

# Properties of Waterborne Nanoscale Pigment Red 122 Dispersion Prepared by Phase Separation Method

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**ABSTRACT:** Waterborne nanoscale pigment red 122 dispersions were prepared by phase separation method and milling method with dispersant, respectively. The properties of these dispersions were studied and compared, and also, the encapsulation process was investigated. It was found that the pigment dispersion prepared by phase separation method had higher stability, smaller particle size, and narrower particle size distribution than those milling method with dispersant. The apparent viscosity of pigment dispersion prepared by phase separation method was lower than that prepared by milling method with dispers-

ant when the weight ratio of styrene-maleic acid copolymer (PSMA) to pigment is below 14%. The change of contact angle indicated that the wettability of encapsulated pigment was greatly improved. On the basis of our results, a schematic representation was given for the illustration of the whole encapsulation process. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3968–3972, 2008

**Key words:** waterborne nanoscale pigment red 122 dispersion; phase separation method; milling method with dispersant; encapsulation

## INTRODUCTION

Waterborne nanoscale pigment dispersion is widely used as inkjet printing inks, dye of fibers, etc.<sup>1</sup> However, most of organic pigments tend to aggregate or coagulate for their hydrophobicity. It is very hard for them to be wetted and dispersed in the aqueous media. In addition, it is necessary to modify the organic pigments before using.

Stabilization of pigments with polymeric dispersants has been proven to be a good way for the preparation of pigment dispersion with high stability, small particles size, low viscosities, and low moisture sensitivity. In aqueous media, the polymeric dispersant can build polymeric shell around the pigment particles and increase the surface charge on the pigment particles,<sup>2</sup> so that the pigment particles can finely dispersed in the aqueous media. Different from the low molecular weight dispersants,

polymeric dispersants always stay on pigment surface even only part of the chain are attached to the surface of the pigment particles. Recently, more and more novel functional copolymers have been synthesized and used for pigment dispersion.<sup>3,4</sup> Encapsulation of pigments with a polymer shell can also facilitate the pigments processing and improve the pigment quality. Miniemulsion polymerization<sup>5,6</sup> and surface grafting technique<sup>7</sup> are the common methods to encapsulate pigment. Moreover, there are many reports on the successful encapsulations of titanium dioxide, colloidal silica, and carbon by polymer<sup>8–11</sup>.

In our previous work, the styrene-maleic copolymer was prepared and used as encapsulated layer to prepare the pigment red 122 dispersion, and we mainly investigated the effect of copolymer structure on stability, Zeta potentials, and particle size.<sup>12</sup> In this article, waterborne nanoscale pigment red 122 dispersion was prepared by phase separation and milling with dispersant, respectively. The properties of these dispersions were studied and compared, and also the encapsulation process was investigated.

## EXPERIMENTAL

### Preparation of waterborne nanoscale pigment dispersion

Preparation by phase separation method

Waterborne nanoscale pigment red 122 dispersions were prepared by phase separation method described in Fu's work.<sup>12</sup> Ten gram PSMA ( $M_n =$

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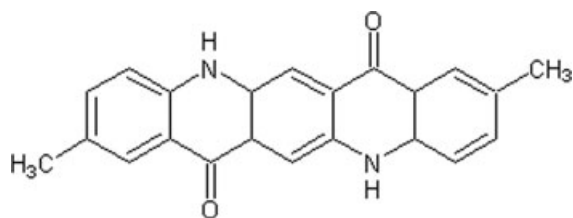


Chart 1. Molecular structure of pigment red 122.

9000, Molar ratio of maleic acid was about 0.56) and 440 g ethanol were mixed together, and then 50 g C.I.P.R122 powder (Chart 1, WuXi XinGuang provided, China) was added into the solution under stirring. The mixed slurry was dispersed by Ultra Turrax IKA T18 Basic (IKA Instruments Ltd) at 4000 rpm for 1 h, and then 250 mL ether was added into the slurry. After PSMA encapsulated onto the pigment surface, the mixture was filtered under vacuum to obtain the slurry of pigment particles coated with PSMA. The slurry washed with distilled water, and dried at 60°C for 24 h to get the powder of pigment particles coated with PSMA.

The pigment dispersion was prepared with 10 g coated pigment powders and 90 g distilled water. pH value was adjusted to 8 by the solution of sodium hydroxide (0.01 mol/L). The system was stirred by Ultra Turrax IKA T18 Basic for 30 min, and then the pigment dispersion coated by PSMA was obtained.

#### Preparation by milling method with disperant

About 10 g PSMANa was dissolved in 440-mL distilled water, and the pH value was adjusted to 8. Fifty gram C.I.P.R122 powder was added into the solution under stirring. The slurry was transferred to a muller and dispersing for 6 h.

The powder of pigment encapsulated by PSMANa was prepared as follows: a quantity of acetone was added into the pigment dispersion prepared earlier, the pigment coated by PSMANa would slowly deposited, dried by freezing method, the powder of pigment coated by PSMANa was obtained.

#### Particle size and its distribution of pigment dispersion

The pigment dispersion prepared earlier was diluted to 2000 times respectively, and pH value was adjusted to 8.0. The prepared samples were put into Nano-ZS90 (Malvern Instruments) for 3 min at 25°C for the measurement of the particle size and its distribution.

#### Stability of pigment dispersion

Centrifuging stability<sup>12</sup>: Pigment dispersion was centrifuged at 3000 rpm for 30 min, then 0.03 g superna-

tant in the centrifugal tube was taken out and diluted to 2000 times by distilled water. The relative absorbency  $r_{30}$  was calculated according to formula.<sup>1</sup>

$$r_{30} = \frac{A_{30}}{A_0} \times 100\% \quad (1)$$

Where  $A_0$  is the absorbency of the dispersion before centrifuged,  $A_{30}$  is the absorbency of the dispersion after centrifuged 30 min.  $r_{30}$  can reveal the stability of dispersion caused by weight, the larger  $r_{30}$ , the higher stability of dispersion is.

Freeze-thaw stability: the pigment dispersion prepared was sealed and placed at -5°C for 12 h and then put into an oven at 50°C, The changing rate of particle size ( $S_T$ ) was calculated according to the formula (2).

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

Where  $d_0$  is the starting particle size of dispersion,  $d_T$  is the particle size of pigment dispersion after freeze-thaw treatment; the smaller the  $S_T$  value, the higher the stability to temperature of dispersion is.

#### Apparent viscosity of pigment dispersion

Apparent viscosity of pigment dispersion prepared with different method was measured by a DV-III Programmable Rheometer (Brookfield).

#### Wettability of coated pigment

Starting C.I.P.R122, the powder of coated C.I.P.R122 with PSMA and the powder of coated C.I.P.R122 with PSMANa were uniformly put onto a glass slide respectively, and then pressed slightly with another a glass slide to ensure a flat surface. The pigment wettability was tested by KrÜss DSA 100.

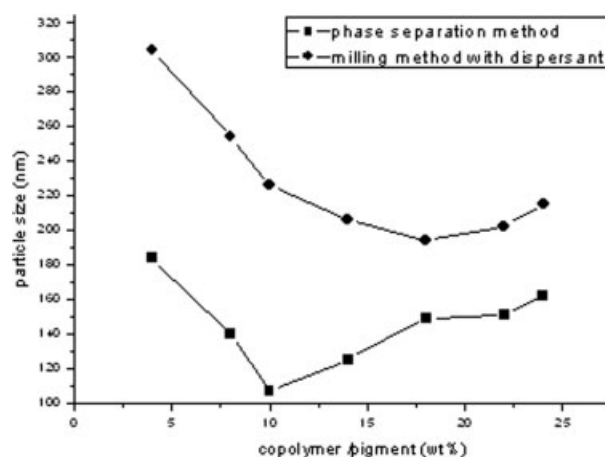
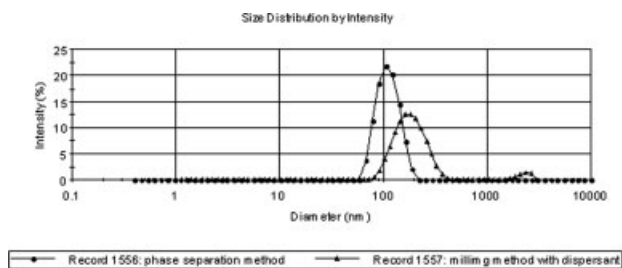


Figure 1 Effect of the dosage of copolymer on pigment particle size.



**Figure 2** Size distribution of pigment dispersion by different method, the weight ratio of copolymer/pigment was about 10%.

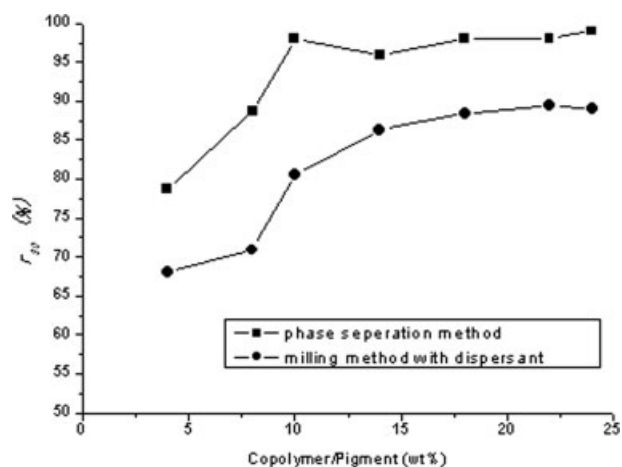
## TEM

Powder of pigment particles coated with PSMA were dispersed in aqueous media by Ultra Turrax IKA T18 Basic for 30 min to get encapsulated C.I.P.R122 dispersion, and then the shape of encapsulated C.I.P.R122 was observed by TEM (H-7000, Japan). Hydrolyzing of encapsulated C.I.P.R122 was prepared as follows: 10 g coated pigment powders and 90 g distilled water was mixed together, and the pH value was adjusted to 8 by the solution of sodium hydroxide (0.01 mol/L). The mixture was stirred by Ultra Turrax IKA T18 Basic for 30 min. The shape of hydrolyzing encapsulated C.I.P.R122 was observed by TEM.

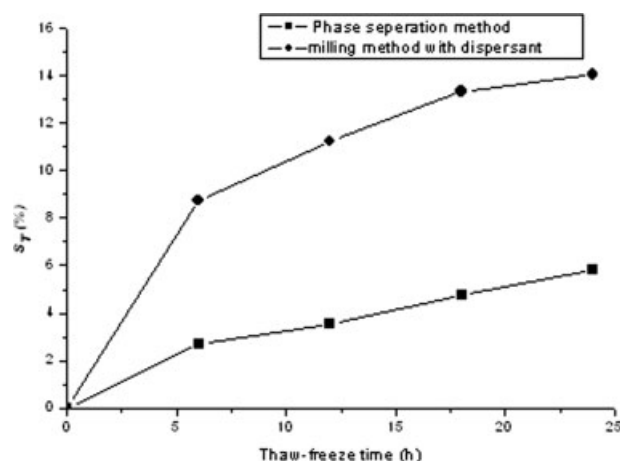
## RESULTS AND DISCUSSION

### Particle size and its distribution

Pigment particle size is greatly affected by the dosage of polymer dispersants. As shown in Figure 1, the particle size decreased first and then increased with increasing the ratio of PSMA/pigment, the particle size reached its minimum when the ratio is about 10% for phase separation method.

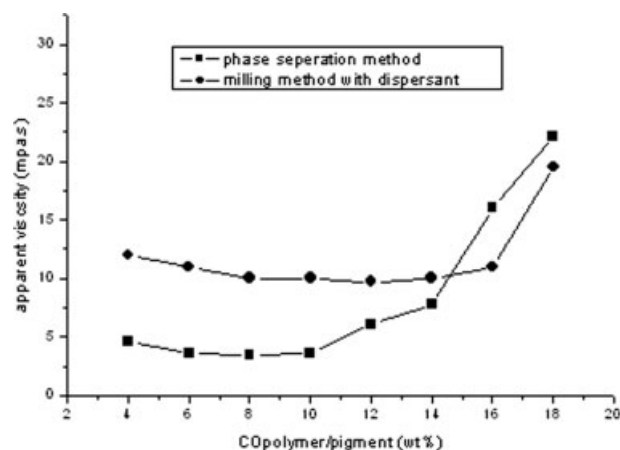


**Figure 3** Effect of the dosage of copolymer on centrifugal stability of pigment dispersion.

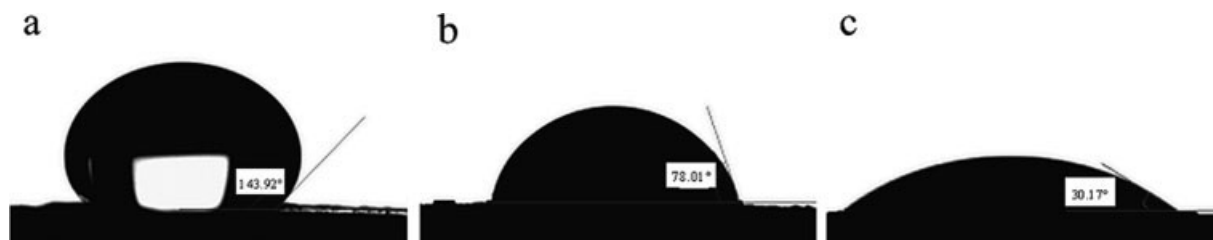


**Figure 4** effect of thaw-freeze time on the changing rate of particle size of pigment dispersion.

The smaller the particle size, the larger the pigment surface is, thus the more amount of copolymer dispersant is needed. While, too much of the copolymer dispersants, higher than 10%, resulted in increasing viscosity of dispersing media, leading to poor wetting performance due to that excess copolymer dispersants would dissolve in media instead of attaching onto pigment surface. Moreover, Figure 1 also shows that, under the same dispersing conditions, the particle size of the pigment dispersion prepared by phase separation was smaller than that prepared by milling with dispersants. Unlike milling with dispersant, the PSMA would completely attached onto the surface of pigment in the phase separation method, while the PSMA was partly absorbed onto the pigment surface in the milling method. The encapsulated polymeric layer would greatly reduce the attraction forces among the particles, and also reduce the desorption between the particles and PSMA, which resulted in improving the dispersing efficiency greatly. On the other hand,



**Figure 5** Effect of the weight ratio of copolymer/pigment on apparent viscosity of pigment dispersion.



**Figure 6** Wettability of pigment powder; (a) starting C.I.P.R122; (b) encapsulation C.I.P.R122 by PSMA; (c) encapsulation C.I.P.R122 by PSMANa.

the polarity of ethanol was lower than that of water, which was more close to the pigment surface, thus resulted in higher dispersing efficiency. So, the phase separation method was more suitable to prepare the waterborne nanoscale pigment dispersion.

As shown in Figure 2, the particle size distribution of waterborne nanoscale pigment dispersion prepared by phase separation is narrower than that prepared by milling method with dispersant. The  $-\text{COO}^-$  group of copolymers encapsulated onto the surface of pigments would form a polymeric shell around the particles and also increase the surface charges of pigment particles. The interaction between pigment particles was weakened due to the existence of these charges and polymeric layer on the pigment particle surface, so that the pigment particles could be finely dispersed in aqueous media.

### Stability of pigment dispersion

As shown in Figure 3, the absorbency reduced with increasing centrifugal time, indicating that the large pigment particles were removed under centrifugal forces. The  $r_{30}$  value of the samples prepared by the phase separation method is bigger than that prepared by milling method through the composition range prepared here, indicating that the stability of pigment dispersion prepared by phase separation method is higher than that prepared by milling method. Figure 3 also told us that the copolymer has an optimal dosage in dispersing or encapsulating the pigment. The surface of pigment could not be coated when the dosage of copolymer was not enough, thus led to poor centrifugal stability. On the other hand, when the dosage of copolymer was high enough, the chain of copolymer would “bridge” each other, thus also led to poor centrifugal stability.

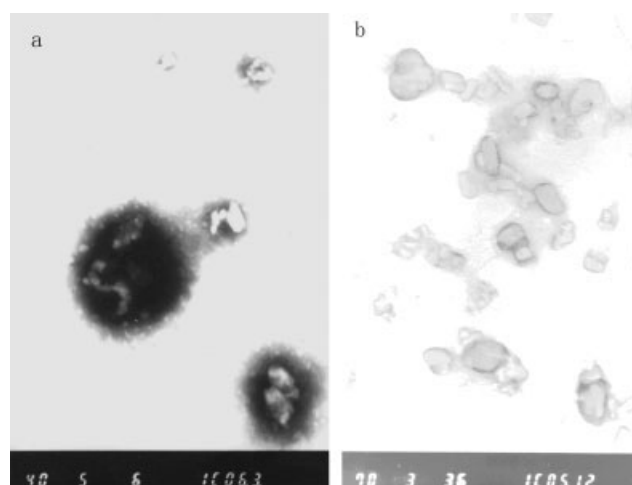
In Figure 4, it is shown that the  $S_T$  value increases with increasing thaw-freeze time, indicating the particle size of pigment dispersions increases with increasing thaw-freeze time. The  $S_T$  value of the samples prepared by the phase separation method is smaller than that prepared by milling method through the composition range prepared here, indicating that the stability of pigment dispersion pre-

pared by phase separation method is higher than that prepared by milling method.

Repulsive and attractive forces among pigment particles determined the stability of the pigment dispersion. When the van der Waals forces between pigment particles were higher than that of steric and static repulsive forces, the pigment particles would combine each other and form large particles. Instead, the dispersion would stably exist in aqueous media. In waterborne nanoscale pigment dispersion, PSMA encapsulated onto the surface of pigments would be ionized at  $\text{pH} = 8$ , and produce some negative charges onto the surface of pigments to create the static forces between pigment particles. Further, the PSMA encapsulated onto the surface of pigments could also produce steric repulsion. The whole steric and static forces were higher than that of van der Waals forces between pigment particles, so the dispersion would exist in long time, even under centrifugal force or treated at high temperature.

### Apparent viscosity of pigment dispersion

Figure 5 shows the apparent viscosity of pigment dispersion prepared by phase separation method



**Figure 7** TEM photo of pigment in different stage, (a) encapsulated C.I.P.R122 (enlarge about 40,000 times); (b) hydrolyzing of encapsulated C.I.P.R122 (enlarge about 70,000 times).

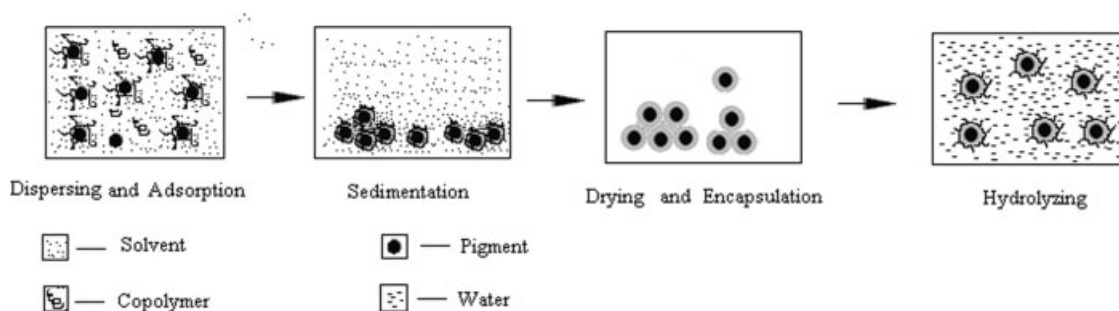


Figure 8 Schematic of encapsulation course by phase separation method.

was lower than that prepared by the milling method with dispersant when the weight ratio of polymer dispersant to pigment was below 0.14. For the phase separation method, the dispersant was completely attached onto pigment surface, and the chain of polymer dispersant cannot stretch freely. While for the milling method, the polymer dispersant was partly absorbed onto pigment surface, and the chain of dispersant freely stretched in aqueous media, leading to higher apparent viscosity.

### Wettability of coated pigment

The pictures of pigments wettability are depicted in Figure 6. It indicates that the encapsulated pigment can be wetted by water more easily than those without modification, especially for the pigment coated by PSMANa. The contact angle of starting pigment (a), the pigment coated by PSMA (b), and the pigment coated by PSMANa (c) were about  $143.92^\circ$ ,  $78.01^\circ$ , and  $30.17^\circ$ , respectively. The changing of contact angles confirmed that the pigment was successfully encapsulated by phase separation method.

### The course of pigment encapsulation

The TEM pictures of two samples: (a) encapsulated C.I.P.R122 and (b) hydrolyzing encapsulated C.I.P.R122 were shown in Figure 7. It is shown that hydrolyzing of encapsulated C.I.P.R122 was more uniformly and smaller dispersed in aqueous media than that of encapsulated C.I.P.R122 by PSMA.

The reason for the fine and uniformly dispersion of hydrolyzing of encapsulation C. I. P. R122 may be attributed to the negative charges on pigment surface, the electric repulsive hinder the particles to combine together. While, for the PSMA encapsulated pigment particles, the PSMA chain onto the surface of C.I.P.R122 would entangle with each other, leading to the formation of large particles.

According to TEM photo, the whole encapsulation process may be divided into four steps (as shown in Fig. 8).<sup>13</sup> (1) Dispersing and adsorption: PSMA was dissolved in a media, at this step organic pigments were added into solution of PSMA and dispersed by

stirring, and then the PSMA was absorbed onto the pigment; (2) Sedimentation: absorption auxiliary which could reduce the solubility of copolymer was added slowly under stirring, and the copolymers precipitated and encapsulated onto the pigment surface by van der Waals forces; (3) Drying and encapsulation: the precipitate was filtered and dried, and then copolymer was tightly encapsulated onto the pigment surface; (4) Hydrolyzing: the copolymer onto the encapsulation pigment was hydrolyzed, and then the pigment was dispersed uniformly in aqueous media.

## CONCLUSIONS

The phase separation method was more suitable for preparation of waterborne nanoscale C.I.P.R122 dispersion than milling method with dispersant. The pigment dispersion prepared by phase separation method has high centrifugal stability and freeze-thaw stability, narrow particle size distribution. The wettability of the pigment dispersion is improved greatly after being encapsulated by PSMA and PSMANa.

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