Dyes and Pigments 5 (1984) 3–14

Studies on Polymorphism of Ni Complexes of Acetoacetanilide Dioxime Pigments During Their Preparation

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(Received 4 July, 1982)

SUMMARY

The possibility of polymorphism during the preparation of some metal-complex pigments (nickel acetoacetanilide dioximates) has been investigated by electron microscopy and X-ray diffraction. The results indicate that two examined pigments exhibit polymorphism depending on the conditions of their preparation In other cases the change of colour and application properties has been the result of morphological differences of pigment crystals

1. INTRODUCTION

In earlier work on the preparation of new organic pigments—nickel complexes of 2,3-dihydroxybutyric acid arylide 2,3-dioximes—it was found that in some cases a change in methods of synthesis gave products of different colour and application properties. These results suggested the possibility of polymorphism of the examined pigments.[1]

It is well known that many azo lakes and pigments and products such as quinacridone or phthalocyanine can crystallize in more than one form. In general a polymorphic form can be obtained by varying the conditions of preparation and conditioning of pigments. So far as we know no observation of polymorphism of Ni complexes of acetoacetanilide dioxime pigments has been reported. In some BASF patents,[2] [3] however, there are comments about variations in colour and application properties

Dyes and Pigments 0143-7208/84/$03 00 © Elsevier Applied Science Publishers Ltd, England, 1984 Printed in Great Britain

of these pigments The question arises as to whether these phenomena are connected with morphological or crystal structure changes. It has been reported that some analytical reagents of similar structure (Ni complexes of 1,2-dioximes, e.g Ni ethylmethylglyoxime) exhibit polymorphism.[4,5]

It is the purpose of the present work to study the cause of variations of the colour and properties of selected pigments An attempt to estimate which factors during the preparation can influence morphological and structural transformations has also been made.

2. EXPERIMENTAL

All laboratory-prepared samples of pigments were subjected to morphological and structural studies. A Tesla BS-250 electron microscope was used to examine the appearance and morphology of pigment powders Samples were dispersed in distilled water or in 5% aqueous ethanol and then collected on microscope slides coated with collodion film. After drying at room temperature the prepared film was placed on the specimen gauze of the microscope

X-ray powder diffraction patterns were obtained using DRON-1,5 apparatus with CuK_α Ni-filtered radiation of wavelength 0 154 18 nm equipped with a radiation intensity recorder with the range $2\theta = 2\text{–}36°$.

Prepared pigments were also subjected to colorimetric studies. Reflection spectra of reduced paints on sheets of white paper were measured using the Specol Rd/O spectrophotometer. Uncoloured white paint was used as standard white.

All pigments had a very soft texture and no additional milling or grinding was needed. Paints were prepared by rubbing the pigment powders with white oil paint on a glass slide under standard conditions. In all cases the colours of the prepared paint and the pigment-powder corresponded

3 RESULTS AND DISCUSSION

3.1. Methods of preparation

The metal-complex pigments were prepared by reaction of 2,3-dioximes of 2,3-dihydroxybutyric acid arylides with nickel salts. This process was carried out by two methods. In the first method the solution or dispersion of dioxime was treated with nickel salt ((i), Fig. 1). In the second method precipitation of a pigment took place during simultaneous reaction of 2-nitrosoacetoacetarylide with hydroxylamine and nickel salt ((ii), Fig. 1). In both methods the reaction mixture was stirred at 50–70 °C for 3–4 h at pH 5–6.

The first method gave higher reaction yields and purer prepared pigments. On the other hand, the time of the second method was much shorter and was useful in those cases where the dioxime formation was difficult or when it was partially hydrolysed to the corresponding ketone in the acid medium of the metallization.

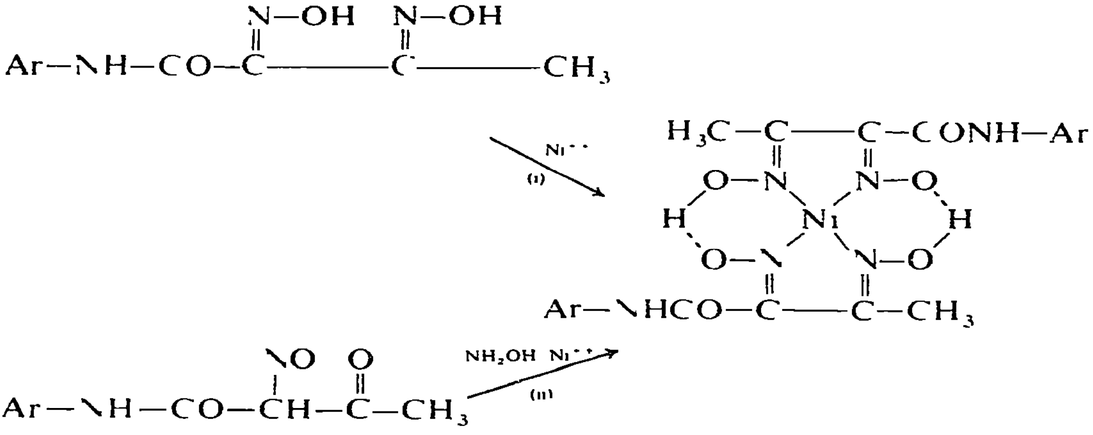

Fig. 1.

In most cases pigments prepared by both methods had similar or identical properties. Usually all pigments prepared by the second method had improved brilliance and purity of colour shade in oil paints. In some cases, however, a definite colour difference between pigments prepared by both methods has been observed.

For example pigment 1 (Ar = 2′,3′-dimethylphenyl) prepared by the method (i) was yellow (pigment **1a**). The same pigment prepared as in method (ii) was orange (pigment **1b**). Reflectance spectra of oil paints gave similar intensities but with orange pigment **1b** a bathochromic shift could be seen (Fig. 2).

Microscopic examination showed a definite difference in morphology of the two pigments. Crystals of yellow pigment **1a** had a ribbon-like

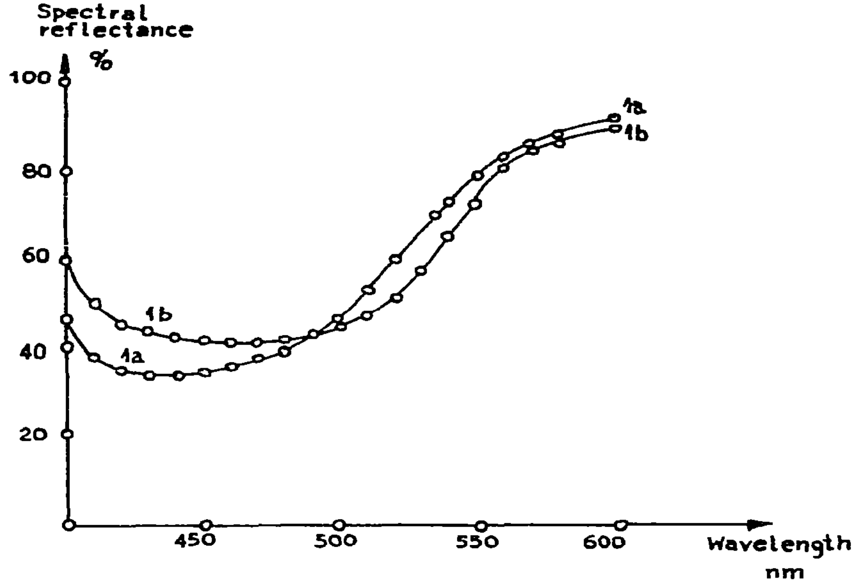

Fig. 2. Spectrophotometric reflectance curves for reduced paints (2/100) of pigments **1a** and **1b** prepared by methods (i) and (ii), respectively

shape Most of the crystals were crushed to plates of different shapes and sizes (Fig 3) Orange-coloured pigment **1b** crystallized in the form of large acicular crystals (Fig. 4)

The difference in crystallographic structure of the two samples was confirmed by X-ray analysis. From the diffraction peaks of both samples, Table 1, it can be seen that there is little similarity in structure between

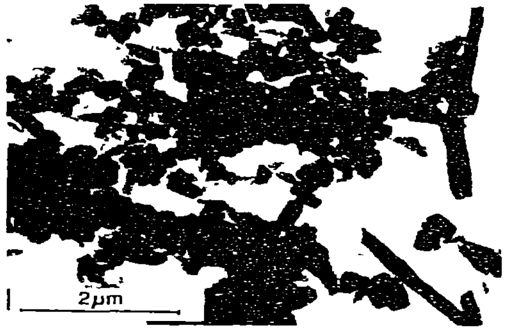

Fig. 3. Pigment **1a** (yellow) prepared by the method (i)

Fig. 4. Pigment **1b** (orange) prepared by the method (ii)

TABLE 1

X-Ray Diffraction Patterns[a] of Pigment **1** (Ar = 2',3'-dimethylphenyl)

Pigment **1a** (*yellow*)		*Pigment* **1b** (*orange*)		*Pigment* **1c** (*orange*)	
d (*Å*)	*I*	*d* (*Å*)	*I*	*d* (*Å*)	*I*
11 04	w	11 48	vs	11 42	s
7 14	vs	9 14	m	7·59	vs
6 13	s	7 63	m	6 73	s
5 90	s	7 01	m	6 04	m
5 15	m	6 60	vs	5 22	w
3 67	s	5 53	s	4 12	vw
3 30	vs	3 73	w	3 73	m
2 58	w	3 59	m	3 47	s
2 33	w	3 47	s	3 32	s
		3 18	m		
		3 06	m		
		2 76	w		
		2 27	w		

[a] According to literature recommendations,[6] the data are presented as a list of interplanar spacings *d* and intensities *I* Intensity of diffraction peaks vs, very strong, s, strong, ms, medium strong, m, medium, w, weak, vw, very weak

yellow and orange pigments. The more intense peaks in the yellow pigment correspond to interplanar spacings of 7·14, 5·90, 3·67 and 3·30 Å while in the orange pigment the more intense peaks are at 11·48, 6·60, 5·53 and 3 47 Å.

It was also found that both polymorphs have different intensity of the absorption peaks in IR spectra in the range 1700–1600 cm^{-1} A third form of the pigment with interesting properties was prepared by a combination of methods (i) and (ii) (pigment **1c**). This pigment was prepared by reaction of 2-nitrosoacetoacet-2',3'-dimethylanilide with hydroxylamine followed by reaction with nickel acetate. Reactions were carried out in the same batch without separation of intermediates The resulting pigment has a yellowish-orange shade and its X-ray data gave evidence for the existence of both polymorphs. In Table 1 it is seen that the diffraction pattern of pigment **1c** includes all the more intense peaks which are present in pigments **1a** and **1b**. The differences in X-ray data are very small and probably are the result of line interference of diffraction peaks of similar interplanar spacing values.

Another example is provided by pigment **2** (Ar = 2′-methyl-3′-chlorophenyl). In this case pigment **2a** prepared by the method (i) gave weak and dull paints as compared with pigment **2b** prepared by method (ii). X-ray diffraction data shown in Table 2 indicate the existence of the same crystal structure in the case of both pigments.

TABLE 2
X-Ray Diffraction Patterns of Pigment **2** (Ar = 2′-methyl-3′-chlorophenyl)

Pigment **2a**		*Pigment* **2b**	
d (Å)	*I*	*d* (Å)	*I*
14.33	m	14.33	m
11.52	m	11.52	m
8.30	ms	8.17	s
3.68	w	5.78	w
3.43	m	5.42	vw
3.36	m	4.13	vw
3.20	w	3.63	w
		3.43	m
		3.36	w
		3.19	w

A more crystalline structure accompanied by better pigment properties was evident in the sample prepared by method (ii). The greater crystallinity and crystal size of pigments prepared by this method (see Fig. 2 and Fig. 4) can be explained by the possible limitation of nucleation and growth processes by the presence of the dioxime in the reaction mixture in the case of method (ii). In the case of pigment **2** the differences in properties are probably the result of morphological differences which are indicated by electron micrographs (Figs 5 and 6).

3.2. The influence of the reaction medium

The last stage of preparation of the pigments, metallization, was usually carried out in water-miscible organic solvents (alcohols, DMF), in mixtures of these solvents with water or in water itself. Replacing an alcohol or water–alcohol medium by water usually has no influence on

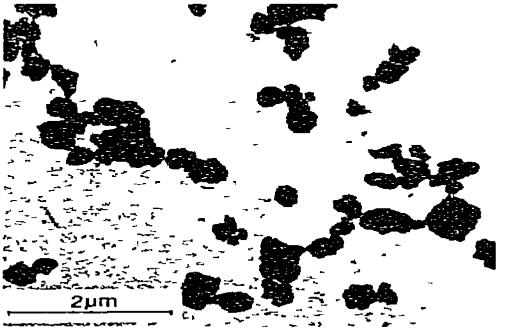

Fig. 5. Pigment **2a** (yellow, weak tinctorial strength) prepared by the method (i)

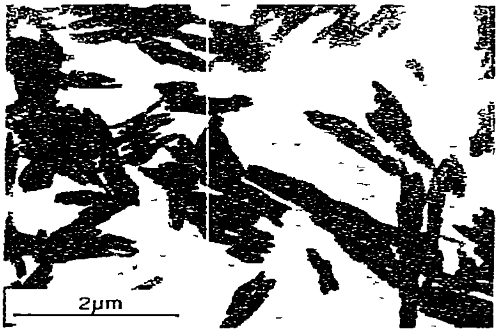

Fig. 6. Pigment **2b** (yellow, high tinctorial strength) prepared by the method (ii)

pigment's colour. All the nitrosoacetoacetarylides and dioximes studied were easily soluble in alcohols and other organic solvents but had rather poor solubility in water. Metallization carried out in water was then a heterogeneous process. Thus it was observed that pigments prepared in water had poor tinctorial strength and even abnormal colour.

For example pigment **3a** (Ar = 2′-chlorophenyl) prepared in aqueous ethanol had a brilliant yellow colour. The same pigment prepared in water (pigment **3b**) was orange with poor tinctorial strength. Reflectance spectra of reduced colour paints of these pigments showed a marked difference in intensity together with a difference in absorption range (Fig. 7).

From the electron photomicrographs it can be seen that pigment **3a** crystallizes in small, more or less aggregated needles (approx. 1 µm in length, Fig. 8) while pigment **3b** prepared in water gives particles irregular in shape and size (Fig. 9).

As in the case of pigment **2**, both samples of pigment **3** have the same crystal structure. As expected, the sample prepared in aqueous ethanol was more crystalline. The colour differences between the samples are then the result of changes in morphology, i.e degree of crystallinity and particle size of pigment crystals.

Similar observations have been made when water-miscible alcohols were replaced by other alcohols (n-buthanol, n-amyl alcohol, glycols) or by other organic solvents such as ethyl acetate, xylene or chlorobenzene. All pigments were crystalline but in some cases (chlorobenzene) considerable increases in crystal size occurred. This phenomenon caused a decrease in colour intensity and such pigments were usually redder than

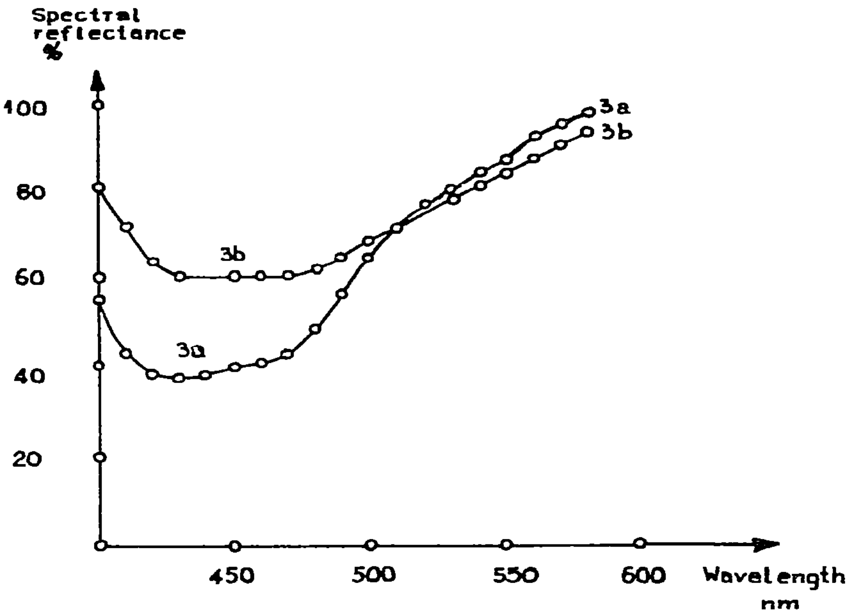

Fig. 7. Spectrophotometric reflectance curves for reduced paints (2/100) of pigment 3 prepared in aqueous ethanol (3a) and in water (3b)

those obtained using other solvents No definite change in crystal structure has been observed in any of the pigments studied.

Dimethylformamide used as a solvent during the metallization gave different results Some of the pigments studied have slight solubility in this solvent at higher temperatures and during the synthesis the possibility exists of recrystallization of the pigment accompanied by a change of

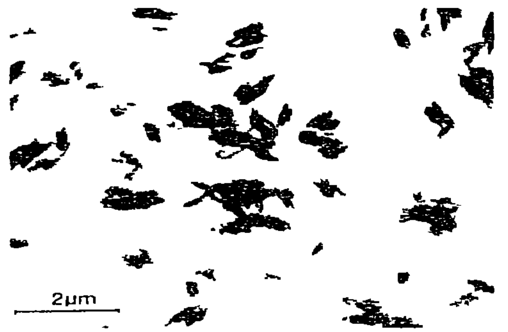

Fig. 8. Pigment 3a (bright yellow) prepared in aqueous ethanol

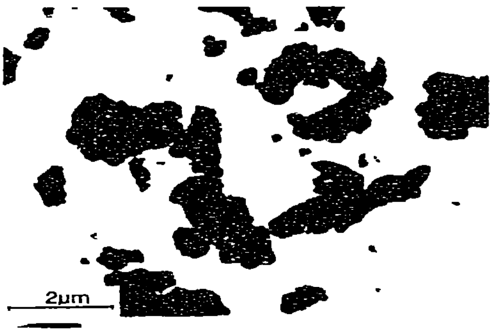

Fig. 9. Pigment 3b (dull, weak orange) prepared in water

crystal structure. This phenomenon evidently takes place during the preparation of pigment **4** (Ar = phenyl). Samples prepared in aqueous ethanol (pigment **4a**) and in 40% aqueous DMF are yellow. Pigment prepared in 80% DMF is orange (pigment **4b**). Yellow pigment **4a** deliberately treated with boiling DMF is red (pigment **4c**).

Electron micrographs of the samples of pigment **4** show visible differences. Sample **4a** synthesized in aqueous ethanol occurs in acicular form as in the case of other pigments prepared in this medium (Fig. 10) After treatment by DMF, sample **4c** occurs as a mixture of plates of different size and singular small needles (Fig. 11)

Fig. 10. Pigment **4a** (yellow) prepared in aqueous ethanol

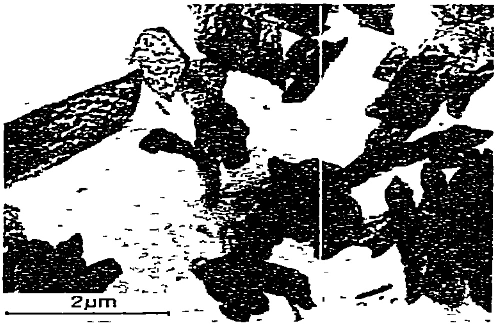

Fig. 11. Pigment **4c** (red) prepared by heating pigment **4a** in boiling DMF

X-ray diffraction peaks of both samples are similar but for sample **4c** there appear strong intensity peaks corresponding to interplanar spacings at 4 75 and 4·13 Å, accompanied by the appearance of a middle intensity peak at 2·60 Å and disappearance of a strong intensity peak at 5 43 Å There are also slight changes in values and intensities of other diffraction peaks (Table 3). These results suggest that pigment **4c** is the mixture of two different crystal structures The appearance of lines of middle and weak intensity at higher 2θ values indicates also that pigment **4c** has a more highly crystalline structure than pigment **4a**

The result of the reaction in aqueous dimethylformamide depends on the concentration of DMF in the mixture. When the solubility of a pigment in the reaction medium is sufficient, both metallization and recrystallization processes can take place. In the case of pigment **4b** prepared in 80% DMF a visible particle size growth accompanied by morphological change to ribbon-like crystals can be seen (Fig. 12).

TABLE 3
X-Ray Diffraction Patterns of Pigment **4** (Ar = phenyl)

Pigment **4a** *prepared in aqueous ethanol (yellow)*		*Pigment* **4b** *prepared in 80% DMF (orange)*		*Pigment* **4c** *prepared by heating pigment* **4a** *in boiling DMF (red)*	
d (*Å*)	*I*	*d* (*Å*)	*I*	*d* (*Å*)	*I*
11 04	vs	10 20	vs (broad)	10 20	vs
10 20	vs	7 18	vs	7 59	m
7 18	vs	5 42	s	6 64	vs
5 43	s	4 97	s	5 66	w
4 97	m	4 59	m	5-22	w
4 59	w	4 20	w	4 97	m
3 66	m	3 92	w	4 84	m
3 38	w	3 63	s	4 75	ms
3 30	m	3 36	m	4 13	ms
3 19	w	3 28	s	3 66	w
2 95	w	3 17	m	3 41	s
		3 03	m	3 32	vs
		2 95	m	2 95	w
		2 88	w	2 60	m
		2 60	w		
		2 53	w		
		2 49	w		
		2 39	m		
		2 29	w		
		2 17	w		
		2 09	w		
		2 06	w		

As has been mentioned above, the colour of pigment **4b** also changes to orange but its tinctorial strength is weaker than in pigments **4a** and **4c**. The X-ray diffraction pattern of this sample is almost unchanged in comparison with pigment **4a**. However, the appearance of weak intensity diffraction peaks at 4·20 and 2·60 Å suggests the presence of a new crystal structure. The presence of numerous lines of weak intensity at higher 2θ values (Table 3) indicates the most crystalline structure among all the samples of pigment 4. It is possible that after a long time of reaction the concentration of new crystal structure would increase and this phenomenon could cause further change in colour and properties.

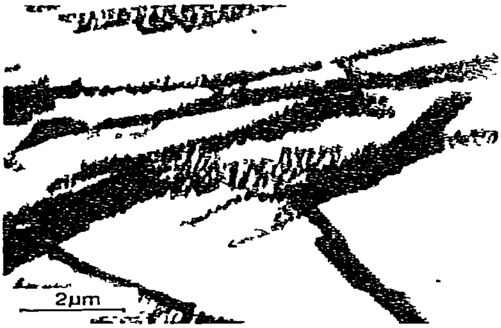

Fig. 12. Pigment **4b** (orange) prepared in 80% DMF

Although in the case of pigment **4** the use of dimethylformamide as a solvent gave rise to polymorphism, it should be mentioned that in other cases (e.g. when Ar = 2′-methylphenyl) only crystal growth without change of crystal structure has been observed.

4. CONCLUSIONS

The purpose of this research was to study the observed changes in colour and application properties of some metal-complex pigment derivatives of 2,3-dihydroxybutyric acid arylide 2,3-dioxime. From a number of possible pigments the yellow pigments **3** and **4** have especially interesting application properties. A detailed study has shown that changes in the process of preparation gave rise to definite variations of their properties.

It was expected that because of the unsymmetrical structure of the 2,3-dioximes used and the possibility of structural isomerism of metal complexes, changes in the morphology of the pigment crystals would be accompanied by changes in their crystal structure. It has been found that each of the pigments examined occurred in a stable form. Changes of crystal structure were observed in the cases of pigment **1** and pigment **4**. However, in the latter the change was incomplete in spite of a long conditioning time. In all other cases the change of colour and application properties was the result of morphological change in the pigment crystals. It is also evident that in spite of similarity in structure and methods of preparation all pigments of this group have to be considered separately in regard to their production. The results of the present work clearly do not exclude the possibility of existence of other polymorphic forms. Other factors which cannot be reproduced in laboratory-scale experiments may give further modifications in morphology and structure in plant production of these pigments

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