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A new type of quaternary ammonium salt containing siloxane group and used as favorable dispersant in the surface treatment of C.I. pigment red 170

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ABSTRACT

C.I. pigment red 170 is an important type of organic pigment. A new type of quaternary ammonium salt containing siloxane group was prepared and then used as a favorable dispersant in the surface treatment of pigment red 170. The quaternary ammonium salt was achieved from the reaction of *N*-(β-aminoethyl)-γ-aminopropyl-methyl-bimethoxy-silane and 3-chloro-2-hydroxypropyl-bimethyl-hexadecyl ammonium halide in isopropanol, and its structure was characterized by IR and NMR techniques. The flowability, dispersing extent, particle size, and wetting behaviors of pigment were determined and the results showed that a small amount of the above dispersant could bring to the high flowability, good dispersing stability, small particle size and excellent wettability of pigment red 170. We also proposed the scenarios of dispersing process of pigment red 170 based on the information obtained from above characterizations.

1. Introduction

Most of the pigments are made into optimum particle sizes so as to yield best performance. During transportation and storage, however, the so-called primary particles build up to form agglomerates and aggregates [1]. This may cause poor flow properties and low tinctorial strength in paints and printing inks. It is important to break down these structures back into fine particles and to stabilize this state during the process of producing paints and printing inks. Dispersants are therefore used to get a fine and homogeneous dispersion [2,3]. These dispersants must enable the pigment particles to withstand the Van der Waals attractive force which would otherwise hold the pigment particles together. During the process of surface treatment, dispersants are adsorbed on the surface of pigment particles so as to prevent pigment particles from aggregating by steric barrier and/or electrostatic repulsion [4,5].

Traditionally, abietic acid and its derivatives, organic amines, surfactants, or other inorganic materials are used in the surface treatment of organic pigments to get good dispersibility [6–15]. However, it may result in low tinting strength and flowability when inadequate amount of dispersant is used [3,16]. Thus, many researchers make their best effort to devise new types of dispersant to meet the demanding needs of the pigment dispersion.

Pigment cannot be used directly to coating. Coatings are mainly composed of pigment, filler and resin. But these components may not be compatible to each other. Siloxane can make pigment and filler well dispersed in organic binders due to their hydrophilic/hydrophobic nature. They convert the hydrophilic surface of pigments and fillers into hydrophobic components, which make pigments and fillers compatible with hydrophobic organic resins.

But latest siloxane types can also convert the existing hydrophilicity of filler into a truly “super-hydrophilic” effect. Treated fillers can be incorporated very easily into liquids and show an increase of storage stability, as they tend to sediment more slowly.

The siloxane mentioned above are generally used as dispersants for inorganic pigments, such as titanium dioxide and iron oxides [17–19]. However, there are few references about the use of siloxane in the dispersing of organic pigment. In our research, we have developed a new quaternary ammonium salt containing siloxane group dispersant (Fig. 1a), and found it greatly improves the flowability, dispersing stability and wettability of organic pigments. Pigment red 170 is a very important type of organic pigments and widely used in inks and coatings. So we use pigment red 170 to test the performance of our dispersant. The dispersion extent of pigment red 170 (Fig. 1b) [20] treated with different amounts of the dispersant in water has been studied.

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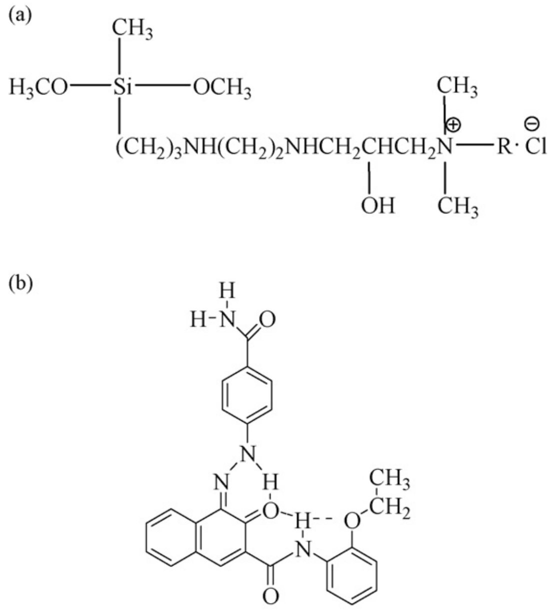


Fig. 1. (a) Structure of cationic siloxane dispersant ($R = C_{16}H_{33}$). (b) Structure of pigment red 170.

2. Experimental

2.1. Materials

Pigment red 170 was provided by Zhejiang Baihe Chemical Holding Group; trimethyl-hexadecyl ammonium halide and nonionic polyether used as contradistinctive dispersants were purchased from Akzo Nobel; other chemicals and solvents were of analytical grade and commercially available.

2.2. Characterization

IR spectra of materials were recorded by Nicolet 5SXC FT-IR spectrometer with pressed KBr. Avance 500 (Bruker) NMR spectrometer (TMS, 500 Hz) was used for the determination of ^1H NMR spectra. CARY 100 Conc UV–vis Spectrophotometer was adopted to measure the transmissivity of pigment–water or pigment–dispersant–water systems. In order to observe the morphology of pigment, JEM-1200EXII transmission electron microscope was used. We also analyzed the particle size distribution of pigment with Mastersizer 2000 particle size analyzer. Wettability of pigement was characterized by Radian Series 3000 surface tension instrument. Finally, the flowability was determined according to the National Standard of People's Republic of China GB1719-79.

2.3. Preparation of cationic siloxane dispersant

The process of the preparation of cationic siloxane dispersant is as Scheme 1.

2.3.1. Preparation of 3-chloro-2-hydroxypropyl-bimethyl-hexadecyl ammonium halide

100 mL water and appropriate amount of hydrochloric acid (37%) were added into a 250 mL flask under agitation. When the mixture was heated to 35 °C, 13.4 g *N,N*-dimethyl-hexadecylamine was continuously dropped into it. Thus, the aqueous solution of tertiary amine salt would be obtained.

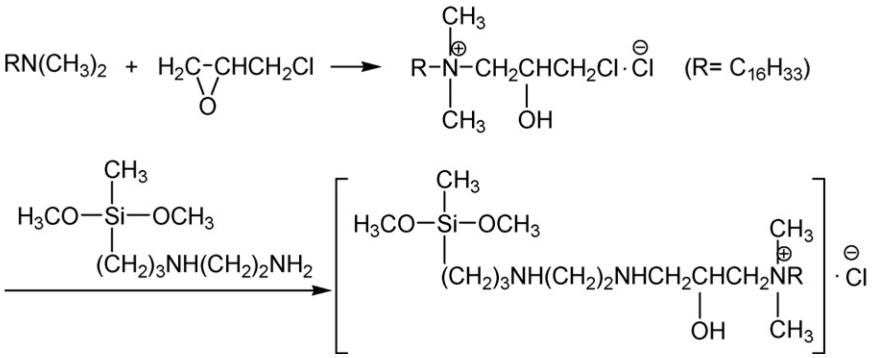
5.2 g epichlorohydrin was then dropped slowly into the above aqueous solution at 5 °C under agitation within 1 h. The temperature of solution was maintained at 5 °C for 1 h after the addition of epichlorohydrin. Then, temperature was raised to 45–50 °C and maintained for 2 h. Finally, 3-chloro-2-hydroxypropyl-bimethyl-hexadecyl ammonium halide could be obtained through removing water and the unreacted epichlorohydrin by reduced-pressure distillation.

2.3.2. Preparation of quaternary ammonium salt containing siloxane group (Fig. 2)

10.3 g *N*-(β-aminoethyl)-γ-aminopropyl-methyl-bimethoxysilane, 19.9 g 3-chloro-2-hydroxypropyl-bimethyl-hexadecyl ammonium halide and 100 mL isopropanol were added into a flask of 250 mL. The mixture was refluxed for 8 h at 80 °C. Then quaternary ammonium salt containing siloxane group, which was light yellow viscous liquid, would be obtained through removing isopropanol by reduced-pressure distillation. FTIR (KBr, cm^{-1}): 3400 (w, ν_{N-H}, ν_{O-H}), 2972–2855 (s, ν_{C-H}, $-CH_3$, $-CH_2-$), 1456 (w, δ_{C-H}, $C-CH_2$), 1258 (s, δ_{sC-H}, $Si-CH_3$), 1186.76 (s, ν_{asC-O}, $Si-O-CH_3$), 1088 (w, ν_{Si-O}), 723.50 (s, δ_{C-H}, $-(CH_2)_n-$). ^1H NMR ($CDCl_3$, 500 Hz) δ (ppm): 0.08 (6H, s, aH, a′H), 0.15 (3H, s, bH), 0.64 (2H, t, cH), 0.88 (3H, t, pH), 1.20–1.26 (20H, m, nH), 1.32–1.35 (2H, m, oH), 4.58–1.66 (2H, m, dH), 1.75–1.77 (2H, m, mH), 2.78 (2H, t, eH), 3.00 (2H, t, gH), 3.10–3.15 (2H, m, fH), 3.39–3.40 (6H, m, kH, k′H), 3.46–3.52 (2H, m, lH), 3.54–3.64 (2H, m, hH), 3.69–3.80 (2H, m, jH), 4.57 (1H, m, iH).

2.4. Dispersing extent of treated pigment in water

0.1 g pigment sample and 10 mL distilled water with different amount of cationic siloxane dispersant were added into a test tube of 25 mL. The aqueous dispersion was allowed to lay aside for 24 h after 30-min oscillating with an ultrasonator. 0.5 mL of the mixture



Scheme 1. Reaction process of the preparation of cationic siloxane dispersant.