# Preparation of a Nanoscale Color Index Pigment Orange 13/Styrene-Maleic Acid Copolymer Composite Dispersion for Ink Jet Printing

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**Abstract.** Color Index pigment orange 13 (PO13) modified with styrene-maleic acid copolymer (PSMA) was prepared via phase separation technique. Experimental results showed that a dispersion with small particle size and high centrifugal stability could be obtained using number molecular weight ( $M_n$ ) of PSMA at 22,500, the weight ratio of PSMA to pigment ( $R_{C/P}$ ) at 0.24, and pigment content ( $C_P$  at 15%. The particles were small and uniformly dispersed in aqueous media. The PO13/PSMA dispersion had high stability and exhibited an improved printing performance when it was applied to preparation of ink jet printing ink. © 2010 Society for Imaging Science and Technology.

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## **INTRODUCTION**

Organic pigments modified by polymers can provide high lightfastness and weatherability;<sup>1</sup> these composites are widely used in textile dyeing and especially in ink jet printing inks.<sup>2–5</sup> In recent years, several techniques have been developed for preparing the composite of pigment and polymer, such as miniemulsion polymerization technique,<sup>6–8</sup> layer-by-layer assembly technique,<sup>9,10</sup> graft method,<sup>11,12</sup> and phase separation technique.<sup>13</sup> Employing these methods, some novel functions are introduced depending on the polymeric materials absorbed onto the pigment. For example, the stability, dispersing performance, and rheological behavior are improved after the pigment is coated with an amphiphilic polymer;<sup>14</sup> the thermal stability, acid, and alkali resistance are enhanced when the pigment is encapsulated with some inorganic materials.<sup>9,10</sup>

In order to widen the color gamut and improve the printing qualities of a product for ink jet printing, we prepared a dispersion of Color Index (CI) pigment orange 13 (PO13) modified with styrene-maleic acid copolymer (PSMA) by phase separation technique. The effects of process conditions on the particle size and stability of the PO13/PSMA dispersion are reported. The properties of the dispersion and its application in ink jet printing were investigated as well.

#### EXPERIMENTAL Raw Material

CI pigment orange 13 (PO13, 99.8% purity) was provided by Wuxi Xinguang Co. Ltd.. of China; its chemical structure is shown in Figure 1. Sodium hydroxide (analytical grade), glycerol (analytical grade), ethylene glycol monomethyl ether (analytical grade), toluene (analytical grade), styrene (analytical grade), maleic acid (analytical grade), and 2, 2-azo*bis*-isobutyronitrile (chemical grade) were all provided by Shanghai Reagent Co. Ltd.. of China.

## Preparation of PO13/PSMA Composite Dispersion

The PSMAs with different molecular weight were prepared according to our team's previous work.<sup>15</sup> The molecular weights of PSMA were determined by gel permeation chromatography (butanone, polystyrene standards) in tetrahydrofuran (THF) at an elution rate of 1ml/min at 25°C. A certain amount of PSMA was dissolved in a mixture solvent of butanone and ethanol. After stirring at room temperature for 30 min, a corresponding amount of PO13 was added. The mixture was then dispersed in a pulverizer (Ultra Turrax IKA T18 Basic, Germany) at 10,000 rpm for 1 h. A certain amount of toluene was added dropwise to the mixture. A slurry of PO13/PSMA composite was obtained after centrifugation and washed three times using a mixture of butanone and ethanol; after another centrifugation, the re-



Figure 1. Chemical structure of CI pigment orange 13.

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sulting slurry was washed three times using distilled water. The slurry was then dried at 60°C.

PO13/PSMA composite powder (15 g) was mixed with 85 g distilled water under stirring. After *p*H adjustment to 9.0 by sodium hydroxide solution (10%), the mixture was dispersed ultrasonically for 15 min to give a composite dispersion.

## Preparation of PSMA-dispersed PO13 Dispersion

PSMA (9 g,  $M_n$ =21,000) was dissolved in 203.5 g water. After pH was adjusted to 9.0 and 37.5 g PO13 was added to the mixture. PSMA-dispersed PO13 dispersion was obtained after the mixture was treated ultrasonically until the particle size did not change further. This dispersion was used for comparison to the composite dispersion.

## Preparation of Ink for Ink Jet Printing

The ink formulation based on weight is given as follows: dispersion 50 wt %, glycerol 15 wt %, ethylene glycol monomethyl ether 10 wt %, Tween-80 (surfactant) 1.2 wt %, and distilled water 22.8 wt %. The ink components were mixed together under stirring at 300 rpm until a homogeneous dispersion was obtained. After filtration through a 0.5  $\mu$ m pore filtering sieve, the inks were loaded for ink jet printing.

## Measurements

## Particle Size and Morphology

Dispersions were diluted 2000-fold, followed by adjustment of *p*H to 8.0. The particle size (*d*) and particle size distribution (PDI) was measured with a Nano-ZS90 (Malvern Instruments Ltd., U.K.). Trasmission electron microscopy (TEM) was performed with an H-7000 (Hitachi, Japan) instrument.

## Centrifuging Stability

PO13/PSMA dispersion was centrifuged at 3000 rpm for 60 min; 0.03 g supernatant was then diluted 2000-fold with distilled water. The optical absorbence ( $A_{60}$ ) was measured using a spectrophotometer. Relativity absorbency ( $r_{60}$ ) was calculated according to Eq. (1) and was used for evaluation of the storage stability of pigment dispersion;

$$r_{60} = \frac{A_{60}}{A_0} \times 100\%,\tag{1}$$

where  $A_0$  is the absorbance of the dispersion before centrifuge. The larger the  $r_{60}$  value, the higher the stability.

## Freeze-Thaw Stability

The dispersions were sealed and stored at  $-5^{\circ}$ C for 24 h and then stored at 70°C for another 24 h. The treated dispersions were diluted 2000-fold using distilled water for measuring the particle size. The freeze-thaw stability was evaluated by the change in particle size (*S*<sub>*T*</sub>) as given by Eq. (2);

$$S_T = \frac{|d_0 - d_T|}{d_0} \times 100\%,$$
 (2)

where  $d_0$  and  $d_T$  are the particle sizes of a dispersion before and after freeze-thaw treatment, respectively. The smaller the **Table I.** Effect of the molecular weight of PSMA on properties of PO13/PSMA dispersion. Note:  $R_{C/P} = 0.24\%$ ,  $C_P = 15\%$ .

<i>M</i> <sub>n</sub> , ×10 <sup>4</sup>	d (nm)	PDI	r <sub>60</sub> (%)
1.43	135.2	0.225	88.9
1.89	127.5	0.195	91.8
2.25	114.2	0.207	91.2
2.78	138.0	0.189	89.4
3.15	149.5	0.237	85.6



Figure 2. Effect of the weight ratio of PSMA to pigment on particle size and centrifugal stability of PO13/PSMA dispersion,  $M_n$ =22,500,  $C_p$ =15%.

 $S_T$  value is, the higher freeze-thaw stability of the dispersion.

## Printing Performance

The printing performances of the inks prepared from pigment dispersions were tested on a pizeoelectric ink jet printer (Mimaki JV4–180, Japan); the diameter of nozzle was about 50  $\mu$ m. The nozzle clogging rate was calculated according to Eq. (3);

$$B = \frac{C_1}{S} \times 100\%,\tag{3}$$

where  $C_1$  is the number of clogged nozzles, and *S* is the total number of nozzles on the printhead. The greater the *B* value, the poorer the printing performance of ink.

## **RESULTS AND DISCUSSION**

## Preparation of PO13/PSMA Composite Dispersion

Table I shows that PO13/PSMA dispersions had a higher  $r_{60}$ , a smaller d, and narrower PDI when  $M_n$  was about 22,500, either a lower or a higher  $M_n$  contributed to a larger particle size and a poor centrifugal stability. We believe that the reason for this result was that a lower  $M_n$  failed to provide sufficient attractive force between PSMA and pigment, while a higher  $M_n$  caused a "bridge" effect among pigment particles.<sup>11</sup>

Figure 2 shows that the weight ratio of PSMA to pigment ( $R_{C/P}$ ) of 0.24 provided the smallest particle size and the highest stability to the dispersion. When  $R_{C/P}$  was lower than 0.24, the PSMA concentration was so low that not



Figure 3. Effect of pigment content on particle size of PO13/PSMA dispersion,  $M_n$ =22,500,  $R_{C/P}$ =0.24.

enough PSMA could absorbed onto the pigment; some pigment particles would be aggregated, leading to larger particles. When  $R_{C/P}$  was higher than 0.24, some PSMA molecules dissolved into the aqueous media so as to raise the viscosity of dispersion, leading to a low wetting speed. The centrifugal stability might be explained by Stokes equation, suggesting that the dispersion having a large particle size should have a poorer stability, providing the viscosity of the dispersion changed little.

Figure 3 shows that the dispersion was obtained with the smallest particle size when  $C_P$  reached 15%. It was known that interaction forces among pigment particles include the shear forces produced by stirring and the impact forces produced by particle collision. The impact forces increase with increasing  $C_P$ , which results in a high dispersing efficiency. However, when  $C_P$  was higher than 15%, the viscosity of the dispersion would increase dramatically, to produce a dispersion with low wetting speed and, therefore, poor dispersing efficiency.

## Properties of the PO13/PSMA Composite Dispersion

The particle morphology of PO13/PSMA composite dispersion is shown in Figure 4. In comparison with PSMAdispersed PO13 dispersion [Fig. 4(b)], PO13/PSMA composite dispersion had a smaller particle size [Fig. 4(a)]. These results confirmed that the PO13/PSMA should have good dispersing performance.

Figure 5 shows that PO13/PSMA dispersion has higher freeze-thaw stability than PSMA-dispersed PO13 dispersion. In the PO13/PSMA composite dispersion, PSMA was completely absorbed onto the pigment and hardly peeled off, while in PSMA-dispersed PO13 dispersion, PSMA was only partly absorbed onto the pigment surface and easily peeled off at high temperature.

# *Physical Properties of Inks and Their Printing Performance*

Table II shows that PO13/PSMA composite dispersion ink (PO13/PSMA ink) had superior physical properties such as a lower viscosity, smaller particle size, and higher freeze-thaw stability to PSMA-dispersed PO13 dispersion ink. As a consequence, the PO13/PSMA composite dispersion ink exhibited better printing performance as presented in Figure 6.



Figure 4. (a) TEM photo of PO13/PSMA dispersion; (b) PSMAdispersed PO13 dispersion, process conditions for PO13/PSMA dispersion:  $M_n$ =22,500,  $R_{C/P}$ =0.24, and  $C_P$ =15%.



Figure 5. Freezethaw stability of PO13/PSMA dispersion and PSMAdispersed PO13 dispersion, process conditions:  $M_n$ =22,500,  $R_{C/P}$ =0.24, and  $C_P$ =15%.

Figure 6 indicates that the nozzle clogging rate of the PO13/PSMA ink was lower than that of PSMA-dispersed pigment dispersion ink. The differences may be ascribed to the fact that the particle size was larger in PSMA-dispersed pigment dispersion ink. Second, some PSMA in PSMA-

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 Table II. Physical properties of the inks prepared from PO13/PSMA dispersion and PSMA-dispersed pigment dispersion.

Dispersion system	$\eta_a \ ({ m mpa \ s})$	$\sigma \\ (\rm mN~m^{-1})$	d (nm)	<b>B</b> (%)
PSMA-dispersed pigment dispersion	6.22	29.5	235.6	10.3
P.O. 13/PSMA dispersion	4.3/	30.2	114./	4./



Figure 6. Printing performance of inks prepared from PO13/PSMA dispersion and PSMA-dispersed PO13 dispersion.

dispersed pigment dispersion ink dissolved into the water, which could change the flow performance of the ink in the printhead. Finally, the resultant higher viscosity, higher surface tension and apparently poorer stability would also lead to poorer printing performance.

## CONCLUSIONS

The optimal process conditions for preparing a PO13/PSMA composite dispersion were obtained when  $M_n$  of PSMA was 22,500,  $R_{C/P}$  was 0.24, and  $C_P$  was 15%. The stability and fluidity of PO13/PSMA dispersion under these conditions were superior to those of a representative PSMA-dispersed pigment dispersion. The PO13/PSMA composite dispersion is suitable for preparation of ink jet printing inks.

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