The Effect of Metal Oxides on the Transformation of Copper Phthalocyanine Crystals in Organic Solvents

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The dimorphic transformation of copper phthalocyanine crystals was examined by means of X-ray diffraction analysis and electron-micrograph observation, for α-copper phthalocyayine and metal oxides of various mixing ratios with respect to weight were ground using a grinder and suspended in an organic solvent. The α-β transformation of copper phthalocyanine is accelerated by the presence of metal oxides such as alumina, magnesia, and zinc oxide. Particularly, alumina has a remarkable effect on the acceleration of β-copper phthalocyanine formation. The rate of transformation increases with the amount of metal oxide and the grinding time for a mixture of copper phthalocyanine and alumina. The activation energy for the α-β transformation in a (1 : 1) mixture of copper phthalocyanine and alumina ground for 30 min was calculated to be 12.0 kcal/mol.

The phthalocyanine pigments are some of the most important colored pigments owing to their excellent properties. They are remarkably resistant to alkalis and concentrated sulfuric acid and are stable under normal storing conditions. Since their tints have exellent durability in exterior finishes, they are used in paints, lacquers, enamels, and plastics. Their resistance to light, acids, and alkalis also makes them valuable pigments for printing on paper and textile goods.[1]

The polymorphic behavior of copper phthalocyanine was first found by German investigators.[2] Hamm and Norman[3] observed the dimorphic transformation of copper phthalocyanine by means of an electron microscope and electron diffraction. It is well known that the α-form crystal is transformed into the stable β-form either by treatment in various organic suspension media or by thermal treatment. The α-β transformation in organic suspensions is of greatest importance with respect to the decrease of tinting strength and the change of tone in the paint and ink industry. Many investigations have been reported on the transformation of copper phthalocyanine in organic suspensions from the viewpoints of practice and crystallography.[4–11]

Furthermore, in the paint industry, mixtures of several kinds of pigments are used to obtain various colors. Usually, mixtures of organic and inorganic pigments are used. In previous work, the grinding process of mixtures of copper phthalocyanine and inorganic pigments was examined.[12–14] There are no reports concerning the effect of inorganic pigments on the transformation of copper phthalocyanine in organic suspensions. In the work reported here, the effect of metal oxides on the transformation of copper phthalocyanine in organic solvents was investigated by means of X-ray diffraction analysis and electron microscopy.

Experimental

Materials. The α-form copper phthalocyanine (abbreviated α-CuPc) used here was supplied by the Dainippon Ink Chemical, Ltd. Metal oxides used were alumina, magnesia, and zinc oxide of a commercially available high purity (99.9%). The specific surface areas of the alumina, magnesia, and zinc oxide obtained using the BET method are about 170 m^2/g, 30 m^2/g, and 5 m^2/g, respectively. *p*-Xylene of commercial spectrograde quality was used as the organic solvent

Apparatus and Procedure. The mixtures of α-CuPc and metal oxides were ground using an Ishikawa-type grinder with an agate mortar in a closed chamber at room temperature at a (1 : 1) weight mixing ratio. Each mixture containing magnesia and zinc oxide was ground for 30 min after mixing. The mixture of α-CuPc and alumina was ground for 10, 30, and 60 min at weight mixing ratios of (2 : 1), (1 : 1), and (1 : 2). The mixtures were suspended in *p*-xylene to investigate the α-β transformation. The concentration of each suspension was always maintained within the range of 3 to 6 weight percent for *p*-xylene. About 30 cm^3 of the suspension was put in a glass tube with a glass stopper. The suspension was placed in a water bath at constant temperature to within ±0.05 °C. After the required interval of time had elapsed at a definite temperature, the suspension was rapidly cooled with cold water. After being quickly separated from the solvent, the precipitate was washed with a cold inert solvent such as methanol or acetone to remove any trace of the solvent. After being dried, these crystals did not tend to undergo further changes either in external appearance or in crystal structure. The immersion time was in the range of 10 min to 10 h depending on the treating temperature.

To determine the composition of each crystal form, X-ray diffraction analysis was employed using nickel-filtered copper radiation at 35 kV and 10 mA as the X-ray diffraction source, with a scanning speed of 1/2° per min, a time constant of 2 s, a divergence slit of 1° and a receiving slit of 0.2 mm. The X-ray diffraction diagrams were recorded by means of an X-ray diffractometer (Geigerflex). The observation of the powder surface was performed using a Hitachi HSM 2 electron microscope.

Results and Discussion

The X-ray diffraction patterns of original α-CuPc and β-CuPc are presented in Fig. 1. It is worth noting that a common characteristic of the X-ray diffraction patterns for the metastable and stable forms is that a pair of strong reflections appear at smaller angles, as indicated by the letters u and v for the α-form, and by s and t for the β-form crystals. These correspond to lattice spacing of 9 to 13 Å, which are closely related to the size and the stacking of the molecules in approximately 10 Å squares, as well as to the normal crystal arrangements of both forms.

The X-ray diffraction pattern of a (1 : 1) mixture of α-CuPc and β-CuPc is shown in Fig. 2(a). The

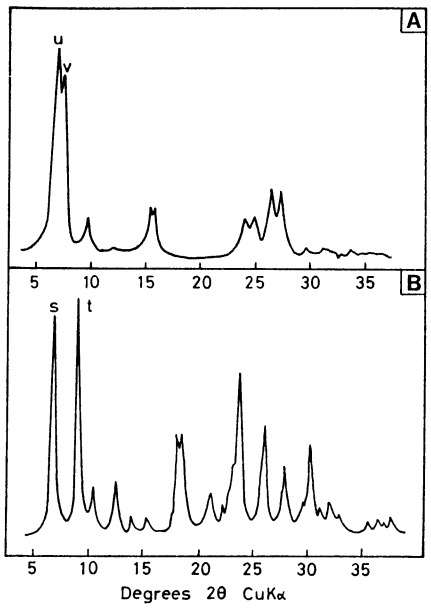

Fig. 1. X-Ray diffraction patterns of dimorphic forms of CuPc. (A): α-CuPc (Metastable form), u: 12.9 Å (200), v: 12.1 Å (002). (B): β-CuPc (Stable form), s: 12.6 Å (001), t: 9.8 Å (20$\bar{1}$).

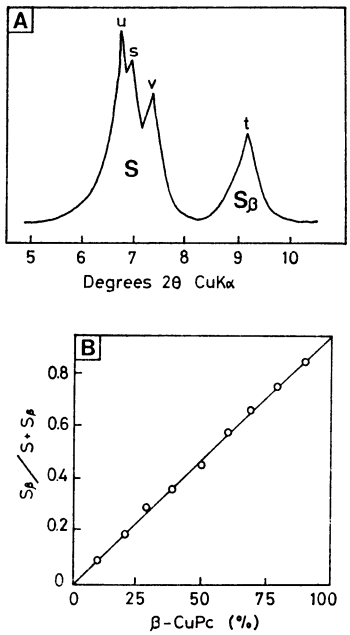

Fig. 2. (a): X-Ray diffraction pattern of a (1 : 1) mixture of α-CuPc and β-CuPc. (b): Calibration curve.

letter Sβ indicates the integral intensities of the reflection of β-CuPc, and S those of α-CuPc overlapping with β-CuPc. Sβ/S+Sβ is plotted against the composition of β-CuPc in mixtures of α-CuPc and β-CuPc of various mixing ratios in Fig. 2(b). The amount of β-CuPc in the samples can be determined from this calibration curve.

The α-β transformation of a mixture of α-CuPc and metal oxides was carried out in *p*-xylene at 50 °C. The reflections characteristic of α-CuPc are gradually

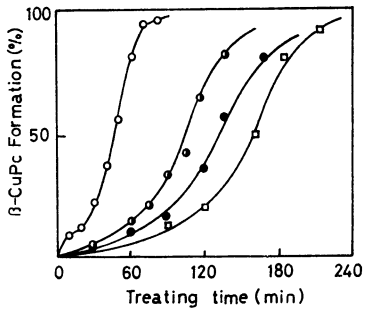

Fig. 3. The amount of β-CuPc formed in mixtures of α-CuPc and metal oxides *versus* the treating time in *p*-xylene at 50 °C.
(□): α-CuPc alone, (●): Mixture of α-CuPc and zinc oxide, (◑): α-CuPc and magnesia, (○): α-CuPc and alumina.

replaced by those of β-CuPc and the two sets of reflections are superimposed at the intermediate stages. By using the calibration curve, the amount of β-CuPc in the mixture of α-CuPc and metal oxide can be calculated. Figure 3 gives the relation between the amount of β-CuPc formed and the treating time. The effect of metal oxides on the transformation of α-CuPc increases in the order: alumina>magnesia>zinc oxide. The addition of alumina produced a remarkable effect on the rate of β-CuPc formation. This order is the same as the increasing order of the surface areas. Consequently, the rate of transformation is considered to depend on the specific surface areas of the oxides.

Our following discussion is mainly devoted to the effect of the addition of alumina on the transformation of α-CuPc.

Scanning electron micrographs of the original specimens and the mixtures of α-CuPc and alumina transformed in *p*-xylene at 40 °C are shown in Photo. 1. The horn-like crystals which formed on the surface of the alumina as shown in Photo. 1(D). It is obvious that almost all the α-CuPc crystals in Photo. 1(E) have transformed into flacky β-CuPc. The nuclei of the β-CuPc crystals formed in the solvent are considered to be adsorbed on the surface of the alumina, and then β-CuPc crystal growth is expected to proceed. The nuclei can be expected to increase with the amount of the addition and the grinding time.

The amount of β-CuPc formed in mixtures of α-CuPc and alumina of various mixing ratios is plotted against the treating time in Fig. 4. The amount of β-CuPc formed in mixtures of α-CuPc and alumina at each treating time increases with the amount of the addition.

This fact is explained by assuming that the adsorption of the nuclei on the surface of the alumina accelerates the β-CuPc crystal growth.

The amount of β-CuPc formed in the mixture ground for various periods is plotted against the treating time in *p*-xylene at 40 °C in Fig. 5. The amount of β-CuPc formed in the mixture increases with the grinding time. This fact indicates that the nuclei of β-CuPc crystals on the surface of the alumina can be formed more easily by mechanical treatment than by

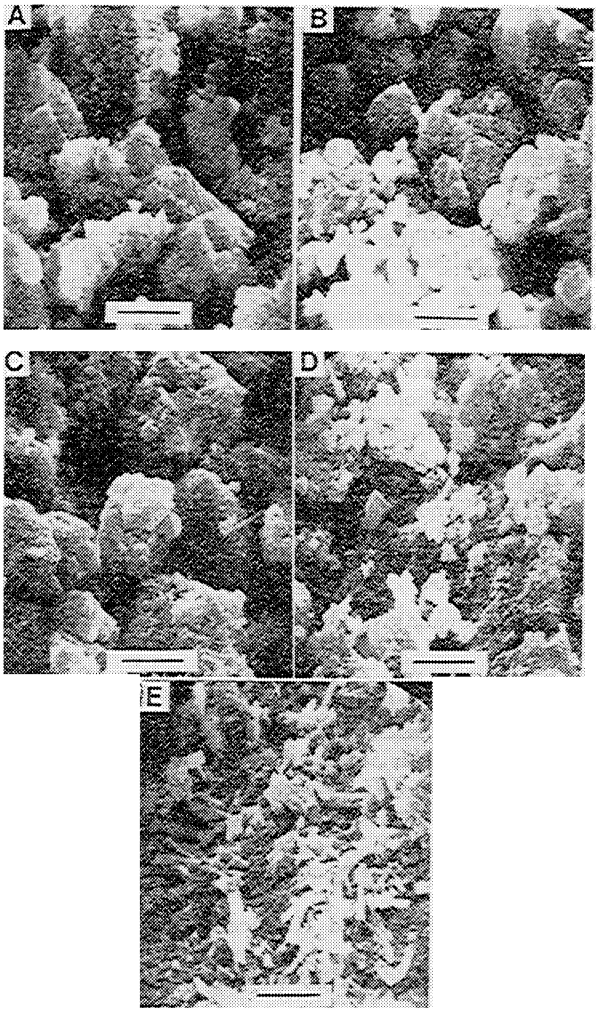

Photo. 1. Scanning electron micrographs of original specimens and the mixtures of α-CuPc and alumina undergoing transformation in *p*-xylene at 40 °C. The bars represent one micron.
(A): α-CuPc, (B): (1 : 1) mixture of α-CuPc and alumina ground for 30 min, (C); mixture treated for 60 min, (D): mixture treated for 75 min, (E): mixture treated for 90 min.

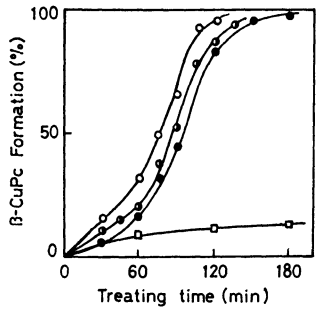

Fig. 4. The amount of β-CuPc formed in mixtures of α-CuPc and alumina ground for 30 min at various mixing ratios *versus* the treating time in *p*-xylene at 40 °C.
(□): α-CuPc alone, (●): (2 : 1) mixture, (◑): (1 : 1) mixture, (○): (1 : 2) mixture.

simple mixing. When the organic pigment is admixed with the inorganic one, the surface of inorganic pigment becomes covered with the former and grinding of the inorganic pigment is impeded by the lubricating action of the organic pigment.[12–14] Particularly, in the grinding of mixture of α-CuPc and inorganic powder, the transformation from α-CuPc to β-CuPc is considered to be accelerated by the absorption of the grinding energy.[14]

Figures 6 and 7 show the amounts of β-CuPc formed in α-CuPc alone and in a (1 : 1) mixture of α-CuPc and alumina, respectively, against the treating time

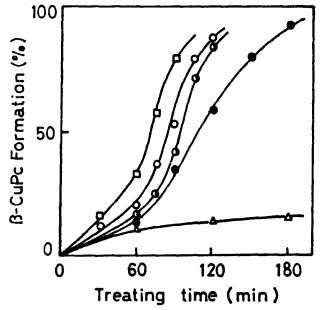

Fig. 5. The amount of β-CuPc formed in a (1 : 1) mixture of α-CuPc and alumina ground for various intervals *versus* the treating time in *p*-xylene at 40 °C.
(△): α-CuPc alone, (◑): Mixture ground for 10 min, (○): Mixture ground for 30 min, (□): Mixture ground for 60 min, (●): Simple mixing.

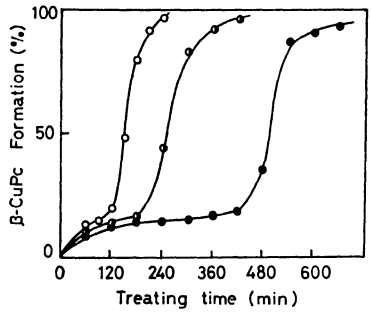

Fig. 6. The amount of β-CuPc formed in α-CuPc alone against the treating time in *p*-xylene at various temperatures.
(●): 30 °C, (◑): 40 °C, (○): 50 °C.

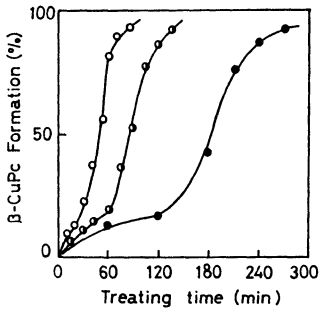

Fig. 7. The amount of β-CuPc formed in a (1 : 1) mixture of α-CuPc and alumina *versus* the treating time in *p*-xylene at various temperatures.
(●): 30 °C, (◑): 40 °C, (○): 50 °C.

in *p*-xylene at various temperatures. It appears difficult to explain the entire curve by a simple mechanism. In the earlier stages of the treatment, it is considered that crystals of meatstable form (α-CuPc) undergo preliminary growth without changing their crystal structure. The latter stages agree with first-order reaction kinetics.

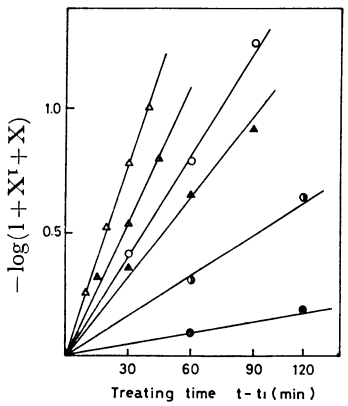

Fig. 8. The logarithm of the amount of β-CuPc formed in α-CuPc alone and the α-CuPc in the mixture *versus* the treating time in *p*-xylene at various temperatures.
(t_1): Induction time, (X_1): The amount of β-CuPc formed for a treating time t_1 in *p*-xylene.
(○): α-CuPc alone, (△): (1 : 1) mixture of α-CuPc and alumina.
(○): 50 °C $X_1=0.286$, $t_1=150$ min, (◑): 40 °C $X_1=0.770$, $t_1=300$ min, (●): 30 °C $X_1=0.897$, $t_1=540$ min, (△): 50 °C $X_1=0.204$, $t_1=40$ min, (▲): 40 °C $X_1=0.323$, $t_1=90$ min, (▲): 30 °C $X_1=0.238$, $t_1=180$ min.

Therefore, the logarithm of the amount of β-CuPc formed was plotted against the treating time, as is shown in Fig. 8. From the result, the activation energy for the transformation of α-CuPc alone and α-CuPc in a (1 : 1) mixture was calculated to be 17.6 kcal/mol and 12.0 kcal/mol, respectively. Other investigators[5,9] have found the activation energy for the transformation of α-CuPc alone in *p*-xylene to be 17.1 kcal/mol. This is in fairly good agreement with our results.

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