Effect of Milling Process on Morphology of Copper Phthalocyanine Particles

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1. INTRODUCTION

In many industrial fields using pigments, making submicron particles of pigments have been so attractive subject for a long time. Nano-scaled pigments could be useful in display industry, especially in color filters. The smaller particle size in the dispersion state produces superior color strength, contrast, and transmittance [1].

For the application of pigments, it is so important to build up and stabilize the process of milling and dispersion to produce submicron pigments particles with narrow particle size distribution.

Copper phthalocyanine (CuPc) pigments have been the most commercially important species in the ink, display and coating industries [2, 3]. The α- and β- crystalline forms of CuPc pigment are one of the polymorphs widely used [4]. When the compound shows more than one crystalline modification, dependence of crystal structure is more considerable. In the case of CuPc, it is well known it shows many polymorphic forms, only β-form crystal has been thoroughly studied because it is the most thermodynamically stable crystal state [5,6]. Other crystal forms, however, have not been studied in detail because it is difficult to get a single crystal. The ε-form had been reported, but the information about this polymorph is not sufficient.

The milling procedure is so important for the pigmentation of crude CuPc. The polymorphs of CuPc is strongly depends on the procedure factor for milling and the chemicals used in milling process. And furthermore, the shear strength induced during milling process is another considerable factor for investigation of crystal form change.

This present work investigated the influence of various factors that affect the polymorphs of CuPc. The crystal forms were studied using wide angle X-ray diffraction (WAXD), IR absorption spectra and SEM. The change of crystal forms during the milling procedure were investigated and considered the most factors which can affect the transformation of crystal forms. Acid pasting method and salt milling method were employed for this study. Many process condition were considered to study the morphological changes of CuPc including polymorphs, aggregation feature and particle size.

2. EXPERIMENTAL

2-1. 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 Chemiclas Co. and we compared the different in morphology of crude CuPc which affect on the polymorphs and final morphologies after milling process.

2-2. Acid pasting and salt milling

α -type CuPc standard were made by acid pasting method using concentrated sulfonic acid (96%). 200 g of crude CuPc were injected at a 0.1~0.2 g/min speed with stirring. CuPc is so temperature sensitive that the color tone and crystal forms are easily changed. So, the inside temperature of reactor were fixed at target temperature to see the temperature effect on the final morpologies. 6 hours stirring was needed to dissolve the crude CuPc completely. This CuPc solution was poured slowly into the 3L of distilled water and filtered. After drying, the particle size, crystal forms and shape of crystals were investigated according the acid pasting condition such as temperature and contents of synergist.

Salt milling was conducted in kneader using grinded fine salt. The original salt was purchased and grinded into so fine salt powder. Final particle sizes of salt were in the rage of 40~50μ m in volume

distribution. The results of CuPc crystal morphology were so dependent on the size and shape of salt crystals. The main factors in salt milling procedure were the size of salt particles, time for milling in kneader and the existence of extra solvent. All the salt millings in this work were conducted under diethylene glycol (DG) as a main solvent.

3. RESULTS AND DISCUSSION

The results showed that the particle size of CuPc was changed in the ranged between few micro orders to submicron orders. Figure 1 showed the WAXD results when the acid pasting temperatures were changed from 0℃ to 40℃.

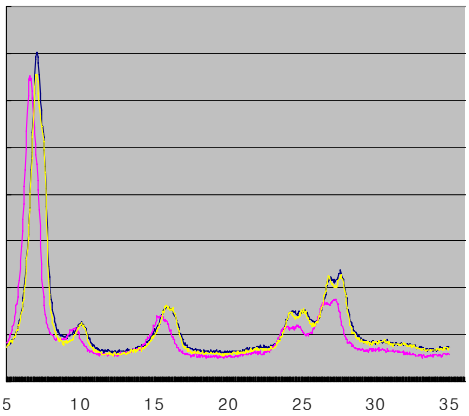

Figure1. WAXD patterns of CuPc according the acid pasting temperature.

Figure 2 showed the particle size distribution measured by particle size analyzer. In the table 1, the particle size calculated from particle size analyzer and WAXD results. In general, X-ray diffraction gives the size of primary particle size before aggregation in the process.

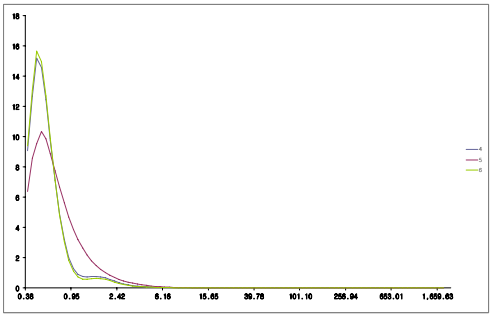

Figure2. Particle size distribution of acid pasted CuPc crystal particles..

Table 1. The summary of particle sized of CuPc after acid pasting.

CuPC		Avergae Particle Size(um)	FWHM	2 theta	d(Å)
Crude CuPC		1.10	0.259	6.88	307
α type	0 ℃	0.67	0.353	6.96	226
	20 ℃	0.84	0.230	6.45	360
	40 ℃	0.65	0.350	6.96	220

4. REFERENCES

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