ELSEVIER

Dyes and Pigments 44 (2000) 1–7

DYES and PIGMENTS

Properties of copper phthalocyanine microencapsulated in polystyrene by phase separation

Zhang Tianyong [a],*, Fei Xuening [b], Song Jian [a], Zhou Chunlong [a]

[a] *Department of Applied Chemistry, College of Chemistry and Engineering, Tianjin University, 300072, Tianjin, People's Republic of China*

[b] *Tianjin Institute of Urban Construction, Tianjin, 300381, People's Republic of China*

Received 19 August 1998; accepted 19 January 1999

Abstract

Copper phthalocyanine (CuPc) was microencapsulated by liquid phase separation in an organic solvent using a polystyrene (PS) wall. Experimental results show that the molecular weight of PS effects properties of CuPc such as flowability, dispersing ability, wetting property and particle size. The wetting angle for the microcapsule is increased, and flowability and dispersing level (in toluene) of microencapsulated CuPc are improved significantly. A better pigment dispersion can be prepared by PS using a loading of 2–5%. Thus it is possible to reduce the viscosity of a dispersion coloured with microencapsulated CuPc and increase the solids loading of the dispersion system. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Microencapsulation; Copper phthalocyanine; Polystyrene; Dispersibility

1. Introduction

While it has long been known that the cells of animals and plants are natural microcapsules, artificial microencapsulation was initially introduced by Green and Schleicher in the 1950s [1] to produce pressure-sensitive dye microcapsules for the manufacture of carbonless copying paper [2]. Since that time, many products of this type have appeared on the market, for applications involving pharmaceuticals, cosmetics, agricultural chemicals, food additives, coatings, printing inks, adhesives, catalysts and dyes [3–5], and others are known to be under development [6,7]. Microcapsules are minute heterogeneous containers that are normally spherical if enclosing a fluid, and roughly the shape of a particle if containing a solid. Shell materials may be natural or synthetic polymers, with diameters in the range of 1–1000 μm. Wall thickness will vary with core shape and amount of shell.

Microencapsulation of organic pigment, can improve the applicable properties of pigments by modifying surface properties. The polymer membrane on pigment particle surfaces cause changes in surface properties leading to specific surface reduction, surface active center deactivation, increased storage stability, decreased powder dust [8,9]. In turn, applicable properties such as dispersibility, shade, hiding power, transparency, flowability, and viscosity are improved [10–15].

---

* Corresponding author.

PII: S0143-7208(99)00047-9

Microencapsulation methods for organic pigment include solvent evaporation, spray drying, liquid phase separation, suspension cross-linking and monomer polymerizing [16]. Although a number of studies involving the microencapsulation of organic pigment have been reported, the effects of physico-chemical properties of microcapsule wall materials on the applicable properties of the pigments have been much less studied.

In this paper, a microcapsule of CuPc (C.I. Pigment Blue 15:3) generated by the liquid phase separation method is described. In this case, a PS wall is employed. The effects of the amount and molecular weight of wall material on the properties of a CuPc microcapsule are reported.

2. Experimental

2.1. Preparation of polystyrene and determination of molecular weight

Distilled water (100 ml), sodium dodecylsulfate (0.7g) and poly(ethylene glycol) 300 (0.5g) were mixed in a four-neck flask. After dissolution, the pH was adjusted to 9–10 by adding NaOH. To this solution was added potassium persulfate (0.16g) in distilled water (20 ml). Styrene (30 ml purified) was added and the mixture was heated to effect polymerization. Various molecular weights of polystyrene were prepared by adjusting the amount of emulsifier and initiator. Molecular weight was measured by a standard viscosity method using an Ubbelohde Viscometer and chloroform as the solvent.

2.2. Microencapsulation by liquid phase separation method

A 2% solution of wall polymer was prepared by dissolving PS in chloroform:acetone (3:1). CuPc (5 g) was dispersed in 30 ml of the same solvent mixture and a predetermined amount of wall material solution was added. The dispersion was stirred as ethanol (70 ml) was added dropwise over 2 hours. The mixture was stirred for 20 min, and ethanol (20 ml) was added. After stirring for 20 min at room temperature, the solid was collected by filtration and dried at reduced pressure, giving microcapsules of CuPc.

2.3. Determination of the properties of microencapsulated CuPc

The flowability of CuPc microcapsules was determined according to the National Standard of P.R. China GB 1719-79. The average microcapsule diameter and distribution were measured using a LKY-1 Type Microparticle Diameter Analyzer equipped with a centrifugal settler. The shape of microcapsules was observed on a HITACHI X-650 Scanning Electron Microanalyzer. The wetting angle was determined on a JJC-1 Model Contact Angle Measurement Instrument. The dispersing extent (in toluene) of pigment was analyzed using a published method [17].

3. Results and discussion

Liquid phase separation is a common microencapsulation method and while often carried out in an aqueous medium, the present experiments were conducted in an organic phase. This was achieved as follows: (1) the wall material was dissolved in solvent (A); (2) CuPc powder was well dispersed into the above solution; and (3) solvent (B), called a coacervation agent, which dissolves solvent (A) to partially desolvate the wall material but does not dissolve the wall material, is added to the dispersion. In this way, CuPc particles are gradually coated by partial desolvated macromolecular aggregates or the coacervates formed. An efficient coacervate should be selected and a suitable addition rate is maintained. If the rate of coacervate addition is too fast, polymer precipitation easily occurs. Thus, polymer coacervation means partial desolvation of polymer molecules versus exhaustive desolvation that occurs in precipitation. Fig. 1 illustrates the relative position of polymer coacervate between polymer solution and polymer precipitation [18]. Two alternative (or complementary) mechanisms of microencapsulation by coacervation are depicted in Fig. 2 [18]. When Method (A) is selected, the core particles are gradually coated by the newly formed coacervate

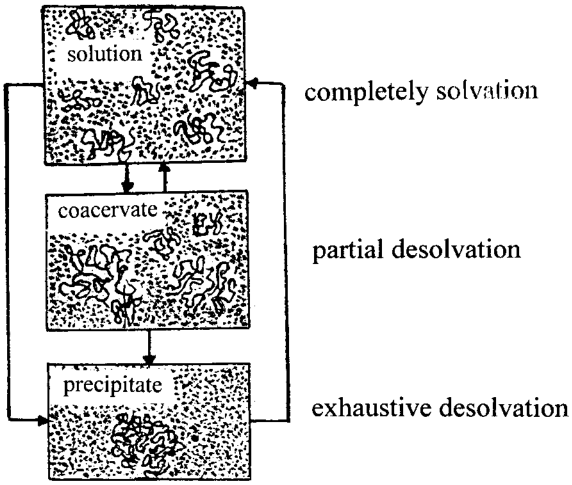

Fig. 1. Schematic representation of the position of polymer coacervate versus polymer solution and polymer precipitate.

nuclei. In our work, three types of polystyrenes were used (PS1, PS2, PS3, having average molecular weight of 0.5, 1.0 and 1.5 million, respectively). The ratios of PS to CuPc by weight for each PS was 2, 5, 10 and 20%, respectively.

3.1. Effect of microencapsulation on the flowability of CuPc pigment

Flowability data for microencapsulated CuPc are shown in Fig. 3. The data show that flowability gradually increases with increasing PS/CuPc value. Furthermore, the increase in flowability was greatest when PS/CuPc is 2–10%, but diminishes when PS/CuPc is 10–20%. This indicates that too much PS offers little benefit on flowabilbity.

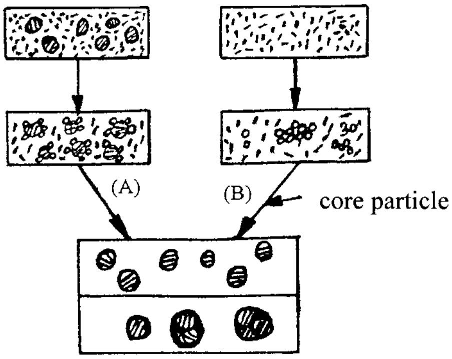

Fig. 2. Schematic representation of microencapsulation mechanisms by coacervation.

The effect of molecular weight on flowability is also observed in Fig. 3. As molecular weight increases, flowability decreases. PS-coated CuPc has higher flowability and reduced oil adsorption. Consequently, the viscosity of dispersions coloured by the microcapsules may be reduced, with increased solids loading. This means that the amount of solvent used in the system may be decreased.

3.2. Dispersing level (in toluene) of microcapsulated products

The dispersing level of pigment in given medium plays an important role in the application of organic pigments. The dispersing extent of CuPc microcapsules in toluene at the different subsidence time varies largely, as shown in Fig. 4. In this case PS/CuPc = 5%. The dispersing extent of microencapsulated CuPc is much higher than that of untreated CuPc. CuPc coated with PS is easily solvated by toluene because the polarity of PS is lower than the surface polarity of untreated CuPc and the aromatic ring in PS moiety has physicochemical similarity to toluene. To a large extent, the solvation of polymer on the pigment surface means that dispersions of the type described here are formed through diffusional processes.

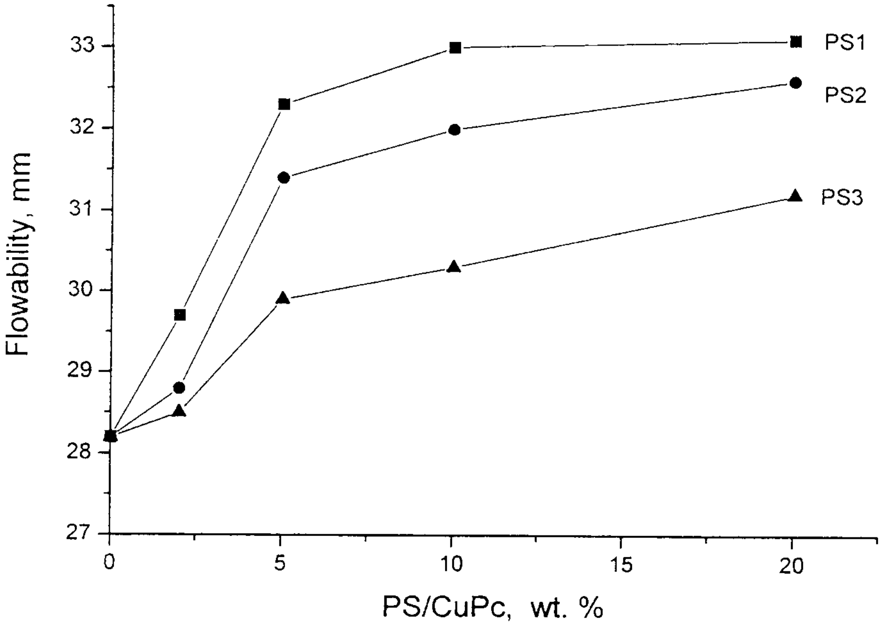

Fig. 3. The flowability of CuPc microencapsulated by polystyrene.

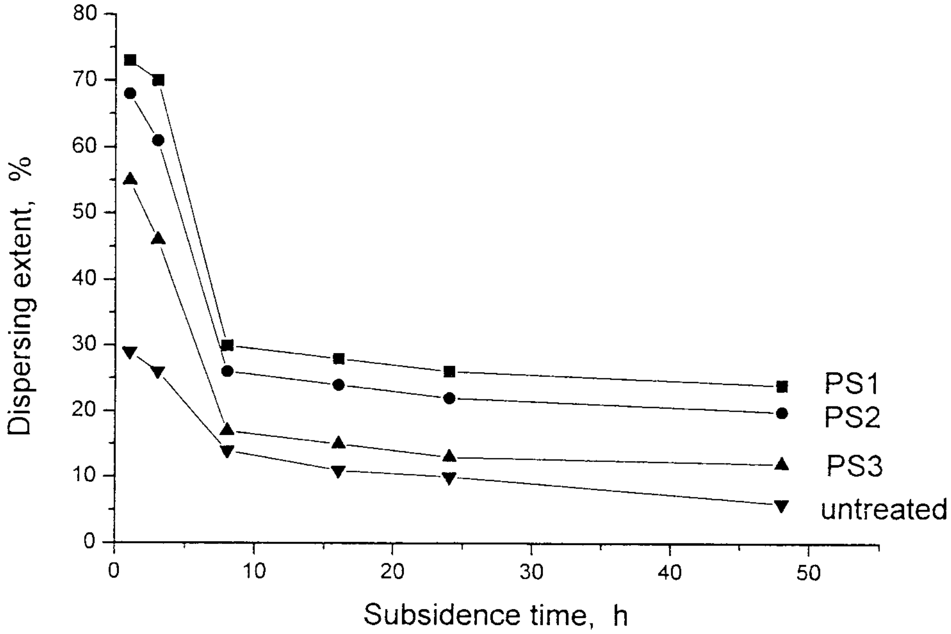

Fig. 4. The dispersing extent (in toluene) of microencapsulated CuPc.

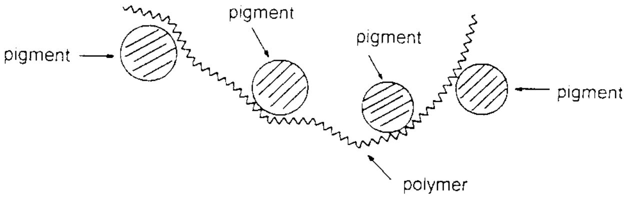

Fig. 5. A possible model for bridging flocculation caused by very long PS chain.

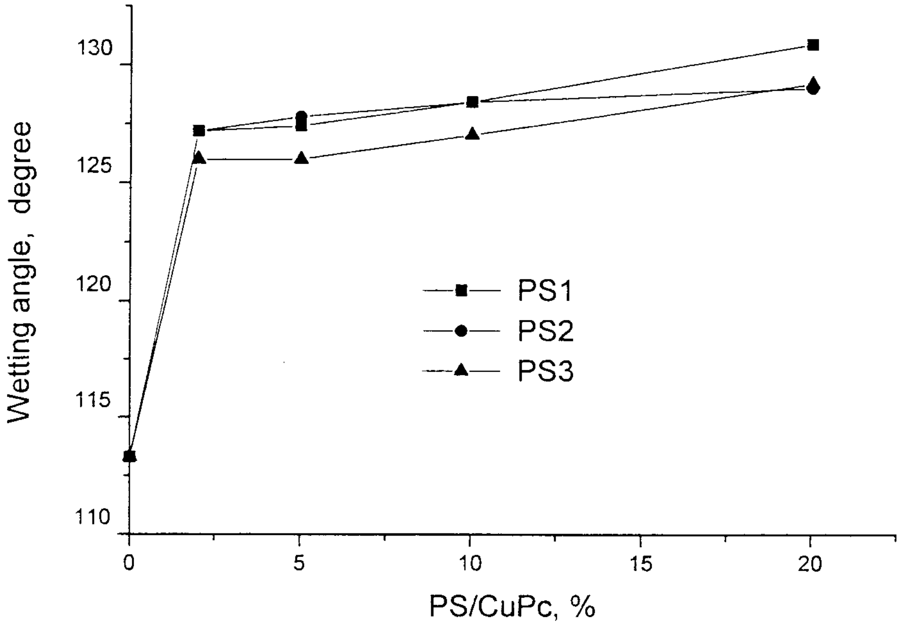

Fig. 6. Wetting angle changes for polysyrene microencapsulated CuPc.

Dispersion level is greatly affected by polymer solvation rate and solvated polymer mobility. Therefore, the dispersing level for coating CuPc pigment decreases rapidly when the subsidence time is 1–8 h; but the dispersing level decreases only a little when the subsidence time is from 8–48 h. This shows that the dispersion system is becoming more stable Since the higher molecular weight PS has inferior solvation rate and mobility, the dispersing power is lower than that of the lower molecular weight of PS (Fig. 4). On the other hand, the solvation chain of PS on the CuPc surface can cause a steric hindrance and prohibit CuPc particles from aggregating again. This also leads to an improvement in the dispersing level of PS-encapsulated CuPc.

Too high a molecular weight PS has an adverse effect on the dispersing level of CuPc. The longer polymer chains may adsorb two or more pigment particles and connect them together, leading to flocculation (Fig. 5).

3.3. Changes of the wetting property of microcapsules

Placing PS on the surface of CuPc changes the wetting angle as shown in Fig. 6. The wetting angle of CuPc enclosed with PS increases compared to untreated CuPc. The data indicate that the surface polarity of CuPc is reduced, causing CuPc to be easily wet out and dispersed in non-polar or lower polar media. Fig. 6 also shows that wetting angle varies little when PS/CuPc is in the range of 2–20% and PS molecular weight changes. Therefore, CuPc particles can be completely coated using 2–5% PS and the surface polarity of CuPc can be reduced effectively. Based on these data, the amount of PS should be carefully controlled, otherwise a reduction in tinctorial strength may occur.

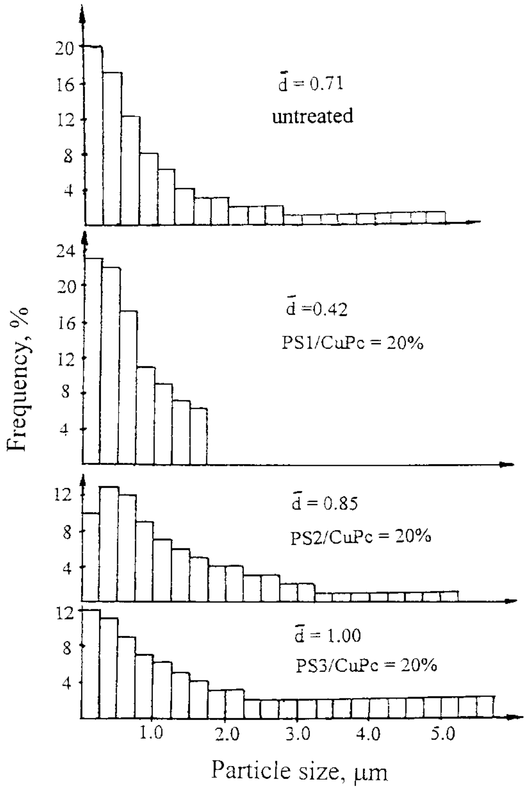

Fig. 7. The average diameter and distribution of PS (PS1, PS2, PS3) microencapsulated CuPc.

3.4. Particle size and shape of microcapsules

Particle diameters and distributions of CuPc coated with different molecular weights of PS are shown in Fig. 7. The differences in molecular weight may cause differences of the extent to be solvated. The higher the molecular weight, the lower the solvation extent. As molecular weight of PS increases, coacervation speed increases, and solvation speed decreases. One capsule product may contain more than one core particle, as a result of much faster coacervation speed. This would give diameter microcapsules. Fig. 7 illustrates that the particle size of microcapsules increase with increasing PS molecular weight. The

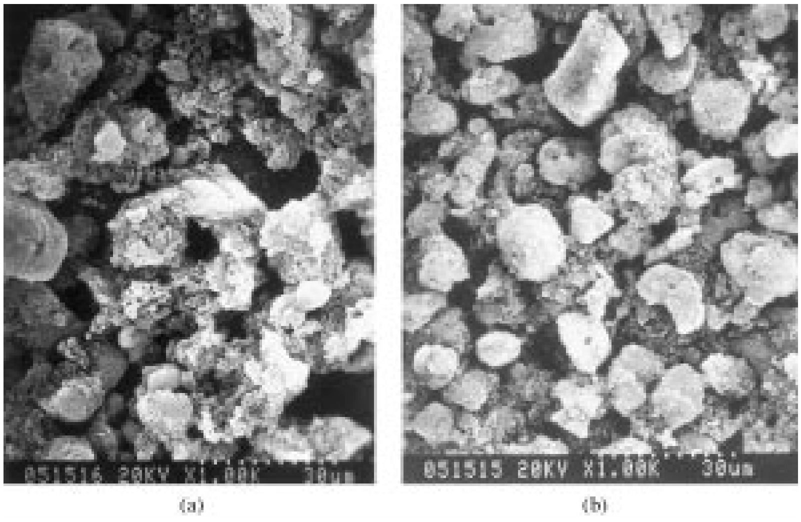

Fig. 8. The SEM of PS1 microencapsulated CuPc. A: PS/CuPc = 5%; B: PS/CuPc = 20%.

average diameter of PS1 microcapsules was lower than that of untreated CuPc, but the average diameters of PS2 and PS3 microcapsules were higher than that of untreated CuPc ($d = 0.71$ μm).

Microcapsules containing a PS1 wall were analyzed by scanning electronic microscopy (SEM), the results of which are shown in Fig. 8. When PS1/CuPc was 5%, a few microcapsules were observed, but the particle distribution was not uniform and many small particles exsisted. When PS1/CuPc was 20%, all particles were nearly microcapsules and particle distribution was uniform. Microcapsule shape was more rounded, and microcapsule was thicker, resulting in a larger particle size.

4. Conclusion

Microencapsulated CuPc can be prepared by organic phase separation, with a wall of polystyrene. The surface properties of polystyrene coated CuPc varied. Wetting angle was raised (for water), and flowability and dispersing extent (in toluene) also improved. These properties correlated with the PS molecular weight and loading levels. A superior pigment dispersion was prepared from PS1 with the loading amount of 2–5%. The viscosity of the dispersions coloured by these microcapsules may be reduced and solids loading may be enhanced.

References

[1] Green BK, Schleicher L. U.S.P 2730456 (1956); U.S.P 273045 (1956).

[2] Ranney MW. Microencapsulation technology. Noyes Development Co., 1969. p. 1.

[3] Nixon JR. Endeavour 1985;9(3):123–8.

[4] Robert ES. Kirk-Othmer Encyclo Chem Technol 3rd ed. 1981, Vol. 15, p. 470–493.

[5] Finch CA. Chemistry and Industry 1985;22:752–6.

[6] Dibiase MD, Morrel EM. Pharmaceutical Biotechnology 1997;10:255–88.

[7] Thies C. Encyclopedia of Polymer Science and Engineering. Vol. 9 New York: Wiley, 1987 [p. 724–725].

[8] Sun Chemical USP 4036652 (1977).

[9] DIC, JP 03221137 (1991).

[10] Dow Chemical USP 4680200 (1987).

[11] Du Pont USP 3806464 (1974).

[12] Williams S. U.S.P 3904562 (1975).

[13] Gutcho MH. Microcapsules and microencapsulation techniques. Noyes Data Co., 1976, [p. 180–181].

[14] Champion International USP 4157983 (1979).

[15] Gunter. U.S.P 5011634 (1991).

[16] Tianyong Z, Chunlong Z. Modern paint and finishing 1997;1:11–13.

[17] Tianyong Z, Chunlong Z. Dyes and Pigments 1997;35(2):123–30.

[18] Arshady R. Polymer Engineering and Science 1990;30(15):905–14.