ELSEVIER

Dyes and Pigments, Vol. 35, No. 2, pp. 123–130, 1997

PII: NOT SUPPLIED IN SGML 0143-7208/97 $17.00 + 0.00

Properties of Copper Phthalocyanine Blue (C.I. Pigment Blue 15:3) Treated with Poly(ethylene glycol)s

Zhang Tianyong and Zhou Chunlong

Department of Applied Chemistry, Tianjin University, Tianjin, People's Republic of China, 300072

(Received 16 August 1996; accepted 18 September 1996)

ABSTRACT

This paper is concerned with the surface treatment of copper phthalocyanine blue (C.I. Pigment Blue 15:3) by adsorption with poly(ethylene glycol)s of various molecular weights. The results from the experiments show that the contact angle for water, the flowability and the mean diameter of treated pigment particles decrease, and that the dispersing stability in aqueous media is increased after treatment. The effect of surface treatment depends largely on the molecular weights of the poly(ethylene glycol)s and on the amount of the poly(ethylene glycol)s used. © *1997 Elsevier Science Ltd*

Keywords: surface treatment, organic pigment, poly(ethylene glycol), dispersing agent.

INTRODUCTION

Organic pigments are dispersed in media as tiny particles. The application properties of pigments, such as the shade, the colour strength, the dispersing properties, and the flowability, depend on their chemical constitutions and on physical properties such as crystal form, particle size, size distribution and surface characteristics. Surface treatment carried out before the addition of pigments in dispersion mediums can significantly improve their applicable properties.

The outstanding chemical stability and physical stability of copper phthalocyanine blue (CuPc) permits their use in most applications for blue organic pigments as well as in some nonpigmentary areas. The hydrophilic stability of untreated CuPc is poor.

Special methods of surface treatment of organic pigments are usually based on abietic acid and its derivatives, organic amines, surfactants and synthetic polymers [1]. Surface treatment with synthetic polymers is one of the more important methods of surface modification of pigments. The good dispersibility of pigments treated with synthetic polymers is due largely to the fact that polymer chains, adhering to the pigment surface, prevent pigment particles from agglomerating via steric stabilization [2],[3].

The poly(ethylene glycol)s (PEG) comprise a series of low to medium molecular-weight, wholly synthetic, water-soluble linear polymers as used in plasticizers, coatings, printing inks, humectants and detergents. For this paper, CuPc was surface-treated with PEG whose molecular weights are 300, 800, 1540, 6000, 20000 g mol^{-1} (referred to as PEG 300, PEG 800, PEG 1540, PEG 6000, PEG 20000, respectively). The dispersing extent in water, the contact angle, the mean diameter and the flowability of the treated pigments were studied.

EXPERIMENTAL

Adsorption of PEG on CuPc

Pigment press cake 12.5 g (β-CuPc is 40%) and given amounts of PEG were mixed in 100 cm^3 of distilled water. The mixture obtained was stirred and kept at 65–70°C for 5 h, filtered and then dried at 50°C in reduced pressure.

Determination of particle size

A pigment sample was prepared as an aqueous dispersion at a loading of 1% by ultrasonic dispersion at 30 ~ 35°C for 5 min. The mean diameter and distribution of pigment particles were measured using a LKY-1 Type Microparticle Diameter Analyzer equipped with a centrifugal settler. The principle of measurement is the centrifugal settling.

Dispersing extent in an aqueous medium [4]

A 20 mg pigment sample and 25 cm^3 of distilled water were shaken vigorously and dispersed in a 40 cm^3 graduated test tube. The aqueous dispersion was allowed to settle over several hours. The upper 1 cm^3 of the dispersion was taken out accurately from the liquid surface 2 cm. This 1 cm^3 of dispersion was then diluted with 5 cm^3 of distilled water. The transmissivity (T) of the diluted dispersion was measured with 751G Model Spectrophotometer. The dispersing extent (D.E.%) was calculated from the following equation.

$$\text{Dispersing Extent } (D.E.\%) = (1 - T) \times 100\%$$

Determination of contact angle

An approximate 1 g sample was pressed into a round disc with a Y30-4 Model Single Piston Universal Liquid Compressor. The contact angle of the round disc was determined on a JJC-1 Model Contact Angle Measure Instrument.

Flowability determination

The flowability was determined according to the National Standard of People's Republic of China GB1719-79.

RESULTS AND DISCUSSION

Wetting properties of treated CuPc pigments

Molecules of PEG consist of ether bonds and hydroxy groups which can form hydrogen bonds with water molecules. Thus PEG is soluble in water. The surface tension of a 10% aqueous solution is about 55 mN/m. That of water is 72.8 mN/m. Thus the surface tension of CuPc containing adsorbed PEG is decreased and the hydrophilic ability of CuPc is increased. An adsorption model of PEG on a CuPc surface is shown as Fig. 1. Contact angle data for the treated pigment are shown in Fig. 2.

The surface of β-CuPc was higher irregularity surface with a dimensional scale 2.45 ± 0.10 according to Mather [5]. W. Heller thought that the multiple contacts were formed when PEG was adsorbed on charcoal [6]. Besides, PEG is a linear homopolymer, so it is suggested that PEG is adsorped on CuPc surface by multiple contact adsorption.

Untreated CuPc (C.I. Pigment Blue 15:3) has a contact angle with water of 104.8° (obtuse angle) and is difficult to wet by water. The contact angles of treated CuPc are reduced to below 90° as shown in Fig. 2. The more PEG is added to CuPc, the more the contact angles are reduced. It shows that the nonpolar surface of CuPc is better covered by PEG. The contact angles are obviously reduced with the increase of molecular weights of PEG, but the contact angles raise oppositely when their molecular weights are higher than 1540.

Hydrophilic ability of PEG is related to its molecular weight. Liquid PEG samples are completely soluble in water, whereas the solubility of solid PEG

in water decreases with the increase of molecular weight [7]. Because the dimension of the polymer chain is shorter and its coverability on the CuPc surface is less, the contact angle is reduced slightly. The contact angle is also decreased slightly because of the reduction of hydrophilic ability caused by the longer polymer chain.

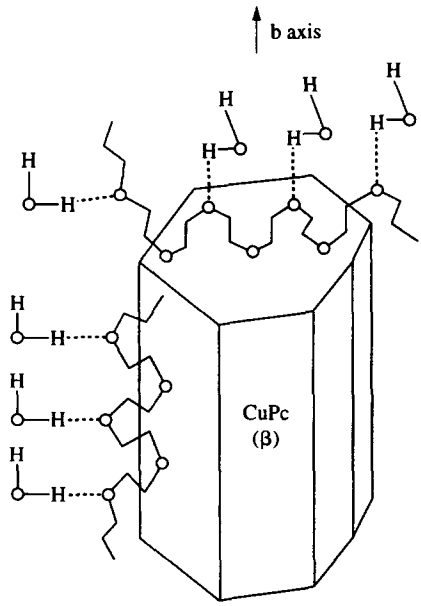

Fig. 1. Assumed adsorption model of PEG on CuPc surface.

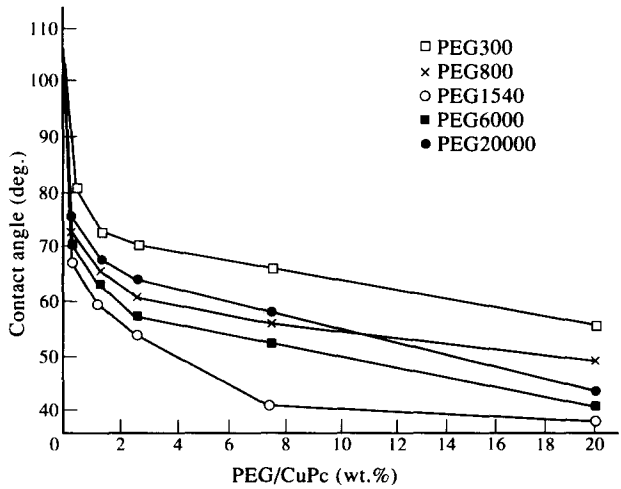

Fig. 2. Contact angle of CuPc treated with various PEG types.

Dispersing extent of treated pigment in water medium

The surface of treated pigment is coated with PEG chains. Water molecules are fixed in PEG chains because of formation of hydrogen bonds. When pigment particles come close to each other, PEG chains adsorbed on the pigment surface will contract. It is necessary to take in energy from the external environment for some of the water molecules fixed in PEG chains to escape from the PEG chains. In addition, the degree of freedom of released water molecules is greater than that of fixed water molecules. Therefore, it is not a spontaneous process. The dispersion system of treated pigment can be stabilized by a steric hindrance effect. It is also called enthalpy stabilization. A reduction of temperature can make hydrogen bonds more stable.

Figs 3 and 4 show that D.E. of treated pigment is increased significantly. The higher the PEG molecular weight is, the more PEG is added and the higher the D.E. is. In those cases, the thicker shell of adsorption benefits the dispersing stabilization. But D.E. begins to reduce in the case of PEG 20 000 when the amount added is more than 2.5%. Fold back on to the pigment may occur if the PEG chain is too long. As a consequence, some flocculation occurs.

Flowability of treated CuPc

There is a relationship between the flowability and the D.E. The D.E. increases with the reduction of flowability in our experiments. Surface properties of CuPc treated with PEG lead to the changes of flowability as shown in Fig. 5.

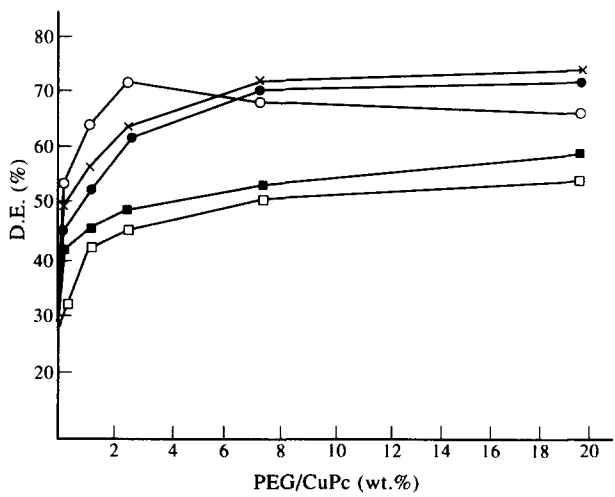

Fig. 3. D.E. of CuPc treated with PEG in water medium. □, PEG 300; ■, PEG 800; ●, PEG 1540; ×, PEG 6000; ○, PEG 20 000; Subsidence time, 8h.

The flowability of treated CuPc varies with the molecular weights and the added amount of PEG. The flowability of untreated CuPc is 29.2 mm. The flowability of CuPc treated with PEG 300 rises slightly. When the added amount of PEG 800 is lower than 1.25%, the flowability rises slightly; on the contrary, the flowability drops largely when the added amount is further increased. The other PEGS lead to a decline in the flowability (compared with the untreated). It is a conclusion from Figs 5 and 4 that the lower the flowability of treated CuPc is, the higher the D.E. of CuPc in water is.

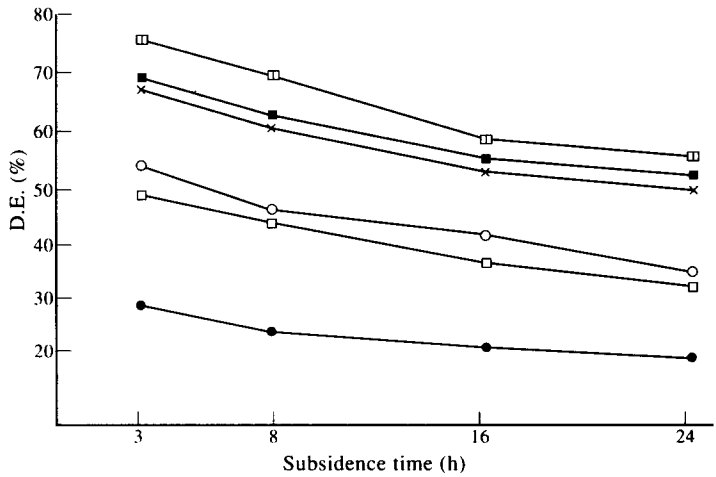

Fig. 4. The relations between the D.E. of treated CuPc and the subsidence time. ◫, PEG 20 000; ■, PEG 6000; ×, PEG 1540; ○, PEG 800; □, PEG 300 ●, untreated PEG/CuPc = 2.5% (wt.%).

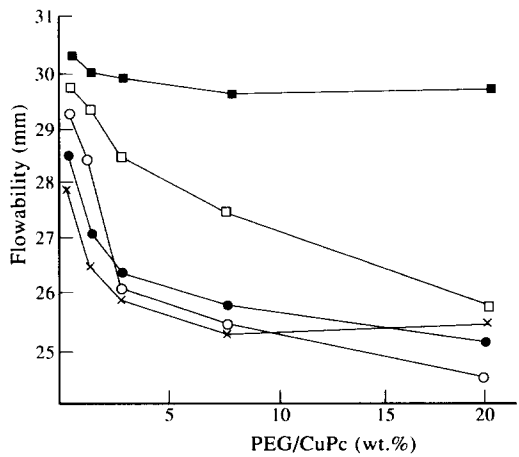

Fig. 5. The flowability of treated CuPc. ■, PEG 300; □, PEG 800; ●, PEG 1540; ○, PEG 6000; ×, PEG ○, PEG 20 000.

Particle size of treated pigment

Surface treatment of pigments can reduce the tendency of pigments to flocculate during drying and when used in the dispersion medium. Figure 6 shows the particle size and distribution of CuPc treated with PEG 20 000, at the loading quoted on Fig. 6.

The treated CuPc have smaller mean diameters, narrower particle size distributions and softer texture aggregates, which help the pigments to be dispersed more stably in aqueous medium.

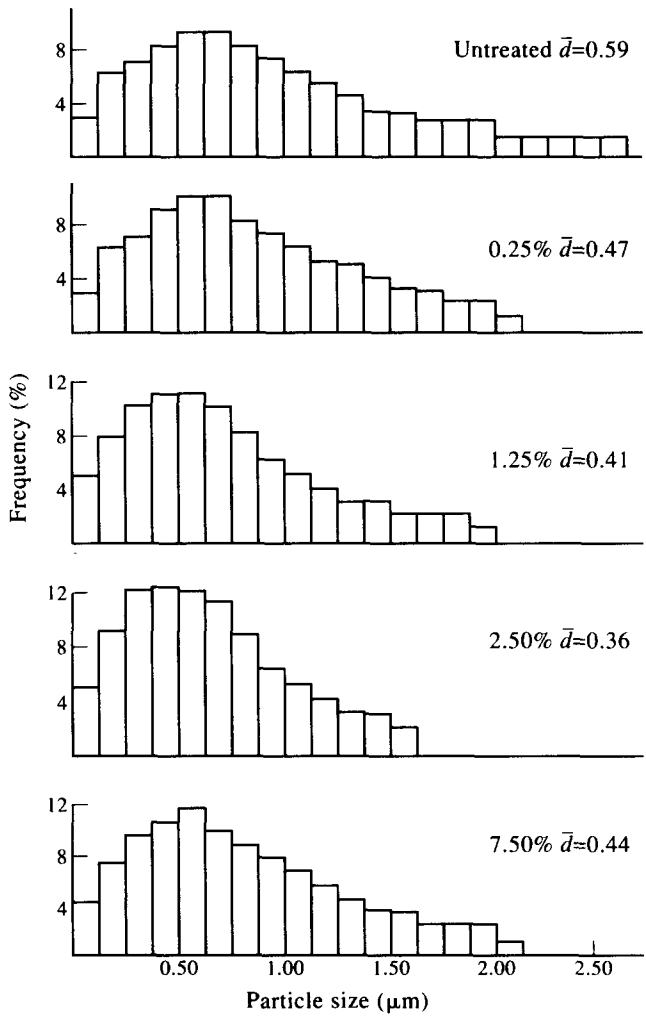

Fig. 6. Mean diameter and particle size distribution of CuPc treated with PEG 20 000.

CONCLUSION

PEG can improve the wetting ability of CuPc in aqueous media by surface treatment. The contact angle of treated CuPc for water is reduced. The D.E. of treated CuPc in water is enhanced largely by a steric hindrance effect. The flowability of treated CuPc is considerably lowered with the increase of molecular weight of PEG. The reduction of mean diameter of treated CuPc makes CuPc easily dispersed in aqueous media.

REFERENCES

1. Merkle, K. and Schafer, H. *Pigment Handbook*, Vol. III (ed. Temple C.). John Wiley and Sons, Inc., 1973, pp. 157–167.
2. Cowley, A. C. D. and Gallon, M. R. *Journal of the Oil and Colour Chemists' Association*, **71**(10) (1988) 310–314, 329.
3. Cowley, A. C. D. and Slater, R., *Plastics Engineering*, **45**(2) (1989) 41–43.
4. Ishigami, Y. and Suzuki, S., *Shikizai Kyokaishi*, **54** (1981) 671–679.
5. Mather, R. R., *Dyes and Pigments*, **14** (1990) 49–58.
6. Heller, W., *Pure and Applied Chemistry*, **12** (1966) 249–274.
7. Davidson, R. L. *Handbook of Water-Soluble Gums and Resins*. McGraw-Hill, Inc., pp. 18-4, 18-5, 1980.