Journal of Imaging Science and Technology® 52(5): 050501–050501-4, 2008.

Preparation of Waterborne Nanoscale Pigment Dispersions for Formulation of Ink Jet Inks

Shaohai Fu, Kuanjun Fang, Xia Zhang, Xue Jiang, Anli Tian and Chaoxia Wang
Key Laboratory for Eco-Textile of Ministry of Education, Jiangnan University, 1800 Lihu Road, Wuxi 214122, Jiangsu, Peoples Republic of China
E-mail: shaohaifu@hotmail.com

Abstract. *Textile ink jet printing as a new dyeing method with higher resolution, lower pollution, and shorter run length has attracted more and more people's attention. Pigment inks have become one of the main colorant materials in this technology for their excellent light fastness and their suitability to all sorts of textiles. However, most organic pigments of low polarity are hard to wet and disperse in aqueous media, therefore the organic pigments must be modified before their application. In this research, waterborne nanoscale pigment dispersion including Copper Phthalocyanine blue (P.B.15:3), Quinacridone Red pigment (P.R.122), and Monoazo Yellow pigment (P.Y.14) have been prepared by the phase separation method and by the method of direct milling with dispersants, respectively. The properties (stability, particle size, and apparent viscosity) of dispersions prepared by the different methods were compared. The results show that the pigment dispersion has higher stability to alcohols, temperature, and storage, and also lower viscosity; the phase separation method was more suitable to preparation of pigment dispersion for formulations of ink jet inks than the method of direct milling with dispersants; TEM images indicated that the pigment particles were uniformly distributed in aqueous media, and the x-ray diffraction spectra indicated that the pigment crystal structure was unchanged after encapsulation in the phase separation method. © 2008 Society for Imaging Science and Technology.*
[DOI: 10.2352/J.ImagingSci.Technol.(2008)52:5(050501)]

INTRODUCTION

Textile ink jet printing as a new dyeing method with higher resolution, lower pollution, and shorter run length has attracted more and more people's attention. Pigment inks with excellent light fastness and suitability for all sorts of textiles have become one of the main colorant materials in this technology.[1] However, most organic pigments with low polarity tend to be aggregate or coagulate and are hard to wet and disperse in aqueous media, so the organic pigments need to be modified for this application. The milling of the pigment with dispersant and the encapsulation of the pigment with polymer are two common methods for pigment modification.

Polymeric dispersants have proven good properties in stabilizing pigments in aqueous media. These properties include higher stability, smaller particle size, and less moisture sensitivity. Hydrophobic chains attach to the organic pigment surface by van der Waals force, and hydrophilic chains form a voluminous shell around the particles and intensify the surface charge to enable dispersion in water.[2] Unlike low molecular weight dispersants, the polymeric dispersants should always stay on the pigment surface, even if some parts of the chain are desorbed. In recent years, different structures of polymeric dispersants have been synthesized and applied to pigment dispersion, especially diblock co-polymers[3] and graft co-polymers.[4] Encapsulated pigments which use pigments as core and polymeric materials as shell could also facilitate pigment processing. In the last decade, a variety of encapsulation techniques, such as emulsion polymerization and graft techniques have been developed to modify pigments.[5–7] Moreover, there have also been reported some other successful encapsulations of titanium dioxide, colloidal silica, and carbon by polymeric materials; these methods include sedimentation, *in situ* polymerization, solvent evaporation, etc.[6,8–10]

Although much research has already focused on pigment dispersion, a big challenge remains to prepare stable waterborne nanoscale organic pigment dispersions suitable for ink jet printing inks. In our research waterborne nanoscale pigment dispersions including Copper Phthalocyanine blue (P.B.15:1), Quinacridone Red pigment (P.R. 122), and Monoazo Yellow pigment (P.Y.14), which utilized styrene-maleic acid copolymer as the encapsulation layer, have been prepared by different methods. The stability, particle size, and apparent viscosity of the dispersions were measured. Moreover, the shape of pigment particles was observed by transmission electron microscopy (TEM), and the pigment crystals were characterized by x-ray diffraction (XRD).

EXPERIMENTAL

Raw Materials

Co-polymer of styrene and maleic acid (PSMA, molar ratio of maleic acid was ca. 0.56, Mn = 9000, Nanocolorants and Digital Printing R&D Centre of Jiangnan University), powders of P.R.122, P.B.15:3, and P.Y.14 (purity 99.7%, 99.8%, 99.3%, respectively, Wuxi Xinguang Chemical Industry Co., Ltd.), and cotton textiles (120 g/m^2, Dongguan Xinlong Textile Industry Co., Ltd) were employed.

Preparation of Pigment Dispersion by Phase Separation Method

Pigment dispersions of P.B.15:3, P.R.122, and P.Y.14 were prepared by the method described in our previous work;[11,12]

Received Feb. 29, 2008; accepted for publication Jul. 9, 2008; published online Sep. 19, 2008.
1062-3701/2008/52(5)/050501/4/$20.00.

10 g PSMA and 440 g media were mixed together, and then 50 g pigment powder was added into the solution under stirring. The mixed slurry was dispersed by Ultra Turrax IKA T18 Basic (IKA Instruments Ltd.) at 4000 r/min for 1 h; after that 250 g distilled water were added into the slurry, PSMA slowly deposited, and encapsulated onto the pigment surface. The mixture was filtered under vacuum, washed with distilled water, and dried at 60°C for 24 hours; encapsulation pigment powder was thus obtained. The dispersion was prepared with 5 g encapsulation pigment powder and 95 g distilled water, adjusted to *p*H 8 using sodium hydroxide solution (0.01 M) and stirred by Ultra Turrax IKA T18 Basic for 30 min.

Preparation of Pigment Dispersion by Milling with Dispersant

Styrene-maleic acid sodium copolymer (10 g) was dissolved in 440 g distilled water, *p*H was adjusted to 8, and then 50 g pigment (provided by WuXi XinGuang) was added into the solution under stirring. The slurry was transferred to a mill and dispersed for 6 h.

Particle Size

Pigment dispersions were diluted 2000-fold and equilibrated at 25°C for 5 min, and then particle size was measured using the Nano-ZS90 instrument (Malvern Instruments, Ltd., England).

Stability of Pigment Dispersion

Centrifuging stability:[12] The pigment dispersion was centrifuged at 3000 rpm for 60 min, then 0.03 g supernatant in the centrifuge tube was taken out and diluted 2000-fold with distilled water. Absorbancy (A_{60}) of the pigment dispersion was measured, and the relativity absorbancy r_{60} was calculated according to Eq. (1):

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

where A_0 is the absorbancy of the dispersion before being centrifuged; r_{60} reflects the stability of dispersion, i.e., the larger r_{60}, the higher the stability of the dispersion.

Freeze-thaw stability:[12] The pigment dispersion was sealed and placed at −5°C for 12 h and then put into an oven at 50°C for another 12 h; the change in particle size (S_T) was calculated according to Eq. (2):

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

where d_0 is the starting particle size of dispersion, d_T is particle size of pigment dispersion after freeze-thaw treatment; the smaller T_d, the higher the temperature stability of the dispersion.

Stability to alcohols: 20 g glycerol and 80 g pigment dispersion were mixed together to prepare the pigment mixture in which alcohol content was 20% and pigment content was ca. 4%. The mixture was diluted 2000-fold and then the change in particle size as a consequence of the alcohol treatment (S_A) was evaluated using an analogous formula:

Table I. Properties of pigment dispersion prepared by phase separation method.[a]

Pigment dispersion	D (nm)	η (mpa s)	Stability (%) r_{60}	S_T	S_A
P.R.122	104.6	3.25	100	0.38	0.49
P.B.15:3	82.7	3.78	100	0.00	0.17
P.Y.14	75.8	4.20	98	0.12	0.30

[a] The content of pigment by weight was ca. 5%.

$$S_A = \frac{|d_0 - d_T|}{d_0} \times 100\,\% , \tag{3}$$

where d_0 is the starting particle size of dispersion, d_T is particle size of pigment dispersion after adding alcohol; the smaller S_A, the higher the stability of the dispersion towards alcohol.

Apparent Viscosity of Pigment Dispersion

The pigment dispersion was equilibrated at 20°C for 5 min, and apparent viscosities were tested using a DV-Ш Ultra programmable rheometer (Brookfield, USA).

Dyeing Cotton Textile and its K/S Value

Pigment dispersion (10 g, 5% pigment by weight) and 90 g deionized water were mixed and stirred for 30 min to prepare the dyeing bath. The cotton fabrics were dyed with an EHP 350 pad machine, the whole processes were done as follows:

> Two-dip-two-pad (wet pickup, 70%) → dry (60°C) → bake (120°C, 3 min).

K/S values were measured with X-Rite-8400 colorimeter.

Characterization of Pigment Encapsulated by Phase Separation Method

The shape of pigment particles prepared by phase separation method were observed using a transmission electron microscope (TEM, Hitachi H-7000, Japan).

X-ray diffraction spectra (XRD) of encapsulated pigments were determined using Cu$K\alpha$ radiation at a wavelength of $\lambda = 1.54183$ Å. The generator settings were 40 kV and 35 m$\AA$. Diffraction data were collected over 15 min over a range of 5°–45°, with a step width of 0.02° and a counting time of 5 s per step. Sample preparation included spreading the powders into the holder (about 3 mm thick) and pressing slightly with a glass slide to ensure a flat surface.

RESULTS AND DISCUSSION

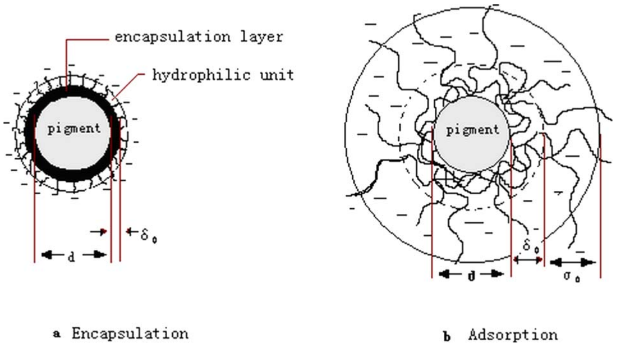
Properties of Pigment Dispersion Prepared by a Different Method

Properties of pigment dispersions are closely dependent on modification method, i.e., phase separation method versus milling with dispersant; the measured properties of the pigment dispersions are and listed in Tables I and II.

Table II. Properties of pigment dispersion prepared by direct milling with dispersant method.[a]

Pigment dispersion	D (nm)	η (mpa s)	Stability (%)		
			r_{60}	S_T	S_A
P.R.122	166.7	7.25	96	0.60	0.61
P.B.15:3	125.7	6.78	93	0.25	0.26
P.Y.14	180.2	11.20	95	0.89	0.47

[a] The content of pigment by weight was ca. 5%.



a Encapsulation

b Adsorption

Figure 1. Schematic of interaction between pigment particles and polymeric dispersants. *d*: diameter of pigment particle, δ_0: encapsulation layer, σ_0: Solvated layer.

Comparing Table I with Table II, we conclude that the phase separation method was superior to the method of milling with dispersant for preparation of pigment dispersion for ink jet application. In the phase separation method, the pigment aggregation or coagulation could be broken initially by shear forces, and the dispersed pigments were then encapsulated by PSMA. The PSMA which encapsulated the pigment would greatly reduce the attractive forces among pigment particles and thereby improve the dispersing efficiency, which led to smaller particle size and higher stability. In the method of milling with the dispersant, the chains of PSMA could be desorbed under certain conditions, which led to poorer stability. In addition, under these conditions not all PSMA could adsorb onto the pigment, and some would dissolve into the media, resulting in an increase in the apparent viscosity and reduced dispersing efficiency. This difference can be described by the schematic shown in Figure 1.

Moreover, the color properties of the dyed fabrics were also different when the pigment dispersions were prepared by the different methods. Figure 2 revealed that with the same dosage of pigment, the K/S values of dyed cotton fabrics were higher when the dispersions were prepared by phase separation method.

The reason for this may be attributed to the different particle sizes of the pigment dispersions. Particles of smaller size were easier to adsorb onto the cotton textiles. In addition, smaller particles provide more surface area, which would result in improved coverage.

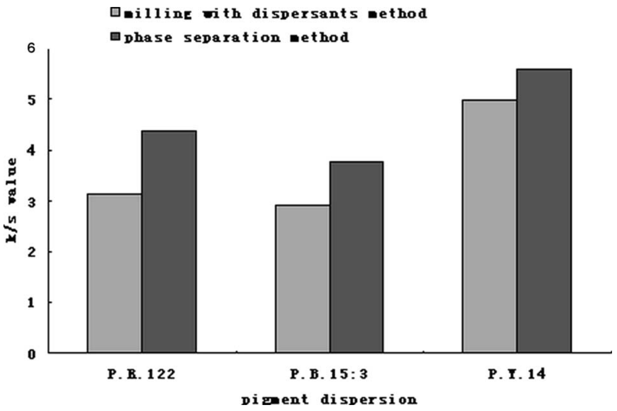
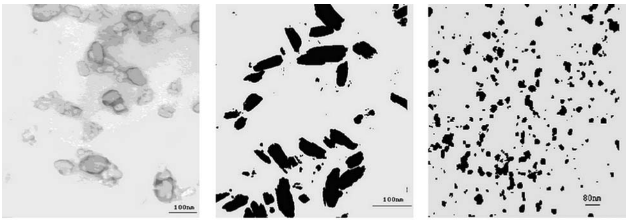


Figure 2. Effect of modification method on K/S value of dyeing cotton textile. The content of pigment by weight was ca. 0.5%.



Encapsulated P.R.122

Encapsulated P.B.15:3

Encapsulated P.Y.14

Figure 3. TEM photo of encapsulation pigment of pigment dispersion: 1-P.R. 122, 2-P.B.15:3, 3-P.Y. 14.

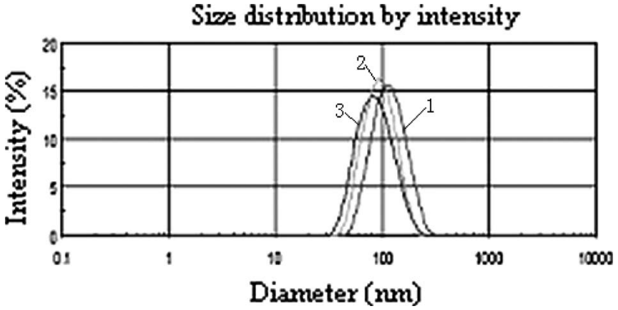


Figure 4. Size distribution of encapsulated pigment.

Particle Shape and Distribution of Encapsulated Pigment

In order to acquire shape information on pigment particles which prepared by the phase separation method, the pigment particles were observed by TEM and their size distribution evaluated by the dynamic light scattering (DLS) method.

Figures 3 and 4 indicate that pigment particle sizes were uniform in aqueous media; the particle shapes of P.R.122, P.B.15:3, and P.Y.14 were elliptical, club-shaped, and round, respectively. In aqueous media, hydrophilic chains of PSMA should build a voluminous shell and intensify the charges on the particles, which would effectively hinder their mutual attraction; thus the pigments could be dispersed stably and homogeneously in aqueous media.

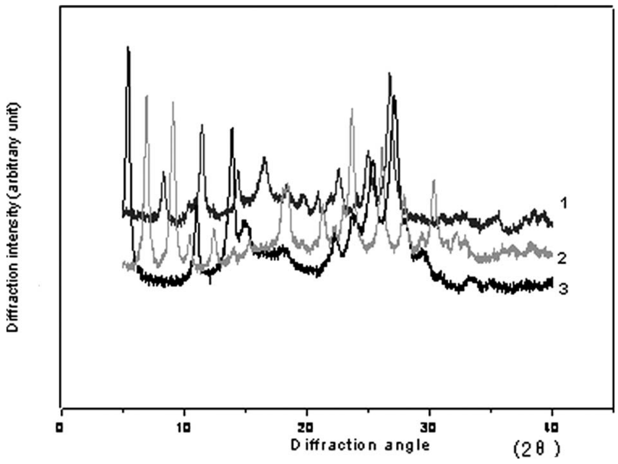


Figure 5. XRD of encapsulated pigments: 1-P.Y. 14, 2-P.B.15:3, 3-P.R. 122.

XRD of Encapsulated Pigment

It is well known that the color performances of pigment dispersion were mainly determined by the molecular structure, as well as by crystal structure; furthermore, crystal structure is a function of molecular structure.

Figure 5 revealed that diffraction spectra of encapsulated pigments were similar to those of the starting materials; the peaks appear at almost the same positions, which told us that the crystal structure was not changed on encapsulation, i.e., pigment crystal structure was unaffected by pigment processing.

CONCLUSIONS

The pigment dispersion prepared in our experimental work have higher stability to alcohol, temperature, and centrifugal force, and also have lower viscosity. The phase separation method was superior for preparation of waterborne nanoscale pigment dispersions compared to the method of direct milling with dispersant. The pigment particles were uniformly dispersed in aqueous media and the pigment crystal was not changed by processing in the phase separation method. Pigment dispersions prepared by the phase separation method are suitable for application in ink jet printing inks.

ACKNOWLEDGMENTS

This work was supported by the National 863 Projects (2002AA327120), National Natural Science Foundation of China (Grant Nos. 20474025 and 50173012); we also thank the Southern Yangtze University for supporting the research.

REFERENCES

[1] K. J. Fang, S. H. Fu, and X. Zhang, "Development of digital ink jet printing", Dyeing Finishing **24**, 48 (2004).

[2] M. A. Banash and G. C. Stuart, "A quantitative study of polymeric dispersant adsorption onto oxide-coated titania pigments", Prog. Org. Coat. **35**, 37 (1999).

[3] H. J. Spinelli, "Group transfer polymerization and its use in water based pigment dispersants and emulsion stabilizers", Prog. Org. Coat. **27**, 255 (1996).

[4] J. A. Simms, "A new graft polymer pigment dispersant synthesis", Prog. Org. Coat. **35**, 205, (1999).

[5] S. Lelu, "Encapsulation of an organic phthalocyanine blue pigment into polystyrene latex particles using a miniemulsion polymerization process", Polym. Int. **52**, 542 (2003).

[6] P. Viala, "Pigment encapsulation by emulsion polymerization, redespersible in water", Macromol. Symp. **187**, 651 (2002).

[7] P. Palumbo, "Surface modification of pigmented colorants and applications to digital printing", *ICPS'02: International Congress of Imaging Science* (SPSTJ, Tokyo, 2002) p. 559–560.

[8] B. P. Singh, "Stability of dispersions of colloidal alumina particles in aqueous suspensions", J. Colloid Interface Sci. **291**, 181–186 (2005).

[9] M. Aslam, L. Fu, S. Li Vinayak, and P. Dravid, "Silica encapsulation and magnetic properties of FePt nanoparticlesv J. Colloid Interface Sci. **290**, 444 (2005).

[10] M. Cechova, T. B. Alince, and G. M. v. d. Ven, "Stability of ground and precipitated CaCO3 suspensions in the presence of polyethylene oxide and kraft lignin", Colloids Surf., A **141**, 153 (1998).

[11] S. H. Fu and K. J. Fang, "Preparation of styrene-maleic acid copolymers and its application in encapsulated pigment red 122 dispersion", J. Appl. Polym. Sci. **105**, 317 (2007).

[12] K. J. Fang, C. X. Wang, X. Zhang, and Y. Xu, "Dyeing of cationised cotton using nanoscale pigment dispersions", Coloration Technol. **121**, 6 (2005).