Study on recrystallization mechanism of phthalocyanine pigments

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1. INTRODUCTION

Copper Phthalocyanine (CuPC) pigments have been widely used in the ink, display and coating industries. Polymorphism is one of the interesting characteristics among the properties of phthalocyanine dye and pigments. The α- and β- crystalline forms of CuPC pigment are most common crystal forms. However, only β-form crystal has been thoroughly studied because it is the most thermodynamically stable crystal state and it is easy to be prepared.

The milling of pigment is a pulverizing procedure to make crude type pigment available in application. We call this procedure pigmentation and, in the case of CuPC, polymorphism during pigmentation is one of the important phenomena. The polymorphs of CuPC is strongly depends on the milling methods and the chemicals used in milling process. Basically, polymorphism of CuPC crystal is a phenomenon resulted from mixed effects of input energy, such as physical and thermal energy, and crystallization kinetics during milling.

Crude CuPC is a non-pigmentary β-crystalline material with crystal size up to around 100 μ*m.* Pigmentary crystal size is achieved by pulverization, but is accompanied by partial conversion of the β-form to the α-form. Organic liquid during milling process is necessary to produce the ε- or β –form crystals. That process was called wet milling process. Salt-milling or kneading in the presence of bulk liquid is one of the wet milling processes. Sometimes dry milling under the presence of a minor proportion of a liquid is used for crystallising the pigment.

Acid pasting has been used to convert CuPC crystalline form from β to α. Conversion to α form is absolutely necessary to get another crystalline form which is used for LCD color filter due to its thermal stability and good color characteristics.

Acid pasting is a recrystallization process of CuPC molecules in the poor- or non-solvent. The poor- or non-solvent is hard to dissolve the solutes and brings about a decrease of solubility of CuPC molecules in the binary solvent mixture. Acid pasting procedure is able to operate at a constant temperature. Only the concentration gradient of the solvents arises in the crystallizer and also leads to broadening of the particle size distribution.

In acid pasting, the crystallization of CuPC molecules starts from the interface of good solvent and poor/non-solvent. It happens that mutual solvents diffusion takes place first and the concentration of solute in good solvent decrease gradually. At the critical concentration, crystals start to form it unique feature and polymorph.

In This work, water, propylene glycol mono methyl ether acetate (PGMEA), methanol, t-butyl methyl ether were selected as non-solvents for CuPC. Sulfuric acid is a strong mineral acid with high polarity, which can dissolve CuPC and soluble in water at all concentration. Non-solvents were selected according to their degree of polarity to observe the effect of mutual affinity of solvent on the crystallization process. Crystal growth has been investigated for CuPC sulfuric solutions in contact with non-solvents to determine the crystal polymorph and particle size distribution. The crystal forms were studied using wide angle X-ray diffraction (WAXD), IR absorption spectra and SEM. Many process condition were considered to study the morphological changes of CuPc including polymorphs, aggregation feature and particle size.

2. EXPERIMENTAL

Synthesis of phthalocyanine

Copper phthalocyanine was synthesized using the procedures as below. Copper sulfate pentahydrate, phthalic anhydride and excess of urea with a catalytic quantity of ammonium chloride and ammonium molybdate were finely ground and the mixture was heated around 180℃ for 4 h. The resulting product was purified using methanol, hydrochloric acid and sodium hydroxide.

For investigating the effect of β-type CuPc crystals size and morphology, another crude CuPc were delivered from Bokwang Chemicals Co. and we compared the different in morphology of crude CuPc which affect on the polymorphs and final morphologies after milling process.

Crystallization by non-solvent

Crud type CuPc crystals were made by acid pasting method using concentrated sulfuric acid (96%). The liquid-liquid interface crystallization was performed by the same apparatus designed by Kazunori Kadota et. Al. [1]. 6 hours stirring was needed to dissolve the crude CuPC completely. This CuPC solution was poured slowly into straight glass funnel and non-solvent was gently added on top of CuPC sulfuric solution with a pipette to from a liquid-liquid interface. The precipitation of CuPC was carried out with changing the contact time of two liquids. The filtration was carried out for the separation of the crystal particles from the solution under vacuum when the crystals grow in a proper size. The crystal shape and particle size distribution were observed by scanning electron microscopy.

3. RESULTS AND DISCUSSION

The results showed that the particle size of CuPc crystals was changed in the ranged between few micro orders to submicron orders.

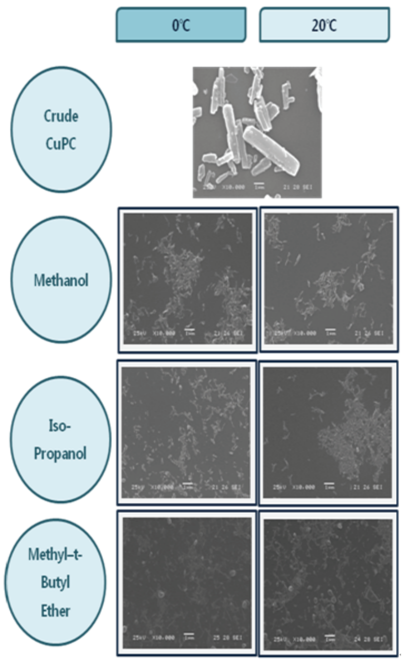

Fig. 1. SEM image of CuPC crystals grown at interface between sulfuric acid and non-solvents.

Fig. 1 shows SEM image of CuPC crystals grown at 0℃ and 20℃ according to non-solvent types.

4. CONCLUSION

Low polarity solvent such as methyl butyl ether could let pigment solution divide into smaller emulsified domain by stirring and smaller crystal size we can obtain. Furthermore such a low crystallization rate due to the slow moving out of sulfuric acid makes other polymorphs of CuPC crystal.

Consequently, to obtain the result of reducing the particle size in the smallest scale and narrowing the size distribution, low polarity solvent and low temperature are preferred. Heptan of which polarity is zero did not mixed with sulfuric acid at any moment, so pigments precipitation did not occur.

5. REFERENCES

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