

## Investigation of Nano-Colorant Master Batch

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### ABSTRACT

*The encapsulation of organic pigment (a copper phthalocyanine blue pigment) with polymer by co-sonication of copper phthalocyanine blue pigment dispersion and a typical miniemulsion polymerization was studied. The pigment containing polymer particles were analyzed in detail by particle size measurements, transmission electron microscopy, UV-Vis spectrophotometry and thermogravimetric analysis. The effect of the polymerization process and type of surfactant and co-surfactant in the efficiency of encapsulation were investigated. The pigment was first suspended into surfactant by sonication, before being encapsulated by miniemulsion polymerization using styrene as monomer and water soluble potassium persulfate as initiator. The final particle size was in the range of 67 to 157 nm. Dynamic light scattering measurements showed that the organic pigment could stabilize the miniemulsion droplets, and be thus satisfactorily encapsulated without introducing any other compound in the formulation.*

**Key words:** Encapsulation, Organic pigment, Miniemulsion, Polymerization

### INTRODUCTION

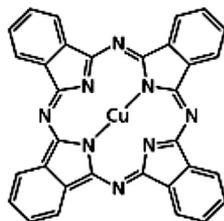
Organic pigments have been extensively used in coating, ink and latic industries or even in color filters for electronics and communication apparatus since they have many advantages such as photosensitivity, color strength, excellent transparency and etc. However, the limited hiding powder, poor dispersion ability, and especially the poor weather are obviously the obstacles for organic pigments in other applications (Marim et al., 2005). The current status to make a color resin or polymer was adopted by using processes after finished the polymerization that are dispersing, compounding, or using mixing equipments like twin screw, kneader and three roller to induce the color inside the polymer. After that the colorful polymer will be obtained, then using to different application. Since the process treat the different phase, solid disperse into the melt viscous liquid phase. The main force to disperse the color particle is not easy to attach boundary of the very small size one. Normally the size, can be treated around 1-5 micron, so the color will show the strong scatter effect, and the lower saturation. There are numbers of method explored so far attempting to address these problems. In real

commercial case (Eastman Kodak) (Yuan et al., 2005) the idea to reduce the size of disperse colorant particle was proposed to get the better properties on saturation, also reduce the scattering effect. Lelu et al., (2003) encapsulated an organic phthalocyanine blue pigment into polystyrene latex particles using miniemulsion polymerization to improve its dispersion ability in aqueous system. This study focuses on a novel process without induce extra energy to mix the color with the resin, just merge them together during the polymerization process, called “*in-situ* polymerization process” to manufacture the plastic (polystyrene, PS), forming the high concentrated color master batch, to enhanced and improve the quality of color chip or color plastic master in easilier use, more uniform color and best color performance when apply it to different applications.

## MATERIALS AND METHODS

### Materials

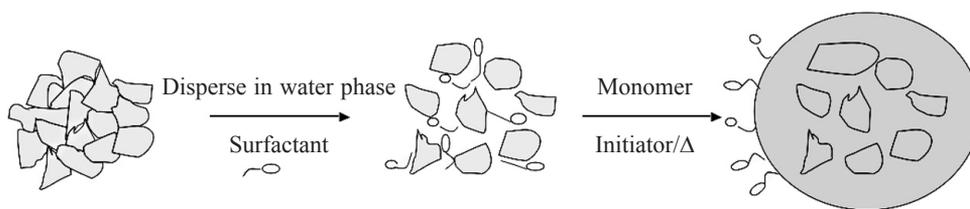
The Copper phthalocyanine blue pigment was supplied by Modern Dye-stuffs @ Pigments with chemical structure as shown in Figure 1. The monomer styrene was purchased from Across. The potassium persulfate of chemical grade from Aldrich, was used as initiator. The surfactant sodium dodecyl sulfate (SDS, BDH), Nonylphenol polyethoxylate (NP-40, Sigma Aldrich) and the co-surfactant hexadecanol (Sigma Aldrich) were used as received. An ultrasonic bath was used to help disperse the blue pigment in surfactant solution.



**Figure 1.** The chemical structure of Copper phthalocyanine blue pigment.

### Encapsulations

A scheme of the methodology utilized in the encapsulation of the Copper phthalocyanine blue pigment was showed in Figure 2. The encapsulation was carried out in a glass reactor of 500 ml. The reactor was initially loaded with water, copper phthalocyanine blue pigment and surfactant and sonified with a 600 W ultrasonic sonifier for 20 minutes, to create the miniemulsion droplets. The system was then kept under agitation for 20 minutes. Then 20% of monomer was added and the system was kept under agitation and heated to 80°C. The polymerization was started with the addition of 0.1% of sodium persulfate. The system was carried out at the same temperature for 6 hours under permanent stirring. After the encapsulation step the latex was precipitated by methanol and centrifuged at 20000 rpm and then washed with de-ionized water to remove all SDS. The encapsulated pigment was dried at 60°C.



**Figure 2.** A scheme of the methodology utilized in the encapsulation of the Copper phthalocyanine blue pigment.

### Characterizations

The particle and droplet sizes were determined by dynamic light scattering (DLS) using Lambda 650, Malvern instrument. Droplet size was recorded immediately after sonication by diluting the sample with a saturated SDS aqueous solution. The autosizer provided average diameter and polydispersity indexes (PDI). The monomer conversions were determined by gravimetry. The morphologies of organic blue pigments and encapsulated blue pigments were characterized by transmission electron microscope (TEM, Jem-2020 200 keV, Jeol). The samples for TEM observation were sonicated in water for 20 min and deposited onto carbon-coated copper grids and air-dried before examination. The amount of encapsulated blue pigment was determined by GmbH 2000, Metter Toledo instrument in air with temperature range from room temperature to 600°C at a scan rate of 20°C/min. The UV-vis spectra were obtained with a Lambda 650 spectrophotometer in the absorption and reflectance mode. The absorption and scattering spectra were determined in film form on glass slide.

## RESULTS AND DISCUSSION

### Preparation of encapsulated blue pigment

In order to investigate the experimental conditions giving the smallest droplet size and the best dispersibility, the formations were compared on the basis of the size and polydispersity of the miniemulsion before polymerization as shown in Table 1. Three surfactant systems were compared as nonionic surfactant (NP-40), anionic surfactant (SDS) and 50/50 of nonionic and anionic surfactant. The smallest droplets were obtained from anionic system as shown in Table 1.

**Table 1.** Effect of surfactant on pigment droplet size.

Pre-Pigment Sample	Surfactant	H <sub>2</sub> O (g)	Droplet size (nm)	PDI
PSB03	NP-40	200	150.7±1	0.1
PSB04	NP-40:SDS	200	182±3.5	0.23
PSB05	SDS	200	94±0.42	0.15

It can be clearly seen from Table 2 that the droplet diameter significantly decreased in the presence of pigment in comparison to the pre-pigment in Table 1. As a direct consequence of the osmotic effect of the solubilized pigment in the

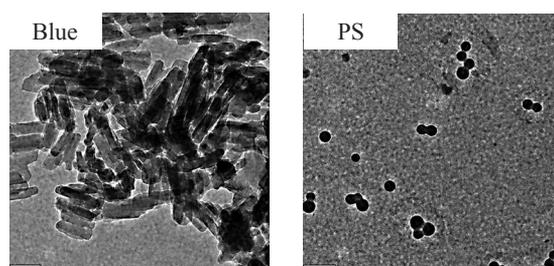
surfactant, the miniemulsion could be converted further into a stable pigmented polymer suspension which displayed an intense blue. TEM images indicated that the pigment particles have been encapsulated with the latex beads. Figure 3 show TEM images of the copper phthalocyanine blue pigment before and polystyrene latex beads. Figure 4 show TEM images of the copper phthalocyanine blue pigment after encapsulation by miniemulsion polymerization. The presence of free polymer particles was verified by the low encapsulation efficiency determined by TGA (3.3 % of pigment encapsulation). These particles were probably formed by a mechanism of micellar nucleation, which is of major importance as it indicates that it could be possible to improve the efficiency of encapsulation by avoiding the particles nucleation and their stabilization in the water phase. Higher values of efficiency could be attained by optimizing the recipes (Viala et al., 2002).

### Stability of encapsulated blue pigment

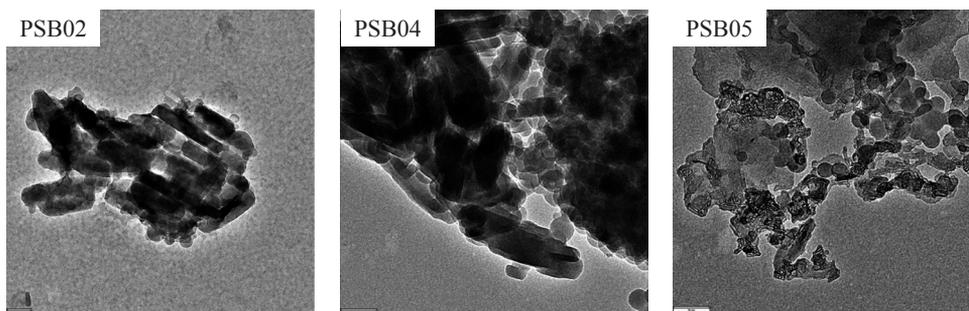
In order to study encapsulated the pigment stability, the encapsulated the pigment size and polydispersity index with varying surfactant were recorded within 28 days as shown in Figure 5. All surfactant systems can stabilize encapsulated blue pigment particles. There are no significant changing in size of all system at anytime.

**Table 2.** Effect of surfactant on pigment encapsulated size.

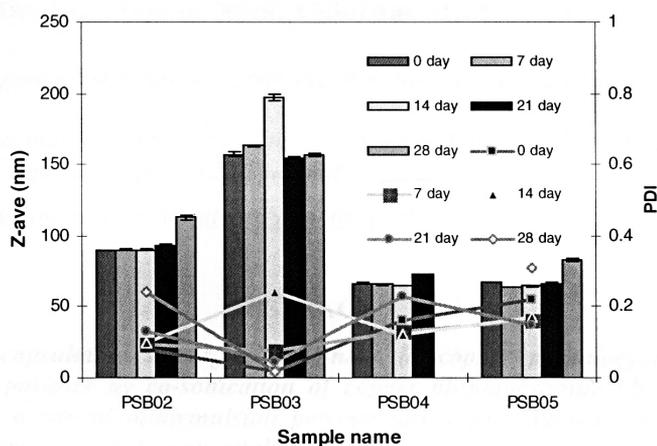
Batch No.	Surfactant	%Solid	Z-ave (nm)
PSB01	SDS	34.5	66.6±0.9
PSB02	SDS:hexadecanol	17.2	89.6±0.21
PSB03	NP-40	-	157±1.7
PSB04	SDS:NP-40	18.5	66.6±0.35
PSB05	SDS	17.2	67.2±0.05



**Figure 3.** TEM images of the blue pigment before encapsulation, latex polystyrene beads.



**Figure 4.** TEM images of the pigment after encapsulation with varying surfactant; PSB02 (SDS:hexadecanol); PSB04 (SDS:NP-40); PSB05 (SDS)



**Figure 5.** Particle size and polydispersity index of encapsulated pigment with varying surfactant PSB02 (SDS:hexadecanol); PSB03(NP-40); PSB04 (SDS:NP-40); PSB05 (SDS) at 0, 7, 14, 21, 28 day

### CONCLUSION

Organic pigment (copper phthalocyanine) was encapsulated with polystyrene through miniemulsion polymerization. The encapsulated pigment with all system show the range of size between 67–157 nm. The smallest size obtained from sodium dodecyl sulfate and sodium dodecyl sulfate/nonylphenol polyethoxylate surfactant system. However, all system can encapsulate pigment and have good stability.

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