

Effects of Alkali on Properties of Nanoscale 2,9 Dimethyl Quinacridone/Poly(styrene-maleic acid) Composite Dispersion

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ABSTRACT: Nanoscale 2,9 dimethyl quinacridone (P.R.122) encapsulated by copolymer of styrene and maleic acid (PSMA) was prepared via phase separation technique followed by the preparation of composite dispersions. Experimental results showed that sodium hydroxide provided the dispersion the smallest particle size and the highest stability when compared with other additives, regardless of it being taken as dispersant or the other neutralization reagent. An optimal process was attained by

using sodium hydroxide with a dosage of 0.60 times of molar amount of $-\text{COOH}$ groups in PSMA when P.R.122/PSMA composite dispersion was treated at 45°C for 30 min. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 526–531, 2010

Key words: 2, 9 dimethyl quinacridone; copolymer of styrene and maleic acid; encapsulated; composite; dispersion

INTRODUCTION

Textiles dyed or printed with coatings have many advantages, such as a simple and short production process, little waste water, and a low production cost.¹ Considering energy saving and environmental protection, the application of coatings in textile has been receiving more attentions from researchers and manufacturers. However, traditional coatings cannot satisfy the demand of the textile industry for its large particles, poor stability, and color performance, which could greatly limit its application in textile.

As a main colorant in coatings, organic pigment modified by dispersant or their derivatives is a common method to prepare the nanoscale waterborne pigment dispersions. In this system, the pigment particle repulsive forces increased when it was absorbed by some dispersant, thus providing stable pigment dispersions.² Polymeric dispersants have become the main additives for their thermal stability and resistance to alkali in pigment processing. At

present, different structural polymeric dispersants have been developed to synthesize and apply in pigment processing.^{3–6} Microencapsulation is another important method to prepare the nanoscale waterborne organic pigment dispersions, in which various techniques were involved, for example, microemulsion or miniemulsion polymerization,^{7,8} cross-linking polymerization,⁹ self-by-self assembly technique,¹⁰ *in situ* polymerization,¹¹ and phase separation method.¹²

In our previous work, P.R.122/PSMA composite was prepared by phase separation method.¹³ In this article, the effects of alkali on the properties of P.R.122/PSMA composite dispersion were further investigated.

EXPERIMENTAL

Materials

Polyethylene oxide sorbitan monooleate (Tween-80, analytical grade); Dodecylbenzene sodium sulfonate (LAS); and Cetyltrimethylammonium bromide (CTAB, analytical grade) were all provided by Shanghai Ling Feng Chemical Reagent Co. (Shanghai, China) Styrene (chemical grade), 2,2-Azo-bis(isobutyronitrile) (AIBN, analytical grade), Maleic acid (analytical grade), Ammonia (analytical grade), Triethanolamine (analytical grade), and Sodium hydroxide (analytical grade) were all provided by

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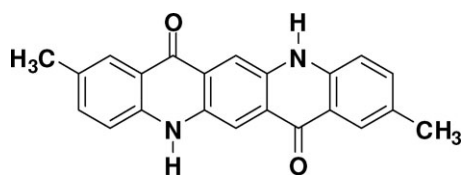


Chart 1 Chemical structure of P.R.122.

Guoyao Chemical Reagent Co. (Shanghai, China) P.R.122 powder (99.7%) was provided by Changzhou North American Chemical Company (Changzhou, China) (Chart 1).

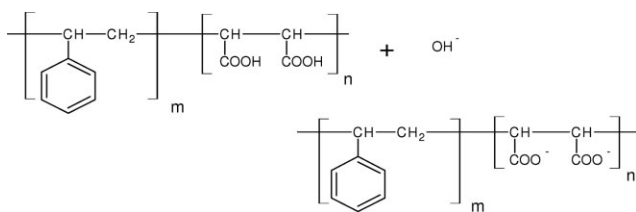
Methods

The experimental process may be depicted as Figure 1.

Styrene was dried by calcium hydride and then distilled before use. AIBN was purified by recrystallization with hot ethanol. The PSMA was prepared according to the Ref. 14, the feeding molar ratio of styrene to maleic acid was about 1.2 : 1, the amount of AIBN to the whole weight of feeding monomers was about 1.8% and the reaction temperature was kept 60°C for 4 h.

P.R.122/PSMA composite was prepared by phase separation method, 2 g PSMA was dissolved in 178 g acetone, and then 20 P.R.122 was added into the solution under stirring. The mixture was transferred to an Ultra Turrax IKA T18 Basic (IKA Instruments) and dispersed for 1 h at 4000 r/min, and then 178 g ethanol was dropwisely added into the mixture. At last, the slurry was filtered under vacuum and dried at 45°C for 24 h in an oven to obtain the P.R.122/PSMA composite.

The P.R.122/PSMA composite dispersion was prepared by two different methods. First, P.R.122/PSMA composite dispersed at 10,000 r/min for 1 h which used Tween-80, CTAB, and LAS as dispersant, respectively. Second, P.R.122/PSMA composite was heated at certain temperature for some time under stirring at 10,000 r/min for 1 h, which used sodium hydroxide, ammonia, and triethanolamine as neutralization reagents, respectively. The neutralization reaction was done as follows:



PSMA-dispersed pigment dispersion was prepared as follows: 20 g PSMA was dissolved into water, and adjusted pH value to 9, the mixture was

heated at 70°C to get a solution with the concentration of PSMA 5%. 20 g P.R.122, 40 g PSMA solution, and 140 g distilled water were mixed and then milled on a bead mill for 4 h.

Measurements

The average particle size (particle size) and its distribution were measured by dynamic light scattering method using Nano-ZS90 (Malvern Instruments Co. England). The morphologies of particles in dispersion obtained under the optimized conditions were characterized by TEM spectroscopy (H-700, Japan). Apparent viscosity was performed with a programmable rotational viscometer (Brookfield DV-III, America) after the dispersion was equilibrated at 25°C for 10 min. To further understand the storage stability of the dispersion in different conditions, the centrifugal stability and freeze-thaw stability was measured as follows.

Centrifugal stability

After the dispersion was centrifuged at 3000 r/min for 30 min, super dispersion in the centrifugal tube was taken out and diluted by distilled water into 2000 times.¹³ The wavelength of maximum absorbance was found at 530 nm by spectrophotometer and then the absorbance was recorded as A_{30} . Relative absorbance (r_{30}) was calculated according to eq. (1).

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

where A_0 is the absorbance (530 nm) of the dispersion before centrifuged, r_{30} can reveal stability of the dispersion against to weight, the larger r_{30} , the higher stability is.

Freeze-thaw stability

The dispersion was sealed kept at -5°C for 24 h and then put into an oven at 50°C for another 24 h, the changing rate of particle size (S_T) was calculated according to eq. (2).¹³

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

where d_0 is the starting particle size of the dispersion, d_T is particle size of the dispersion after freeze-thaw treatment, S_T can reveal the stability of the composite dispersion to temperature, the smaller S_T , the higher freeze-thaw stability of the dispersion is.

RESULTS AND DISCUSSION

Effect of dispersants and sodium hydroxide

Table I shows the particle size (D), centrifugal stability (r_{30}), and freeze-thaw stability (S_T) of P.R.122/

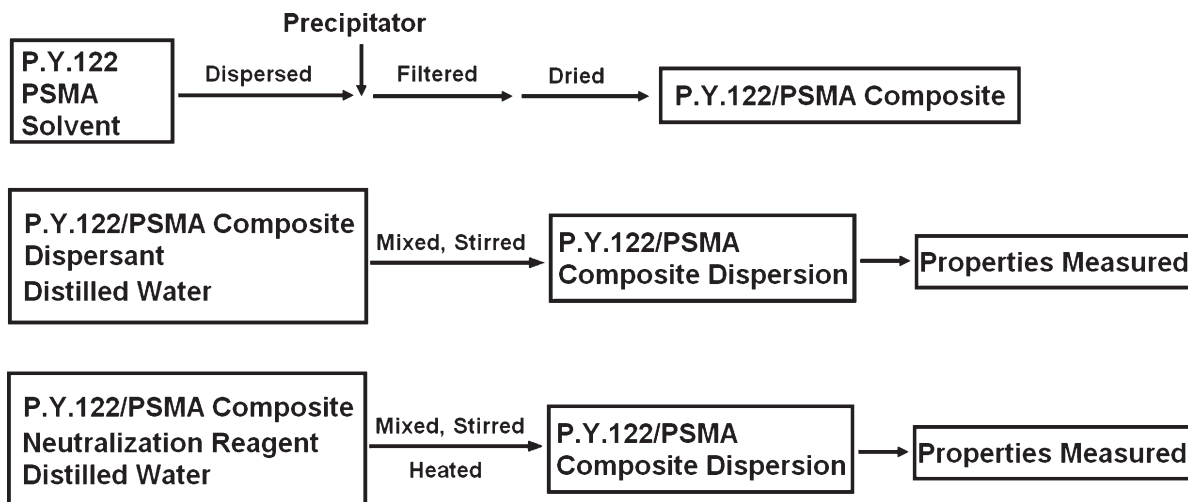


Figure 1 The scheme of experimental process.

PSMA composite dispersion obtained from different dispersants or sodium hydroxide. It was found that when the composite was dispersed with aid of different auxiliary at the same dispersing conditions, sodium hydroxide can provide the smallest particle size and the highest stability, and CTAB provide the largest particle size and the poorest stability to the dispersion.

In alkaline conditions, PSMA that encapsulated onto the pigment reacted with OH^- and produced negative charges, which would give rise to high stability and small particle size for the repulsive forces among particles. However, when P.R.122/PSMA composite was dispersed with aid of dispersant, the dispersant would be adsorbed onto the composite surface due to the possible interactions of electrostatic forces, van der Waals forces. In the dispersion prepared with aid of CTAB, there may be two layers were formed between CTAB and composite surface, the first layer is that CTAB absorbed onto composite

surface via electrostatic forces, the second layer is that the hydrophobic part of CTAB absorbed onto the first layer via van der Waals forces, resulting in an increase of solvated layer thickness and thus producing a large particle size.

The poorest centrifugal stability of composite dispersion dispersed with aid of CTAB may be explained by Stokes-Einstein equation. That is, when the viscosity of composite dispersion changed slightly, the larger particle size, the worse centrifugal stability of the dispersion was. The poorer freeze-thaw stability of composite dispersion that dispersed with aid of CTAB indicated that the attractive forces among the CTAB and P.R.122/PSMA composite were so small that it was easily peeled off.

Effect of neutralization reagents

Table II shows that sodium hydroxide and ammonia can provide the smaller particle size and higher centrifugal stability to the P.Y.122/PSMA composite dispersion than that of triethanoamine. It is known that sodium hydroxide and ammonia could easily penetrate into solvated layer and then react with $-\text{COOH}$ for their small molecular size, the amount

TABLE I
Effect of Dispersant and Sodium Hydroxide on Properties of the Dispersion^a

Dispersant and sodium hydroxide	D (nm)	r_{30} (%)	S_T (%)
LAS	135.3	93	6.1
Tween-80	132.7	94	5.8
CTAB	167.2	91	9.3
Sodium hydroxide ^b	104.1	100	2.9

^a Note : The weight ratio of dispersant to P.Y.122/PSMA composite is about 0.4, the mixture was stirred at 10,000 r/min for 30 min.

^b Note : $M_{\text{NaOH}} = M_T/M_P = 0.64$, M_T : molar amount of adding sodium hydroxide; M_P : the molar amount of $-\text{COOH}$ in PSMA coated onto pigment; neutralization reaction time 30 min; neutralization reaction temperature 45°C; stirring rate 10,000 r/min.

TABLE II
Effect of Neutralization Reagents on Properties of the Dispersion^a

Neutralization reagent	D (nm)	r_{30} (%)	S_T (%)
Sodium hydroxide	106.6	100	1.4
Ammonia	128.5	100	28.4
Triethanolamine	488.7	78	7.3

^a Note : The molar amount of neutralization reagent = $0.6 \times M_p$, M_p : the molar amount of $-\text{COOH}$ in PSMA coated onto pigment surface; neutralization reaction temperature 45°C; neutralization reaction time of 30 min; stirring rate : 10,000 r/min.

of $-\text{COO}^-$ increased on the surface of composite particles. Therefore, the composite particles were easily separated for the repulsive forces which produced by negative charges onto the composite particles, thus resulting in smaller particle size.

Unlike the sodium hydroxide and ammonia, triethanolamine was a Lewis base which reacted with $-\text{COOH}$ via isolated electrons on nitrogen atoms, its large molecular size prevents it penetrating into the solvated layer. As a result, $-\text{COOH}$ groups on composite could not be neutralized enough. Thus, the particles could not be separated under shear forces for the weak repulsive forces, which resulted in larger particle size.

The stability of the composite dispersion is dependent on the repulsive forces among the particles. The higher salt formation degree of $-\text{COOH}$, the more negative charges would be produced, which could provide the high-repulsive forces among the composite particles, thus led to high stability. On the other hand, according to the Stokes-Einstein equation, the P.R.122/PSMA composite dispersion got a poor centrifugal stability when it was dispersed with aid of triethanolamine for its large particle size.

In addition, we found that P.R.122/PSMA composite dispersion had poor freeze-thaw stability when P.R.122/PSMA composite was dispersed by ammonia. The reason was that $-\text{COONH}_4$ is not stable and could be decomposed at high temperature, and then the repulsive forces among the particles decreased, and then some particles could be easily combined together, thus led to poor freeze-thaw stability.

Effect of amount of sodium hydroxide

The amount of sodium hydroxide used in the preparation of P.R.122/PSMA composite dispersion was important as well. Table III shows that the composite dispersion would obtain satisfactory properties when M_{NaOH} was equal to 0.60. Obviously, when

TABLE III
Effect of Amount of Sodium Hydroxide on Properties of the Dispersion^a

M_{NaOH}	D (nm)	r_{30} (%)	S_T (%)	Viscosity (mpa.s)
0.00	307.4	deposited	deposited	13.87
0.40	169.4	43	17.3	25.32
0.60	106.6	100	1.4	6.58
0.64	104.1	100	2.9	6.71
0.68	107.6	100	5.3	6.76
0.80	128.8	98	15.8	6.84
0.90	141.8	96	21.9	7.04

^a Note : Neutralization reaction temperature 45°C; neutralization reaction time 30 min; stirring rate 10,000 r/min.

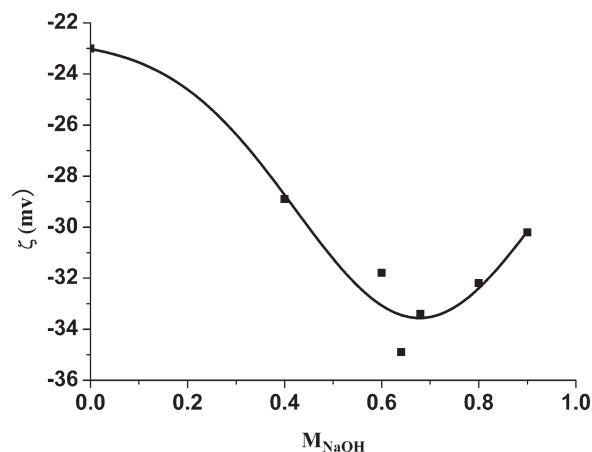


Figure 2 Effect of amount of sodium hydroxide on Zeta potentials of composite particle, neutralization reaction temperature 45°C; neutralization reaction time 30 min; stirring rate 10,000 r/min.

amount of sodium hydroxide was small, little $-\text{COOH}$ would be reacted with OH^- and produced few negative charges, thus resulted in large particle size and poor stability of P.R.122/PSMA composite dispersion.

Moreover, PSMA would be peeled off when amount of sodium hydroxide was high enough, which also led to few negative charges onto P.R.122/PSMA composite surface, and then P.R.122 would attract each other via van der Waals forces, thus resulting in large particle size and poor stability. These explanations may be verified by the relationship between the amount of sodium hydroxide and Zeta potentials as well (Fig. 2).

Table III also indicates that the viscosity of composite dispersion reached to its maximum and its minimum when M_{NaOH} was about 0.40 and 0.60, respectively. When M_{NaOH} was equal to 0, the composite particles combined together for small repulsive forces, the P.R.122/PSMA composite particles were large which led to high viscosity. When M_{NaOH} was small, little $-\text{COOH}$ in PSMA would be reacted with OH^- , therefore, the molecular of PSMA tangled each other for small repulsive forces, thus also produced a large viscosity. In addition, when M_{NaOH} was high enough, PSMA would be peeled off from P.R.122 and then stretched freely, thus also led to a large apparent viscosity. From Table III and Figure 2, we may conclude that the optimal amount of sodium hydroxide is about 0.60 times of molar amount of $-\text{COOH}$ groups in PSMA.

Effect of salt formation temperature and time

The effects of neutralization reaction temperature on particle size of P.R.122/PSMA in dispersion are shown in Figure 3. The particle size decreased with

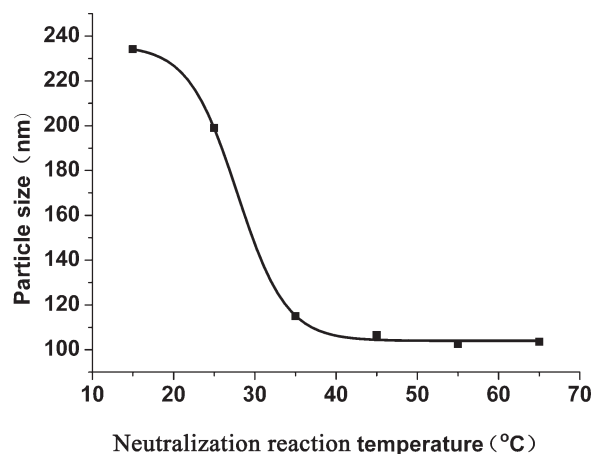


Figure 3 Effect of neutralization reaction temperature on particle size of the dispersion, $M_{\text{NaOH}} = 0.64$; neutralization reaction time 30 min; stirring rate 10,000 r/min.

increasing the neutralization reaction temperature and attained its minimum when neutralization reaction temperature was about 45°C. Generally, a low temperature is unfavorable for the neutralization reaction of PSMA and sodium hydroxide. Therefore, the neutralization reaction degree of PSMA increased with increasing the reaction temperature, which resulted in high-repulsive forces and thus led to small particle size. Once the neutralization reac-

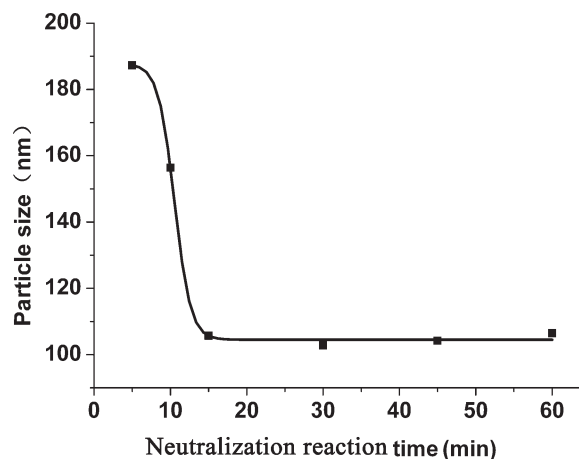
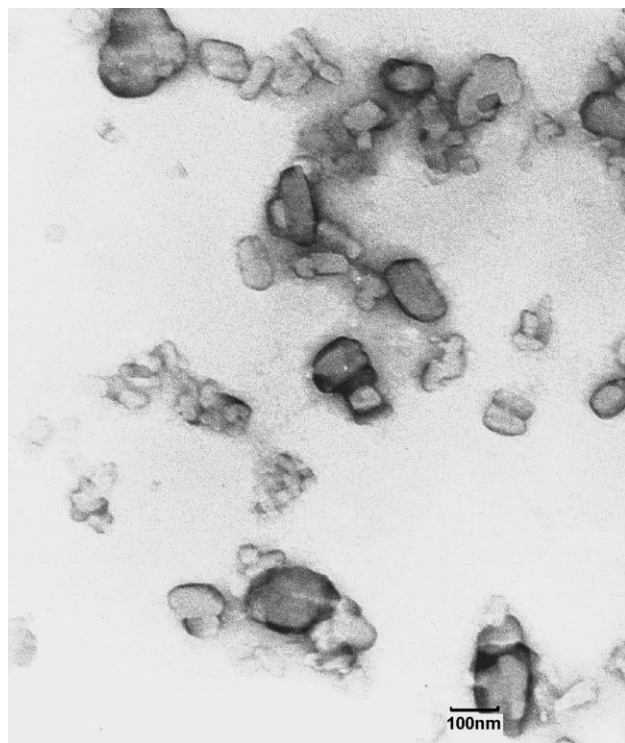


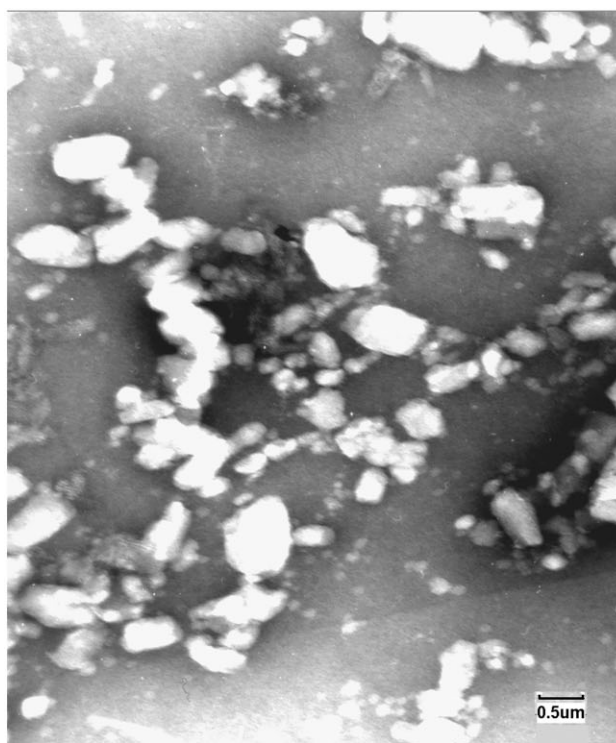
Figure 4 Effect of neutralization reaction time on particle size of the dispersion, $M_{\text{NaOH}} = 0.64$; neutralization reaction temperature 45°C; stirring rate 10,000 r/min.

tion degree was reached to its balance in certain time, the particle size of P.R.122/PSMA in dispersion did not decrease even if the temperature was increased.

Figure 4 shows that particle size of P.R.122/PSMA in dispersion had a sharp drop in 15 min, while becoming stable after that. When neutralization reaction time is short, the neutralization reaction degree of PSMA could not reach to its balance, resulting in



(a)



(b)

Figure 5 TEM photo of particles in composite dispersion (4a) and PSMA-dispersed pigment dispersion (4b), 4a : $M_{\text{NaOH}} = 0.64$; neutralization reaction temperature was kept 45°C for 15 min; stirring rate 10,000 r/min.

those small repulsive forces among particles, which led to larger particle size. When neutralization reaction time was more than 15 min, the neutralization reaction degree of PSMA reached to its maximum, all the P.R.122/PSMA particles were separated, and thus the particle size was not changed with the increase of neutralization reaction time any more.

Morphologies of composite particles

The TEM photo of P.R.122/PSMA composite in dispersion [Fig. 5(a)] and P.R.122 in PSMA-dispersed pigment dispersion [Fig. 5(b)] indicated that the particles of P.R.122/PSMA composite particles was small and uniformly dispersed with little aggregation or coagulation, on the contrary, some P.R.122 in PSMA-dispersed pigment dispersion was combined with each other.¹³

CONCLUSIONS

P.R.122/PSMA composite dispersion with small particle size had the highest stability when it was dispersed with aid of sodium hydroxide. Sodium hydroxide was more suitable for the preparation composite dispersion than ammonia and triethanolamine. The process of P.R.122/PSMA composite dis-

persion was optimized as that the composite was dispersed in 15 min at 45°C, with the molar amount of sodium hydroxide being about 0.60 times of -COOH in PSMA.

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