Physical mixtures	18·9	16·4	14·4	11·2	8·2	5·9

synergistic pigments affects not only the crystal structure of the pigments and the interaction of molecules in the crystal lattice but also the aggregation and dispersibility and the size of the pigment particles.

We have attempted to correlate particle size with the synergistic effect; specific surface areas were measured and compared. It is known that the S_{BET} of mixed synthetic pigments is larger than that of the corresponding physical mixtures. Our results show that S_{BET} of the mixed synthetic pigments is larger than that of the corresponding physical mixtures, and this implies that the particle size of the former is much smaller than that of the latter. In this context, fractal analysis can also be used.[8,9] Our results demonstrate that the mixed synthetic pigments can prevent the growth of particles.

Table 5 lists the specific surface areas of the synergistic system A + D and its components determined by nitrogen-gas absorption. Increase in the specific surface area of pigments means the sizes and aggregation of the tiny pigment crystals are improved. Figure 7 shows examples of electron-micrography of one synergistic pigment and its components measured with a JEM-200CX Transmission Electron Micrograph. The observed crystals are typically blade-shaped. The size of the crystals of the synergistic

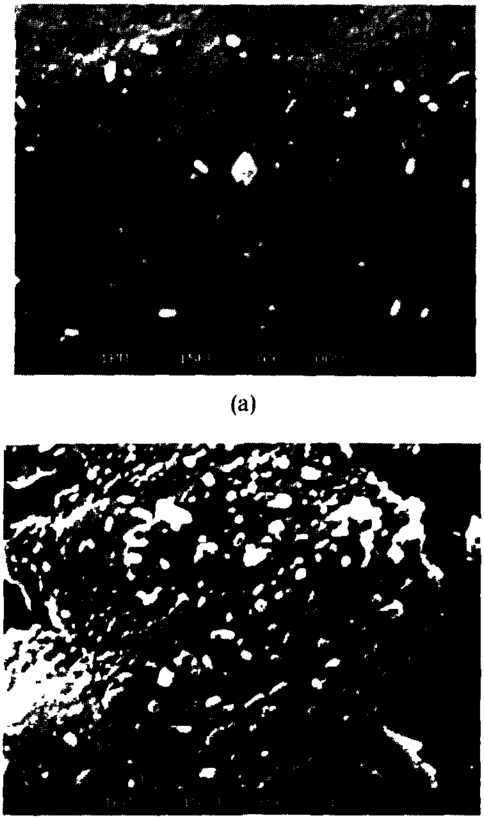
Fig. 7. Transmission electron micrographs of the synergistic pigment (b) and its components C.I. Pigment Yellow 1(a) and C.I. Pigment Yellow 5(c).

TABLE 6
The Average Dimensions of the A + D Synergistic Pigment System (μm)

	A	*Molar ratios between pigment A and D*				*D*
		80:20	*60:40*	*40:60*	*20:80*	
$\bar{D}_0$	0·9856	0·8245	1·063	0·7831	0·8059	1·8846

pigment is much finer than that of the components C.I. Pigment Yellow 1 and C.I. Pigment Yellow 5.

The particle-size distributions of the synergistic pigments were also measured, and the average dimensions of the A + D pigment system are listed in Table 6. The average dimensions of the particles were measured with


(a)

(b)

Fig. 8. Two SEM photographs showing the particle sizes of (a) the mixed synthetic pigment and (b) the corresponding physical mixture.

a Joyce–Loebl disc centrifuge. The pigments used for the measurements were milled in a mortar with OP and then dispersed in water with ultrasonic dispersion for 15 min before the measurements were made. This process may lead to the result that the average dimensions are around 1 μm; the particles may appear as a γ-cluster. Hansa Yellows are soft and can be easily dispersed in the media as single particles, although the particles are larger before use. Two SEM photographs are shown in Fig. 8 as examples of the particle sizes of the mixed synthetic pigments and the physical mixture when they are used in inks and printed on paper; the background is the paper used in our experiments. (a) Is the mixed synthetic pigment and (b) is the corresponding physical mixture.

It is found that the particle size distributions of the synergistic pigments favour small pigment sizes, and the results also show that the particles of the synergistic pigments become finer than those of their components, thus leading to superior tinctorial strength.

All these results suggest that the formation of a solid solution will prevent the crystal growth of the pigments and so lead to a higher colour strength of the synergistic pigments.

3 EXPERIMENTAL

3.1 Synthesis of the individual pigments

The amines (0·05 mol) were diazotized in dilute aqueous hydrochloric acid by using well-established procedures, within a temperature range of 0–5°C, a slight excess of nitrous acid being maintained during the diazotization procedure (starch/KI test). The diazonium-salt solutions were decolourized by using activated charcoal and excess nitrous acid was destroyed with urea prior to coupling. The acetoacetanilides (0·05 mol) were dissolved in aqueous sodium hydroxide with stirring and slight heating, and acetic acid was then added dropwise to adjust the pH to 6·5. Sodium acetate (10·5 g) was added and the volume made up to 400 ml with water. The diazonium liquor was added to the stirred slurry, to ensure that there was no excess diazonium salt. When coupling was complete, the pigments were filtered, washed salt-free, and dried below 60°C.

3.2 Synthesis of mixed synthetic pigments

The same procedure was used as in 3·1 above. The amines used for diazotization were a mixture of different amines.

3.3 Single crystal

Single crystals were obtained from the experimental synthetic pigments containing 40% C.I. Pigment Yellow 1 and 60% C.I. Pigment Yellow 5 by slow cooling of a saturated toluene solution from 85°C to room temperature. The crystal chosen for the crystal-structure determination was of approximate size 0·2 * 0·3 * 0·4 mm.

4 CONCLUSION

In these studies of monoazoacetoacetanilide pigments, some synergistic pigments were obtained and their properties examined. It was found that synergism is one effective method in improving the application properties of classical pigments. Since the formation of a solid solution of pigments affects not only the interactions of molecules in the crystal lattice but also the crystal growth of pigments, which determines the properties of aggregation and dispersibility, we conclude that an appropriate crystal packing, enabling a solid solution to form, is one of the reasons for the synergism effect.

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