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Study on the transformation of metal-free phthalocyanine polymorph crystals by organic solvent treatment

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Abstract

Five organic solvents, sulfolane, *N*,*N*-dimethylethanolamine, iso-propanol, *N*,*N*-dimethylformamide (DMF), and acetone have been used to precipitate the sulfuric acid slurry paste of metal-free phthalocyanine and the pigments were analyzed by the X-ray powder diffraction method. The morphology was investigated by scanning electron microscopy. The organic solvents provided certain influences on the formation of the polymorphs. The α-form metal-free phthalocyanine was obtained by precipitation of the phthalocyanine acid-paste in DMF, iso-propanol, and 2-dimethylethanolamine. The β-form of the metal-free phthalocyanine was obtained by direct synthesis in 2-dimethylethanolamine or by precipitation of the phthalocyanine acid-paste in sulfolane. Finally the γ-form of metal-free phthalocyanine was obtained in acetone. The dispersibility of the metal-free phthalocyanine was improved after the solvent treatment process. These results gave an interesting and potentially commercially important improvement for polymorph transformation of metal-free phthalocyanine.

Keywords: X-ray powder diffraction; Scanning electron microscopy; Polymorphs; Metal-free phthalocyanine

1. Introduction

It is known that polymorphism, the existence of a chemical compound in more than one crystalline packing arrangement, is a generally common phenomenon. In organic molecular crystals the intermolecular forces are relatively weak and a variety of molecular stacking arrangements of similar energy are often possible. Since the structure of metal-free phthalocyanine (H_2Pc) was determined [1], it has been shown to exist possibly in the following polymorphism modifications: α [2], β [3], χ [4], π [5], ε [6], η [7], τ [8], η′ [9], τ′ [9], and γ [10]. Most of the polymorphs of H_2Pc mentioned above, and the reliability of the X-ray diagrams were reviewed by A. Whitaker [11]. The polymorphs of H_2Pc can be prepared mainly by methods such as vacuum deposition [12], direct synthesis [13], mechanical grinding [14], and organic solvent treatment [10] etc. Among those methods, mechanical grinding is the most commonly used, and has been widely applied in

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industrial processes for post-treatment of pigment products. The organic solvent treatment process could be considered an interesting one, which does not need mechanical grinding and inorganic ingredients, and simplifies the purifying process. In the investigation of polymorphic transformations by solvent treatment, phthalocyanine was solubilized or pasted in concentrated sulfuric acid and then precipitated by dilution with solvents. The process can be illustrated as follows [15]:

$$H_2Pc \xrightarrow{H_2SO_4(conc.)} H_2PcH^+ \cdot HSO_4^- \xrightarrow{solvent} H_2Pc$$

It is common knowledge that the α-type particles are formed after the H_2Pc acid paste is dispersed into water. One could expect that organic solvents might influence the precipitating process due to their different intrinsic properties. It was noted that this process should be carried out at low temperature in order to avoid decomposition of the macrocyclic ring of the phthalocyanine molecule. At room temperature, metal-free phthalocyanine is decomposed thoroughly after 20 h in 50% sulfuric acid [16]. Water-miscible solvents were chosen in this process for ease of handling of the dilution process, separating and washing of the phthalocyanine precipitates. The organic solvents used and conditions are shown in Table 1.

2. Experimental

2.1. Preparation of the polymorphs of metal-free phthalocyanine

In this programme, the method reported by P. J. Brach et al. [3] has been used to prepare the metal-free phthalocyanine in high purity and high yield (>90%). The product was washed with water, methanol, acetone and vacuum dried. Analysis calculated for $C_{32}H_{18}N_8$: C, 74.70; H, 3.53; N, 21.71. Found: C, 74.52; H, 3.53; N, 21.58.

Ten grams of metal-free phthalocyanine was added into 100 grams of 96% concentration by weight of sulfuric acid at a temperature below 5 °C and stirred until it completely dissolved. The solution was then poured into 500 ml of organic solvents as shown in Table 1, and the mixture was stirred at room temperature for about 10 h. The precipitate was then filtered off, washed with water, methanol, and acetone and dried at 50 °C under reduced pressure.

2.2. Characterization of the polymorphs of metal-free phthalocyanine

A D/MAX-RB X-ray diffractometer was used to characterise the polymorphism of the precipitate. In the measurement, an X-ray source of Cu target ($\lambda = 1.5418$ Å), tube voltage of 40 kV, DS (radiate slit) of 1°, RS (receipt slit) of 0.3 mm, SS (scan slit) of 1°, scan speed of 4°/min, scanning step of 0.02° and scanning region of 3–50° were chosen, and the results are shown in Fig. 1 and Table 2.

2.3. Investigation of the morphology of metal-free phthalocyanine particles by SEM (scanning electron microscopy)

The SEM (S-2150 Hitachi Ltd.) was used to investigate the morphology of the H_2Pc polymorphs and the tested specimens were prepared as follows.

In a 50 ml beaker, 5 mg of the H_2Pc specimen was added into 20 ml of acetone containing 0.5% of AEO-3 (polyethylene oxide monododecyl ether of

Table 1
Precipitation conditions for metal-free phthalocyanine polymorphs

Specimen	Solvent for treatment	Temp. of precipitation (°C)	Tint of H_2Pc powder
A	*N*,*N*-dimethylethanolamine	132	Reddish blue
B	Sulfolane	0–5	Greenish blue
C	*N*,*N*-dimethylethanolamine	0–5	Reddish blue
D	Iso-propanol	0–5	Reddish blue
E	*N*,*N*-dimethylformamide	0–5	Reddish blue
F	Acetone	Room temperature	Greenish light blue

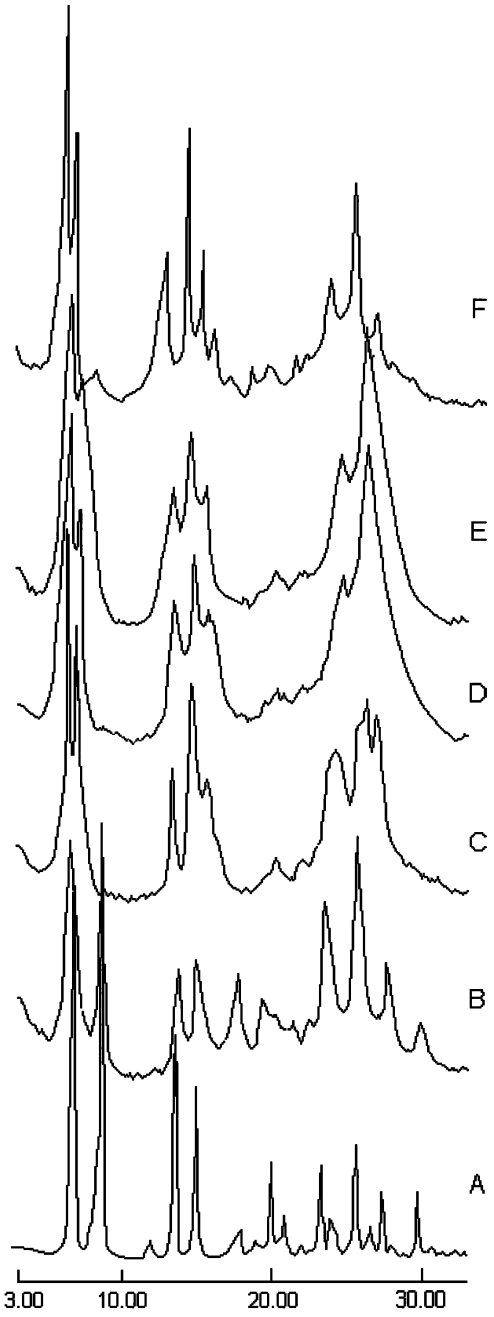

Fig. 1. XRD diagrams of metal-free phthalocyanine particles: A, direct synthesis of metal-free phthalocyanine in *N*, *N*-dimethylethanolamine; B, precipitated in sulfolane; C, precipitated in *N*,*N*-dimethylethanolamine; D, precipitated in isopropanol; E, precipitated in DMF; F, precipitated in acetone.

3 mole ethylene oxide) as dispersant. The mixture was homogenized by an ultrasonic blender. About 3–5 min were needed to obtain a homogeneous suspension. Then 2–3 drops of the suspension were coated on the stainless steel testing base and evaporated at room temperature. The specimens were tested directly without further treatment. The testing voltage and magnification rate are shown on the SEM images in Figs. 2–7.

3. Results and discussion

3.1. Characterization of the polymorphs of metal-free phthalocyanine by X-ray powder diffraction diagram

As shown in Fig. 1 and Table 2, specimen A, the polymorph of metal-free phthalocyanine synthesized directly from *N*,*N*-dimethylethanolamine was the pure β-form, identical to the result reported by P. J. Brauch et al. [3]. Although the interplane spacing d or Bragg angles 2θ of specimen A were entirely identical to the standard diffraction data [17], the diffraction peak heights or relative intensities I/I_0 were obviously different. Comparing XRD diagrams of specimen A and specimen B, it can be seen that the XRD diagram of specimen B precipitated from sulfolane was similar to specimen A. However, specimen B gave remarkably different relative intensities and width of diffraction peaks. The values of the interplane spacings of specimen B were a little larger than the standard XRD data of the β-form, while the relative intensities of diffraction peaks more closely fitted than specimen A. It is considered that specimen B is mainly composed of the β-form. Also comparing with other XRD diagrams, it appears that specimen B contains a small amount of γ-H_2Pc. These two specimens were different in their color tint, specimen A was reddish blue while specimen B was greenish light blue. It has been known that the XRD diagrams are dependent on measurement conditions and the physical properties of the specimens. The different transformation processes or conditions resulted in different physical properties such as aggregation status and grain size of the phthalocyanine particles.

Table 2
Data of XRD peaks and relative intensities of metal-free phthalocyanine particles

A		B		C		D		E		F	
d (Å)	I/I_0 (%)	d (Å)	I/I_0 (%)	d (Å)	I/I_0 (%)	d (Å)	I/I_0 (%)	d (Å)	I/I_0 (%)	d (Å)	I/I_0 (%)
12.690	62	12.912	99	13.301	100	13.182	100	13.182	100	13.341	100
9.905	100	10.040	75	12.133	75	12.133	74	12.233	75	12.133	63
6.329	37	8.051	10	6.582	38	6.553	47	6.544	46	9.972	11
5.778	29	7.296	13	5.980	59	6.013	60	6.029	61	6.573	37
4.945	47	6.365	50	5.569	36	5.576	44	5.654	46	5.972	64
4.354	17	5.839	53	5.368	20	4.539	20	4.349	23	5.590	38
3.754	16	4.995	48	4.337	15	4.333	23	3.618	55	5.323	20
3.419	20	4.562	38	4.058	15	3.598	54	3.365	90	4.945	10
3.208	12	4.148	30	3.877	18	3.365	91			4.599	12
2.962	13	3.965	30	3.738	38					4.362	13
		3.757	77	3.556	35					4.008	15
		3.424	100	3.432	50					3.621	31
		3.215	52	3.358	56					3.426	53
		2.985	29	3.259	49					3.236	25
				3.027	13					2.980	10

Specimen C, specimen D and specimen E were very similar in their XRD diagrams. Those were typical α-form phthalocyanine as reported in the literatures. It was clearly seen that specimen C had some impurity, most likely of the β-form. The color tints of the three specimens were all reddish blue. It is interesting to observe that specimen C and specimen A gave different polymorphs although the organic solvent used for precipitation was the same. The temperature for precipitation of specimen A was much higher than that for specimen C. Also specimen A was prepared under basic conditions in which gaseous ammonia was used as catalyst while specimen C was precipitated under acid conditions.

The XRD diagram of specimen F shows that it is a γ-form metal-free phthalocyanine [10]. It is first reported here that it is possible to prepare γ-form metal-free phthalocyanine by precipitation from acetone as the solvent. Although it has been reported in a former work [10] that the γ-form metal-free phthalocyanine was obtained by precipitation of sulfuric acid paste in DMF solution, only the α-form metal-free phthalocyanine has been formed in our experiments.

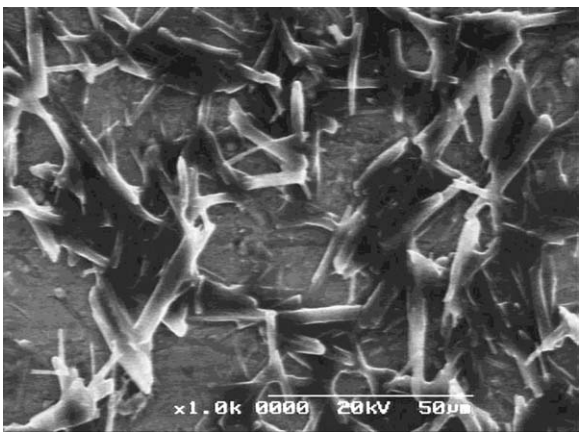

Fig. 2. Scanning electron micrograph of metal-free phthalocyanine particles of specimen A.

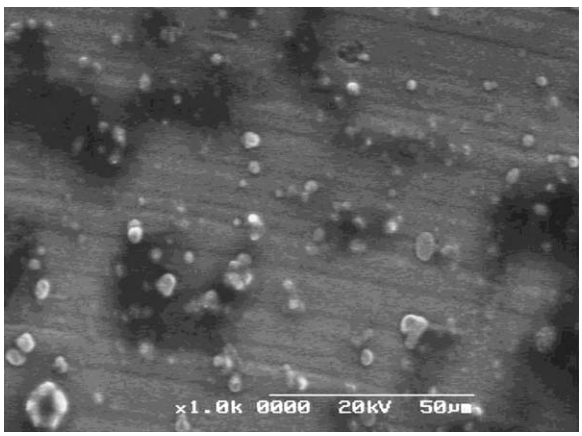

Fig. 3. Scanning electron micrograph of metal-free phthalocyanine particles of specimen B.

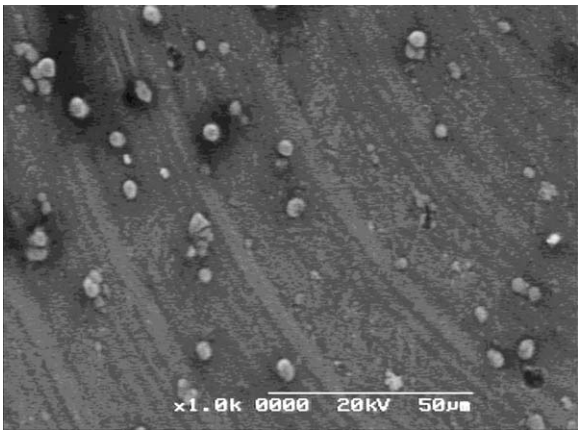

Fig. 4. Scanning electron micrograph of metal-free phthalocyanine particles of specimen C.

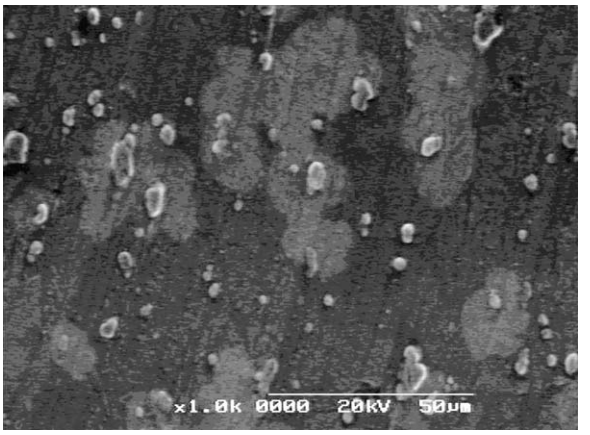

Fig. 6. Scanning electron micrograph of metal-free phthalocyanine particles of specimen E.

3.2. Scanning electron micrographs of solvent treated metal-free phthalocyanine particles

Fig. 2 shows scanning electron micrographs of H_2Pc particles synthesized in *N*,*N*-dimethylethanolamine and Figs. 3–7 show scanning electron micrographs of H_2Pc particles precipitated in sulfolane, *N*,*N*-dimethylethanolamine, iso-propanol, *N*,*N*-dimethylformamide, and acetone respectively.

The original particles, specimen A, were in needle-like form with large grain size and were very difficult to disperse. After the acid–solvent treatment, phthalocyanine particles changed in grain size and shape. According to the general classification of solvents [18], iso-propanol is a neutral amphiprotic solvent, *N*,*N*-dimethylethanolamine is a protophilic solvent, and the other three solvents, sulfolane, *N*,*N*-dimethylformamide, and acetone are dipolar aprotic solvents. In the present experiments, we could not correlate the exact relationship between solvent and polymorph type, but general observations of the mechanism of acidification and precipitation of H_2Pc can be made. Further work should be done on the precipitation dynamics of H_2Pc sulfuric solution

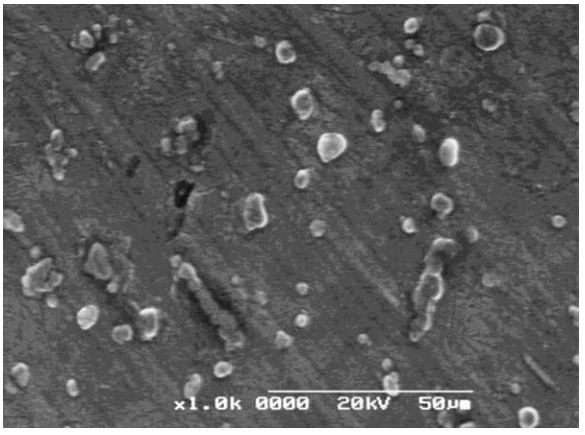

Fig. 5. Scanning electron micrograph of metal-free phthalocyanine particles of specimen D.

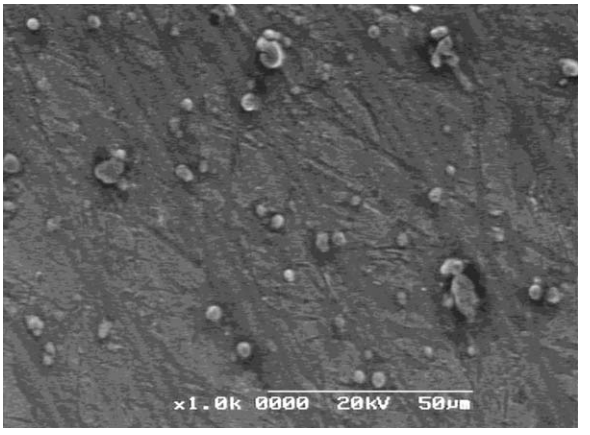

Fig. 7. Scanning electron micrograph of metal-free phthalocyanine particles of specimen F.

under the influence of different organic solvents. The solvents mainly influenced the polymorphism type of H_2Pc, but did not give distinct differences on particle agglomeration. The scanning electron micrographs showed that both the shape and size of five specimens of H_2Pc particles were very similar to each other. The average diameters of the specimens were between 3 and 5 μm, and the particles were spherical in shape.

4. Conclusions

Polymorphous transformation of metal-free phthalocyanine by precipitation in five organic solvents, sulfolane, *N*,*N*-dimethylethanolamine, iso-propanol, *N*,*N*-dimethylformamide, and acetone, has been studied and the products analyzed by X-ray powder diffraction method. The organic solvents gave certain influences on the formation of the polymorphs. The α-form metal-free phthalocyanine was prepared by precipitation of phthalocyanine acid-paste in DMF, iso-propanol, and 2-dimethylethanolamine. The β-form was prepared by direct synthesis in *N*,*N*-dimethylethanolamine under ammonia atmosphere or by precipitation of the phthalocyanine acid paste in sulfolane. Also the γ-form of metal-free phthalocyanine was obtained in acetone. The dispersibility of metal-free phthalocyanine was improved after the solvent treatment process. This result gave an unexpected and potentially commercially interesting improvement for polymorph transformation of metal-free phthalocyanine.

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