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A Study on the Synergism and Crystal Form of some Dichlorobenzidine Disazo Yellow Pigments

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ABSTRACT

Three series of synergistic pigments of the disazoacetoacetanilide yellow type, mainly related to C.I. Pigment Yellow 12, 13, 14, 17, and 63, were synthesized. The synergistic effect was examined and comparison of the color properties of the synergistic pigments with those of the corresponding physical mixtures and of the individual pigments indicated that the classical pigments could be modified by synergism. An attempt was also made to ascertain the reasons for the synergism by using X-ray powder diffraction and scanning electron microscopy. It was found that solid solutions were formed over a large range of concentrations of the components. This leads to improvements in the aggregation and the dispersibilities of the pigments, and, as a result, improves the pigment properties. The isomorphism of C.I. Pigment Yellow 14 and 63, as well as the polymorphism of C.I. Pigment Yellow 17, is also discussed.

1 INTRODUCTION

For some applications, mixtures of pigments are synthesized to improve the properties of the final products. In most cases, in what is called a synergism effect, the properties of the synthesized mixtures are better than those of individual components or of physical mixtures. In current industrial applications, synergism is usually used to modify the application properties of classical pigments such as the Hansa Yellows and Benzidine Yellows.

The synergism of pigments has been utilized for many years.[1–5] In this

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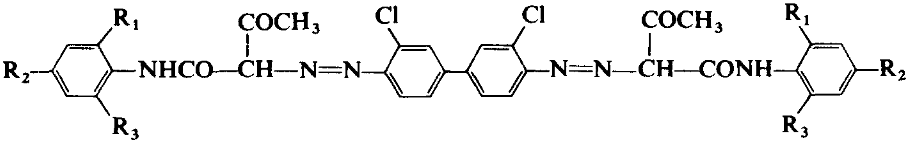
TABLE 1
The Dichlorobenzidine Yellow Pigments



Pigment	*Name in color index*	R_1	R_2	R_3
a	C.I. Pigment Yellow 12 (C.I. 21090)	H	H	H
b	C.I. Pigment Yellow 13 (C.I. 21100)	CH_3	CH_3	H
c	C.I. Pigment Yellow 14 (C.I. 21095)	CH_3	H	H
d	C.I. Pigment Yellow 63 (C.I. 21091)	Cl	H	H
e	C.I. Pigment Yellow 17 (C.I. 21105)	OCH_3	H	H

present paper, an attempt is made to study the synergism of the disazo dichlorobenzidine yellow pigments, by using the industrially important C.I. Pigment Yellows 12, 13, 14, and 17, by X-ray powder diffraction and SEM (scanning electronic micrography). The crystal structure, and the aggregation and dispersibility of the pigments is then related with the synergistic effect. The isomorphism and polymorphs of the disazo yellow pigments were also examined.

The pigments used in the study are shown in Table 1.

2 RESULTS AND DISCUSSION

2.1 Preparation of the individual and synergistic pigments

2.1.1 Synthesis of individual disazo yellow pigments

The series consisted of five dichlorobenzidine pigments, of some industrial importance, namely, C.I. Pigment Yellow 12, 13, 14 and 63,[6] all of which were prepared from tetrazotised dichlorobenzidine by well established azo-coupling procedures. Melting points, infrared data and the elementary analysis are listed in Table 2.

In some previous investigations, it has been shown that mono-azoacetoacetanilides exist in a ketohydrazone configuration.[7-11] The solid-state IR spectra of such pigments show a single carbonyl absorption in the range 1658–1690 cm consistent with the ketohydrazone forms with extensive intramolecular hydrogen-bonding. In this present study, the disazo pigments gave IR spectra similar to those of the monoazo pigments, showing a single carbonyl absorption in 1660 cm (Table 2). This indicates

TABLE 2

Infra-red Spectral Data, Melting Points, and the Elementary Analysis

Pigment	*Melting point* (°C)	*C=O Stretching frequency* (cm^{-1})		*Elementary analysis**		
				C%	*N%*	*H%*
a	300	1660, 1670	f.	61·17	12·96	4·07
			c.	61·05	13·35	4·13
			f.	63·07	12·32	5·06
b	305	1670	c.	63·08	12·60	4·96
			f.	62·10	13·30	4·21
c	280	1670	c.	62·10	12·79	4·57
			f.	55·33	11·77	3·43
d	302	1670	c.	55·01	12·03	3·43
			f.	58·72	12·12	4·35
e	280	1660	c.	59·22	12·19	4·35

* c. = calculated; f. = found.

that the dichlorobenzidine disazo pigments also exist, in the solid state, as ketohydrazone forms.

2.1.2 Synthesis of the synergistic pigments

The mixed synthetic pigments were obtained in a similar manner to the individual pigments but differed in the stages of the coupling process. The dichlorobenzidine tetrazonium-salt liquor was first slowly added to a 2-methylacetoacetanilide suspension, and coupling continued until no anilide remained. The second acetoacetanilide was then added, and the coupling continued until the mixed pigment was formed.

Three series of mixed pigments, each containing two different acetoacetanilide moieties in various molar ratios were prepared, namely:

(i) by using 2-methylacetoacetanilide and acetoacetanilide in molar ratios of 9:1, 7:3, 5:5, 3:7, and 1:9 as coupling components, giving the synergistic pigments 1a, 1b, 1c, 1d, and 1e, respectively; the corresponding physical mixtures of the main components, i.e., C.I. Pigment Yellows 14 and 12, are designated as 1a′–1e′;

(ii) by using 2-methylacetoacetanilide and 2,4-dimethylacetoacetanilide in molar ratios as above, giving pigments 2a–2e, respectively; the corresponding physical mixtures of C.I. Pigment Yellows 14 and 13 are designated 2a′–2e′;

(iii) by using 2-methylacetoacetanilide and 2-chloroacetanilide in molar ratios as above, giving pigments 3a–3e, respectively; the corresponding physical mixtures of C.I. Pigment Yellows 14 and 63 are designated 3a′–3e′.

TABLE 3
X-ray Powder-Diffraction Data

Pigment c	2θ (Å)	8·2	11·4	14·3	16·4	18·4	19·6	20·8	21·8	22·4	24·0	25·0	26.6
	d (Å)	10·78	7·76	6·19	5·40	4·82	4·53	4·27	4·08	3·97	3·71	3·56	3·35
	I/I_0	22	63	18	24	9	9	10	11	21	10	34	100
Pigment d	2θ (Å)	8·1	11·4	14·4	16·4	18·5	19·6	20·9	21·6	22·6	24·0	25·4	26·6
	d (Å)	10·92	7·76	6·15	5·40	4·80	4·53	4·25	4·11	3·94	3·71	3·51	3·35
	I/I_0	9	69	7	11	5	9	8	9	20	13	44	100

2.2 The isomorphism of the dichlorobenzidine pigments

Some isomorphs of monoazoacetanilide pigments have been reported.[12] An example is that of monobromo and dibromo analogues of C.I. Pigment Yellow 3. In this case, it was reported that the X-ray diffraction patterns were similar but that there were differences of intensities. In this present study, a similar phenomenon was observed for C.I. Pigment Yellow 14 and 63 on examination of the crystal structures of the two dichlorobenzidine pigments. The X-ray powder-diffraction patterns of the two pigments are shown in Fig. 1 and the data are listed in Table 3.

Comparison of the patterns and data of the two pigments c and d indicates that the inter-planar distances are very similar and that there are only slight differences in the diffraction intensities. The results imply that pigments c and d are isomorphs.

Additionally, color-measurement data of the two pigments show that their color properties are very similar (Table 4), also demonstrating their isomorphism.

With respect to the molecular structures of the two pigments, it is evident that they have very similar structures, one with a methyl group and the other with a chloro group in the same position. The differences in the diffractional intensities of the two isomorphs are due to the greater scattering of the chlorine atom compared to that of the corresponding methyl group.

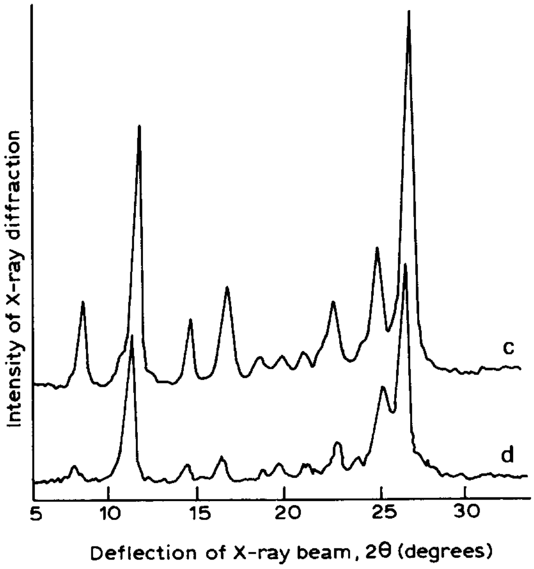


Fig. 1. X-ray diffraction patterns from C.I. Pigment Yellow 14 and 63.

TABLE 4
The Color Properties of Pigments c and d

Pigment	λ_{max}	*K/S* (*Color strength*)	*L* (*Lightness*)	*C* (*Chroma*)	*h* (*Hue*)
c	450·0	9·462	74·04	79·62	84·40
d	450·0	9·430	73·81	80·69	83·16

2.3 The polymorphism of C.I. Pigment Yellow 17

The X-ray diffraction patterns show that C.I. Pigment Yellow 17 is polymorphic. Figure 2 shows the X-ray powder-diffraction patterns of the pigment obtained in different treatments after synthesis.

Comparison of the X-ray powder diffraction patterns from the two samples shows that their diffraction data are different (listed in Table 5), indicating that they are polymorphs; the polymorph obtained by heating at 90°C for 1 h after synthesis was designated α-form and the other β-form.

It is known that the color imparted by a pigment depends not only on the way in which it is applied to a substrate but also on the crystallographic arrangement of the molecules. Polymorphs, since they have a different

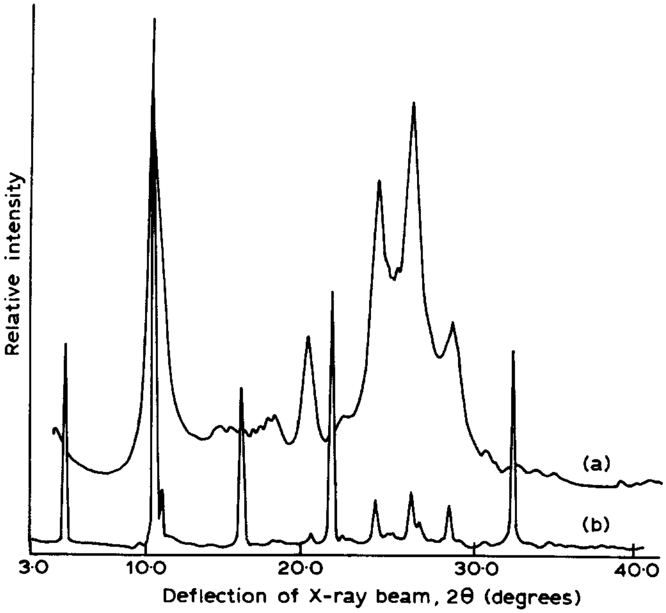
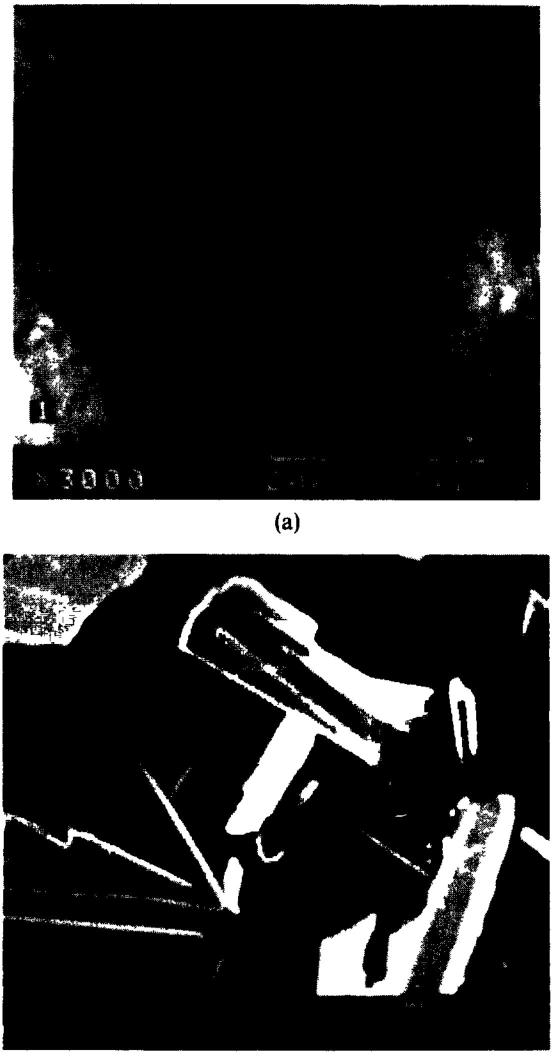


Fig. 2. X-ray powder-diffraction patterns of pigment e. (a) Heated at 90°C for 1 h after synthesis and (b) recrystallised from nitrobenzene.

TABLE 5
X-Ray Powder-Diffraction Data on Pigment e

α-Form	2θ(Å)	10·96	18	19·9	24·02	26·08	28·34			
	d(Å)	8·066	4·924	4·458	3·701	3·413	3·146			
	I/I_0	90	31	48	83	100	51			
β-Form	2θ(Å)	5·28	10·62	11·08	16·0	21·42	24·06	26·22	28·54	32·4
	d(Å)	16·72	8·323	7·979	5·534	4·145	3·695	3·396	3·125	2·76
	I/I_0	40	100	10	31	49	10	11	9	38



(a)

(b)

Fig. 3. SEM photographs of C.I. Pigment Yellow 17. (a) α-Form and (b) β-form.

TABLE 6
The Color Properties of the Polymorphs of Pigment e

Polymorphs	*K/S* (*Color strength*)	*L* (*Lightness*)	*C* (*Chroma*)	*h* (*Hue*)
α-Form	9·846	67·37	62·38	74·70
β-Form	8·985	79·51	86·96	85·66

crystallographic arrangement of the same molecules, could give rise to differences in physical characteristics, such as color and morphological properties. The best-known example of the same compound having different coloring properties in different polymorphs is copper phthalocyanine.[13]

Polymorphism in C.I. Pigment Yellow 17 also results in different color properties. Table 6 lists the results of color measurements of each polymorph. Figure 3 shows examples of the crystal forms of the two modifications of pigment e. This also gives direct confirmation that different crystal packing of the same molecules will lead to modification of the physical properties of the pigments.

2.4 The synergism of dichlorobenzidine pigments

It has already been mentioned that synergism will modify the application properties of the classical pigments. After synthesis of the pigments, their color properties and relative tinting strength were measured in accord with ISO International Standard 787/24 and then compared with those of the individual and corresponding physically mixed pigments.

2.4.1 The color and relative tinting strength of pigments

The results (Table 7) show that the color properties of the mixed synthetic pigments, e.g. color strength, brightness, chroma, when compared with that of the individual and corresponding mechanically mixed pigments, are improved. We can take a series of the synergistic pigments as an example to explain the synergism of the pigments. The data in Table 7 show that the *K/S* values are larger than those of the two main components a and c, which are measured as 9·462 and 9·684, respectively, and their brightness and chroma are also improved with respect to the individual pigments a and c and to the corresponding physical mixtures. It is well known that color strength of pigments is related to the tinctorial strength; the greater the color strength, the better is the tinctorial strength of the pigment. This means that synergistic relations between C.I. Pigment Yellow 14 and 12 between C.I. Pigment Yellow 13 and 63 exist.

TABLE 7
Comparison of the Color Properties of Pigments

Pigment		*K/S* *(Color strength)*		*L* *(Lightness)*		*C* *(Chroma)*	
		P_S	P_M	P_S	P_M	P_S	P_M
c		9·462		74·04		79·62	
1a	1a′	9·650	9·351	75·78	74·82	82·90	80·89
1b	1b′	9·600	9·000	77·00	74·70	81·70	80·01
1c	1c′	9·753	9·258	74·05	71·90	80·75	77·00
1d	1d′	9·755	9·340	73·98	73·65	80·80	79·83
1e	1e′	9·690	9·350	73·54	73·00	79·59	78·67
a		9·684		72·94		78·78	
c		9·462		74·04		79·62	
2a	2a′	9·650	9·340	74·80	74·00	81·13	79·91
2b	2b′	9·550	9·360	74·93	71·40	82·21	79·70
2c	2c′	9·463	9·462	75·48	74·01	81·94	81·00
2d	2d′	9·550	9·300	77·26	74·06	84·35	80·09
2e	2e′	9·550	9·405	73·98	73·50	80·80	80·07
b		9·550		73·13		80·64	
c		9·462		74·04		79·62	
3a	3a′	9·580	9·500	74·28	73·29	80·00	79·88
3b	3b′	9·700	9·450	74·85	74·77	82·10	79·49
3c	3c′	9·480	9·300	76·47	73·50	83·25	79·08
3d	3d′	9·800	9·000	76·92	74·00	86·20	80·20
3e	3e′	9·700	9·100	73·89	73·38	80·90	80·60
d		9·430		73·81		80·69	

* P_S = Synergistic pigments; P_M = Physical mixtures.

2.4.2 X-ray powder diffraction and SEM studies

The problem of how synergistic pigments can improve the properties of the classical pigments arose when we examined the synergistic effect of the dichlorobenzidine disazo pigments. It is recognized that, since pigments are used in the solid state, not only are the color properties observed in the application dependent on the molecular structures, but the crystal structures of the pigments also have a major effect. An attempt was therefore made to examine the changes in the crystal structures of the synergistic pigments in order to establish the case of the synergism.

X-ray powder-diffraction patterns of the synergistic pigments, individual pigments, and mechanical mixtures were obtained and are shown in Figs 4, 5, 6, and 7, respectively. It is found that the patterns of the synergistic pigments are similar to each other and all are similar to that of a main component,

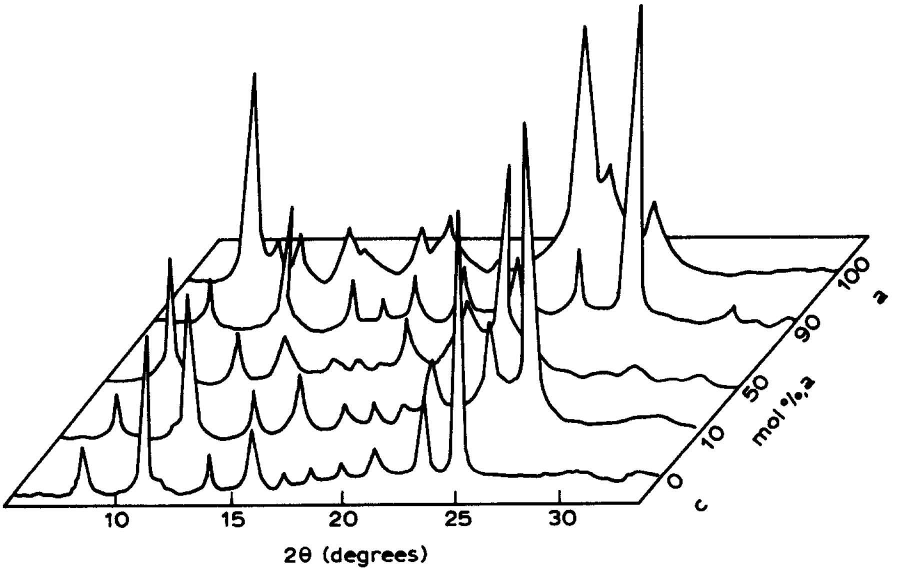


Fig. 4. X-ray powder-diffraction patterns of the mixed synthetic pigments and their components a and c.

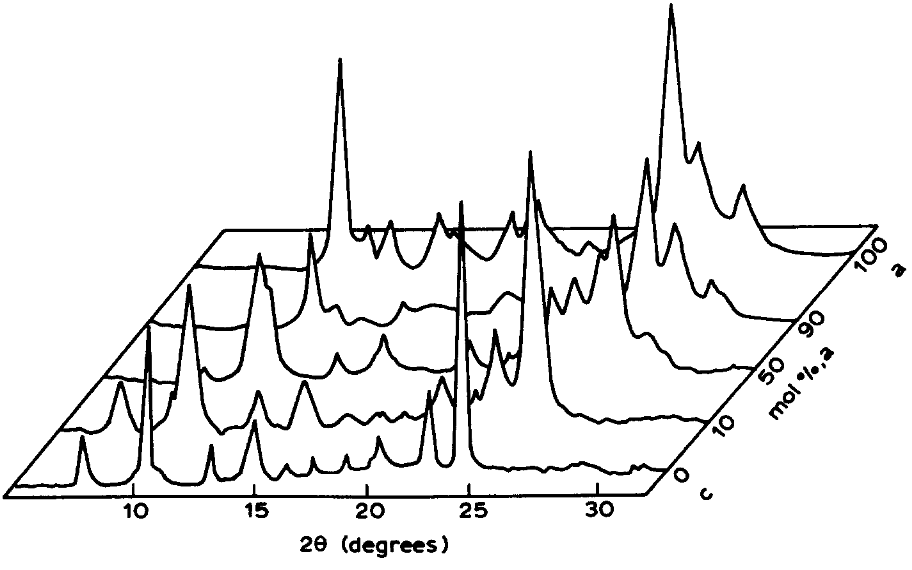


Fig. 5. X-ray powder-diffraction patterns of the physical mixtures of pigment a and pigment c.

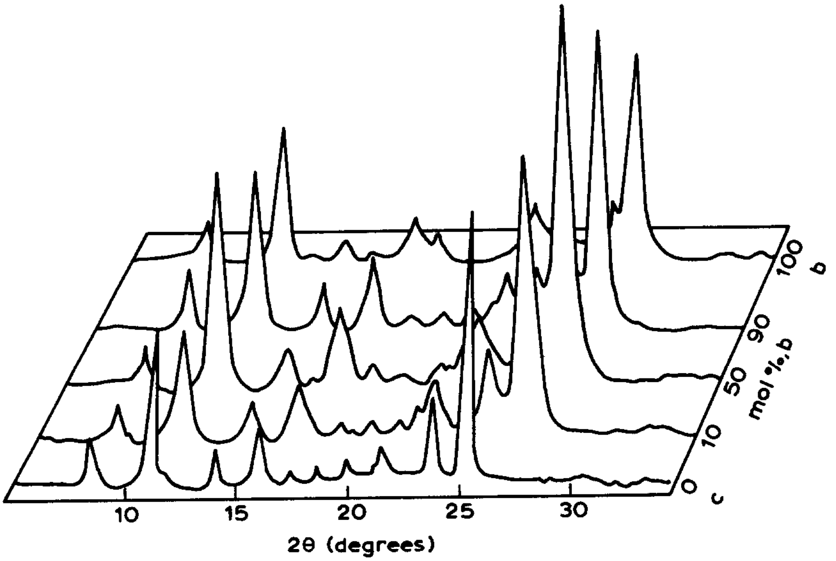


Fig. 6. X-ray powder-diffraction patterns of the mixed synthetic pigments and their components, pigments c and b.

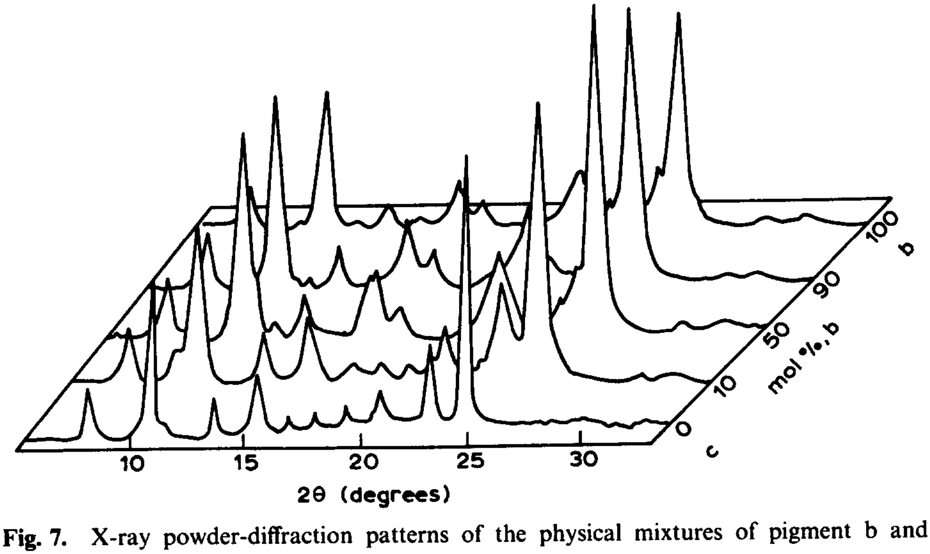


Fig. 7. X-ray powder-diffraction patterns of the physical mixtures of pigment b and pigment c.

namely, C.I. Pigment Yellow 14, although there are some differences in the intensities of the diffractions with change in the composition of the synergistic pigments (Figs 4 and 6). The patterns are however, different from those of the corresponding mechanical mixtures, which reverse the diffraction patterns of the components (Figs 5 and 7).

It is therefore apparent that a substituted solid solution is formed between the synergistic pigments over a wide range of composition, with the crystal structure of C.I. Pigment Yellow 14 as a worthy packing. In the solution, the molecules of pigments a, b, or d are introduced into the crystal lattice and substitute the molecules of pigment c at random. These will affect the interactions of the close-packed chromophores of the pigment molecules in the crystal lattice and thus further influence the color properties of the pigments. This could be one of the reasons for the synergism of dichlorobenzidine diazo pigments.

The particle sizes and dispersibilities of the synergistic pigments were examined by using scanning electron microscopy. The results indicate that the dispersibilities and the aggregation of the synergistic pigments are improved and the crystal sizes also become smaller than those of the individual pigments. It is clear that the formation of the solid solution of the synergistic pigments will not only affect the interaction of the molecules but also prevent the growth of the pigment crystals, both of which effects can lead to modification of the application properties of the classical pigments.

3 EXPERIMENTAL

3.1 Instrumental measurements

The X-ray powder-diffraction patterns were obtained by using a Shimadzu XD-3A X-ray powder-diffraction meter; infra-red spectra were recorded (KBr) with a Nicolet FT-IR 20SX Infra-red Spectrometer; melting points were measured on a CDR-1 differential calorimeter; the color properties were measured with an MM-350 color-measurement meter; scanning electron microscopy was carried out on an SEM 150 Mk 3 instrument (Cambridge Instrument) to observe the micro-state of the pigments.

3.2 Synthesis of dichlorobenzidine disazo yellow pigments

The 3,3-dichlorobenzidines (0·025 mol) were tetrazotized in dilute aqueous hydrochloric acid, by using well-established procedures maintaining the temperature in the range of 0–5°C and a slight excess of nitrous acid during the tetrazotization procedure (starch/KI test). The tetrazonium salt solutions were decolorized by using activated charcoal and then filtered. Residual 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 sodium acetate (10·5 g) was then added and the volume made up to 400 ml with water. The diazonium salt solution was added to the stirred slurry, in maintaining no excess diazonium salt. When coupling was complete, the solution was heated at 90–95°C for 1 h, filtered, the residue washed salt-free and dried below 60°C.

The synergistic pigments were synthesized by the same procedure; the acetoacetanilides used for coupling were mixtures as listed in section 2.1.2.

4 CONCLUSION

A series of dichlorobenzidine disazo yellow pigments was synthesized and their crystal forms were examined. It was found that C.I. Pigment Yellow 14 and C.I. Pigment Yellow 63 were isomorphic and that C.I. Pigment Yellow 17 was a polymorph. The synergistic effect (relationship) between C.I. Pigment Yellows 12, 13, 63, and 14 was investigated. Experimental results showed that the properties of the synergistic pigments, e.g., color strength, brightness, chroma, and particle size, as compared with the individual pigments and the mechanically mixed pigments were modified. X-ray powder diffraction and electron microscopy indicated that the formation of a substituted solid solution is one of the reasons for the synergism of the disazo yellow pigments.

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