TiO₂ Pigment Suspension Behaviour upon Adsorption of Polymeric Dispersants

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ABSTRACT

The influence of polymeric dispersants containing different functional groups on TiO₂ pigment particle suspension was investigated at pH 6.0 and 9.5, using rheology and particle size data. The dispersants chosen were polyacrylic acid and modified polyacrylamides including homo and copolymers modified with carboxylate and/or hydroxyl groups. The pigment suspension was strongly affected by both pH and dispersant functional groups. The pigment suspension exhibited a maximum yield stress and particle size at the pigment isoelectric point. The presence of carboxylate groups in both polyacrylic acid and anionic polyacrylamide copolymer altered the pigment dispersion behaviour, reducing the suspension yield stress and mean particle size. The polyacrylamide homo-polymer had negligible effect on the pigment dispersion properties at pH 9.5, while it caused pigment particle aggregation at pH 6.0. The hydroxyl-modified polyacrylamide had negligible effect on the pigment dispersion at pH 6.0, but decreased the yield stress and the mean particle size at pH 9.5. Prog. Color Colorants Coat. 3(2010), 66-72 © Institute for Color Science and Technology.

1. Introduction

TiO₂ is one of the most important white pigments currently used in the world, with a total annual production of about 6 million [1]. TiO₂ pigment suspension properties are very important for consumer industries such as paints, papermaking and plastics; if aggregates are present, the end-use properties including gloss, opacity and storage stability will be highly affected [2]. Dispersion properties can be greatly improved by addition of a polymeric dispersant [3]. It is therefore very important to understand the interaction between the pigment particles and polymeric dispersants of varying functionality [4].

Pigment dispersion stabilisation in water is generally provided by two major mechanisms of electrostatic and steric stabilisation (Figure 1). Electrostatic stabilisation in an aqueous pigment suspension involves adsorbed ions building up a charged layer around the pigment, preventing aggregation by electrostatic repulsion [5]. Steric stabilisation, on the other hand, is generally described to arise from two factors: an excluded volume component and a mixing or osmotic component,

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involving compression of the adsorbed layer causing an increase in polymer concentration [6]. It is also possible to combine chemical functional groups within the same dispersant molecule to provide both steric and electrostatic stabilization [3].
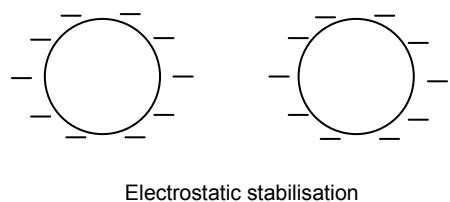
Particles in aqueous electrolyte acquire a charge due to either chemical dissociation of their surface groups, preferential physicochemical adsorption of electrolyte ions, or from preferential desorption or adsorption of ions. The ions involved in the charging process are called 'potential determining ions' and the surface charge of the colloid varies with the concentration of those ions. For common metal oxides (such as TiO_2, Al_2O_3 and SiO_2), H^+ is the potential-determining ion, and so the surface charge is a function of the pH. All oxides thus tend to be positively charged at low pH and negatively charged at high pH. Obviously, then, there is normally a pH somewhere on the scale where the particles have no charge (it is called isoelectric point or iep). Therefore, pH is an important factor in pigment dispersion stabilization in water.

This paper aims to examine the effect of pH and polymeric dispersant functional group architecture on the TiO_2 pigment rheology and particle size in concentrated suspensions. The yield stress (τ_B) of the pigment suspension reflects the shear stress required for breakdown of the structure or particle aggregates [6], and is commonly measured in rheological investigations [7-10]. Knowledge of the effect of polymeric dispersant adsorption on the rheological properties and particle size of pigments has great importance for paint and coating industries [11].

2. Experimental

2.1. Materials

The pigment sample used throughout this study was a rutile with a density of 4.1 g/cm³. The BET surface area of the pigment particles measured by N_2 adsorption was 19.0 m²/g. The mean diameter of the particles measured by TEM was 230 nm. The major surface elements determined by X-ray Photoelectron Spectroscopy (XPS) were Al, Ti, Zr and O (19, 6, 0.6 and 74 at%, respectively, after removing the adventious carbon contribution). The pigment isoelectric point (iep) was at pH 7.8 ± 0.3.

The polymeric dispersants used were polyacrylic acid and modified polyacrylamides (Figure 2). Polyacrylic acid (Polymer-A) was obtained from Sigma-Aldrich Corp., USA, as sodium salt.
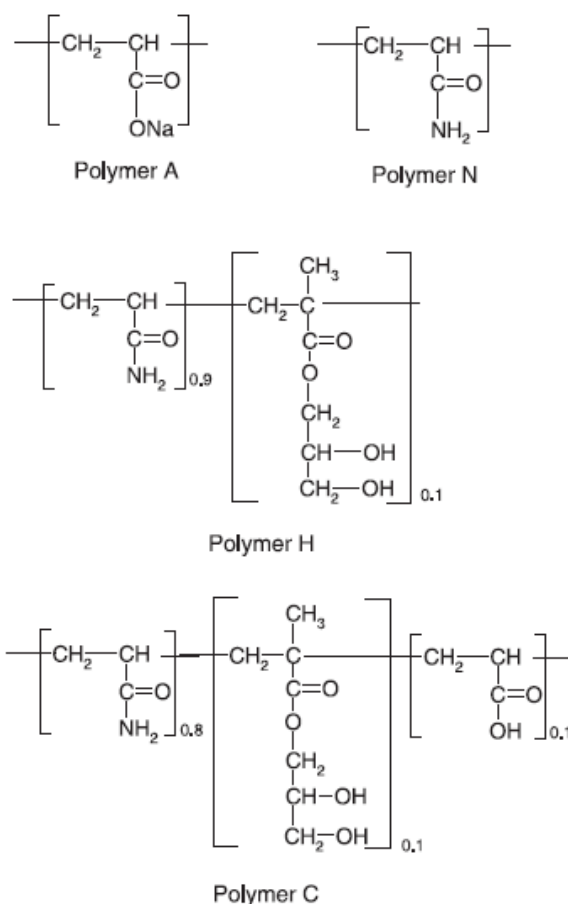

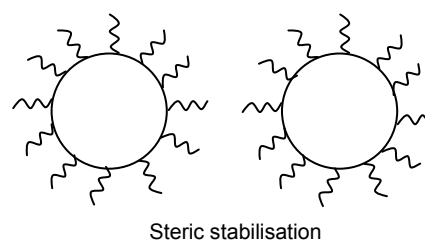Figure 2: The polymeric dispersant schematic structure.

Figure 1: Two common mechanisms of colloidal stabilisation.

The polyacrylamide reagents (Polymer-C, Polymer-H, and Polymer-N) were obtained from Cytec Industries, Inc., USA; Polymer-N was a polyacrylamide homo-polymer, Polymer-H was a polyacrylamide copolymer modified with 10% hydroxyl groups, and Polymer-C was an anionic polyacrylamide copolymer modified with 10% carboxylate and 10% hydroxyl groups. The molecular weights of the polymeric dispersants, measured using size exclusion chromatography relative to polyethylene glycol standards were 13,600, 17,000, 13,100 and 12,600 g/mol for Polymer-A, Polymer-C, Polymer-H, and Polymer-N, respectively; values which are characteristic of dispersants used in the paint industry. The physicochemical properties of the polymeric dispersant samples have been discussed previously [12].

2.2. Pigment suspension rheology

Shear stress of the pigment suspensions was determined at 25 °C as a function of polymeric dispersant concentration using a Haake CV20 couette-type rheometer fitted with a Mooney-Ewart concentric cylinder sensor (45 mm diameter, 0.5 mm gap). As the yield stress of the pigment suspension may decrease in the presence of anionic dispersants, the pigment concentration should be carefully chosen to be high enough to obtain reproducible results. Thus, a pigment concentration of 50 wt.% (20 vol.%) was used for rheological studies, as identified previously [1].

The pigment suspension was stirred overnight at its natural pH ($\sim$ 6.8) and the pH was then adjusted to the desired value with a small amount of HCl or KOH solution before conducting the experiments. The pigment suspensions were sheared at an increasing shear rate,

from 0 to 300 s^{-1} and back to rest in 2 min with the torque sensor continuously determining the shear stress.

The yield stress (τ_B) of the pigment was obtained using the Bingham model (equation 1) where η_{pl} is the plastic viscosity, D the shear rate and τ the shear stress [9]:

$$\tau = \tau_B + \eta_{pl} D \tag{1}$$

2.3. Particle size measurements

The TiO$_2$ pigment particle size in concentrated suspensions was measured using the attenuation mode of the Acoustosizer II (Colloidal Dynamics Inc., Australia). O'Brien [13] has shown that Electrokinetic Sonic Amplitude (ESA) can be used to determine the particle size. The amplitude of the sound wave generated by a given electric field in the electroacoustic method depends on the particle size; larger particles are more sluggish so the amplitude of their motion is smaller. More importantly, when the frequency of the applied field is very high, the colloidal particles are unable to keep pace and a phase lag develops between the applied field and the resulting sound wave response. By measuring that phase relationship it is possible to directly measure the particle size distribution. The size range covered by the electroacoustic method is from about 0.07 to 10 μm.

3. Results and discussion

3.1. Pigment suspension rheology

Typical shear stress versus shear rate curves for the TiO$_2$ pigment particles at pH 6.0 and 9.5 (in the absence of dispersant) are presented in Figure 3.
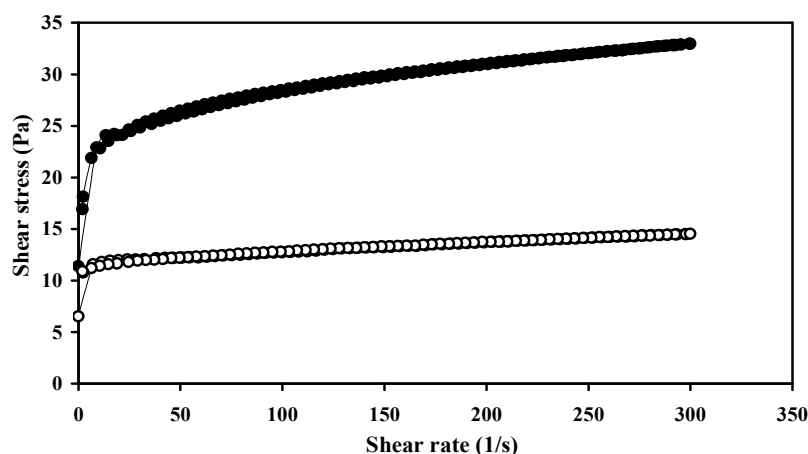

Figure 3: Shear stress versus shear rate for 20 vol% suspension of the TiO$_2$ pigment particles in 0.01 M KCl at pH 6.0 (○) and pH 9.5 (●).

It is observed that pigment particles exhibit non-Newtonian behaviour, showing a minimum stress required for generating flow in the suspension, commonly referred to as 'yield stress'. Clearly, the suspension pH has a pronounced effect on the pigment suspension rheology with higher shear stress values obtained at pH 9.5. The upward and downward curves of each pH values are concomitant revealing no thixotropy hysteresis or settling [14].

Typical shear stress versus shear rate curves for TiO₂ pigment as a function of dispersant at pH 6.0 and 9.5 are presented in Figures 4 and 5, respectively. Clearly, at both pH values, the type of dispersant and their associated functional groups have a large effect on the suspension rheology. At both pH values of 6.0 and 9.5, at the dispersant concentration used in this study (20 mg/g), the pigment particles exhibit non-Newtonian behaviour (curvature in the shear stress versus shear rate plots) in the presence of polymeric dispersants, however, systems including Polymer-N and Polymer-H exhibit a yield stress, while Polymer-A and Polymer-C do not. The upward and downward curves in all cases are concomitant revealing no evidence of thixotropy or settling.
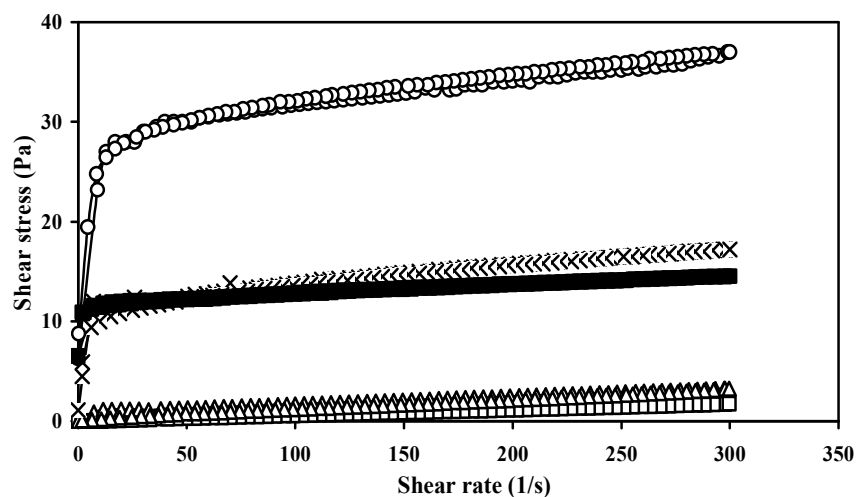

Figure 4: Shear stress versus shear rate for the TiO₂ pigment suspensions at pH 6.0 in the absence of dispersant (■) and presence of 20 mg/g Polymer-N (○), Polymer-H (x), Polymer-C (Δ) and Polymer-A (□) in 0.01 M KCl (pigment concentration 20 vol%).

Figure 5: Shear stress versus shear rate for the TiO₂ pigment suspensions at pH 9.5 in the absence of dispersant (■) and presence of 20 mg/g Polymer-N (○), Polymer-H (x), Polymer-C (Δ) and Polymer-A (□) in 0.01 M KCl (pigment concentration 20 vol%).
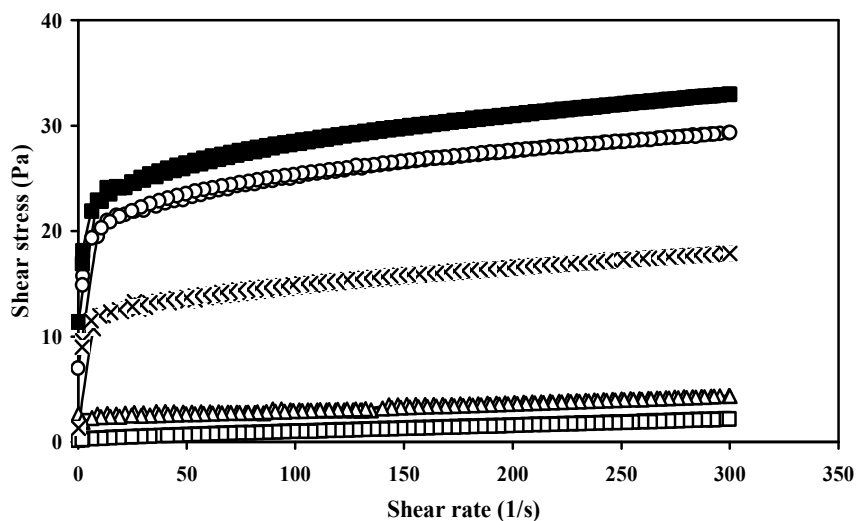
The yield stress values for the pigment suspension obtained using the Bingham model (equation 1) are shown in Figure 6, as a function of pH and type of polymeric dispersants. Results indicate that the pH and the polymeric dispersant functional group architecture significantly affect the rheology of the pigment suspension. The yield stress in the absence of dispersant increases with pH, until a maximum at approximately the pigment iep (pH=7.8), after which it decreases. These results are indicative of pH-dependent particle interaction as reported previously for mineral oxides such as TiO_2 pigment, with maximum yield stress or particle attraction occurring at the pigment iep [7, 10, 15, 16]. The reduction in the yield stress with addition of anionic dispersant (Polymer-A and Polymer-C) is the result of enhanced electrostatic repulsion between particles and/or steric stabilisation. The negatively charged carboxylate functional groups present in Polymer-A and Polymer-C considerably decrease the yield stress of the pigment suspension. In addition, the hydroxyl functional groups present in Polymer-C also contribute to the polymer steric stabilisation combining to provide a significant steric barrier. The increased yield stress in the presence of Polymer-A and Polymer-C at low pH values (pH<4.0) coincides with the shifting of the pigment iep to pH values of about 3.5 in the presence of these two dispersants [17]. The acrylamide functional group, of which Polymer-N is completely composed, has a negligible effect on the pigment particles dispersion. However, under acidic conditions the pigment particles aggregate upon Polymer-N adsorption, proposed to be due to the specific interaction with positive pigment surface sites, reducing the surface charge and consequently reducing colloidal stability. The unexpected increased pigment yield stress in the presence of Polymer-N at pH values below the pigment iep coincides with a reduction in the pigment zeta potential for Polymer-N, as reported previously [17, 18]. For Polymer-H, which is non-ionic, only steric stabilisation is expected to occur. The hydroxyl functional groups in polyacrylamide copolymer decrease the yield stress and the mean particle size.
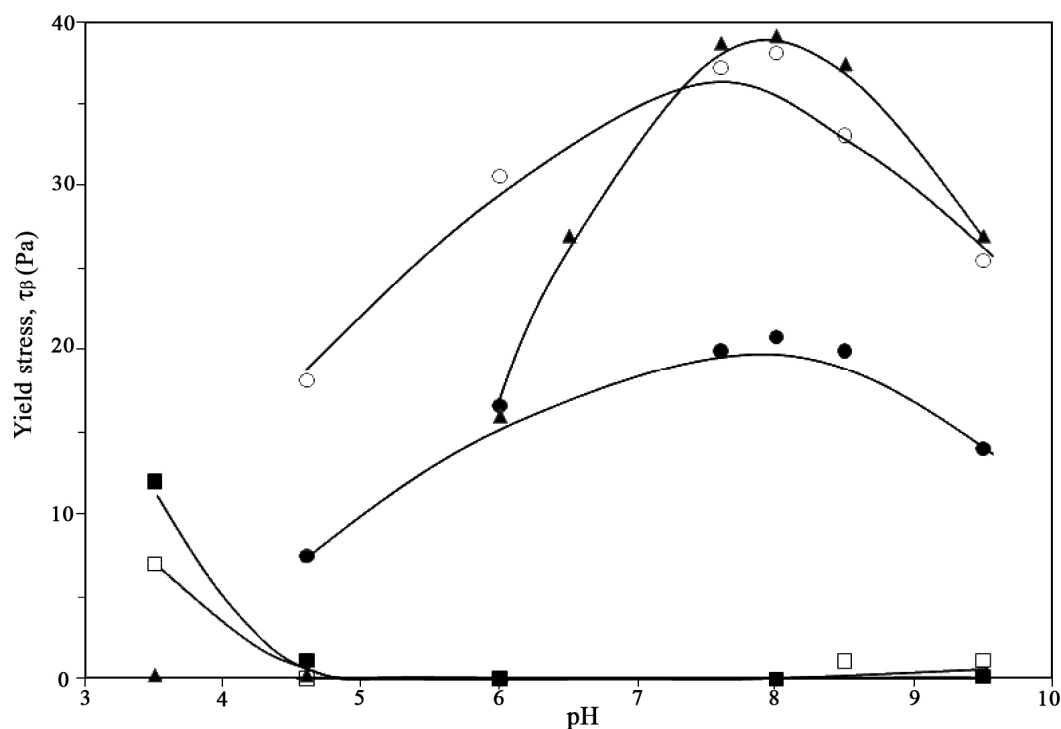

Figure 6: Yield stress of the TiO_2 pigment particles obtained using the Bingham model as a function of pH in the absence of dispersant (▲) and presence of 20 mg/g Polymer-A (■), Polymer-C (□), Polymer-H (●) and Polymer-N (○) in 0.01 M KCl (pigment concentration 20 vol%; pH was changed from high to low values).

3.2. Pigment particle size

Figure 7 shows the 50% values of the cumulative pigment particle size distribution (d_{50}) in the absence and presence of polymeric dispersant, as a function of pH. The average pigment particle size at neutral pH in the concentrated suspensions was 0.73 μm which is larger than 0.34 μm obtained for a very dilute pigment suspension using laser diffractometry. Therefore, the pigment particles in the concentrated suspension show a degree of aggregation. Figure 7 shows that the suspension pH has a significant effect on the TiO₂ pigment particle size, with the particle size increasing with pH until a maximum at approximately the pigment iep, after which it decreases. At the iep, the pigment zeta potential is zero, which results in minimal electrostatic repulsion between the particles and therefore aggregation occurred.

In general, the change in particle size upon adsorption of different dispersants as a function of pH coincidences with the changes observed in the suspension yield stress (Figure 6). In the presence of Polymer-A and Polymer-C, the pigment particle size decreases at neutral and alkaline pH values, however, at low pH values the particle size increases due to the presence of carboxylate groups in agreement with the pigment zeta potential [17]. In the presence of Polymer-H, the pigment particle size decreases via steric stabilisation. Evidentially, Polymer-N has a minimal effect at pH values above the pigment iep (pH>7.8), but at pH values below the iep it even causes the pigment particle to aggregate, which is similar to the behaviour observed in the rheological studies (Figure 6).

4. Conclusions

The pH and the dispersant functional groups have a significant effect on the rheology of the TiO₂ pigment suspension and the pigment particle size. The pigment suspension exhibited maximum yield stress and pigment particle size at the pigment iep. The negatively charged carboxylate functional groups present in Polymer-A and Polymer-C considerably decreased both the yield stress of the pigment suspension and the mean pigment particle size by electrostatic and steric stabilisation. The acrylamide functional group, of which Polymer-N is completely composed, had a negligible effect on both pigment dispersion and mean particle size at pH values above the pigment iep.
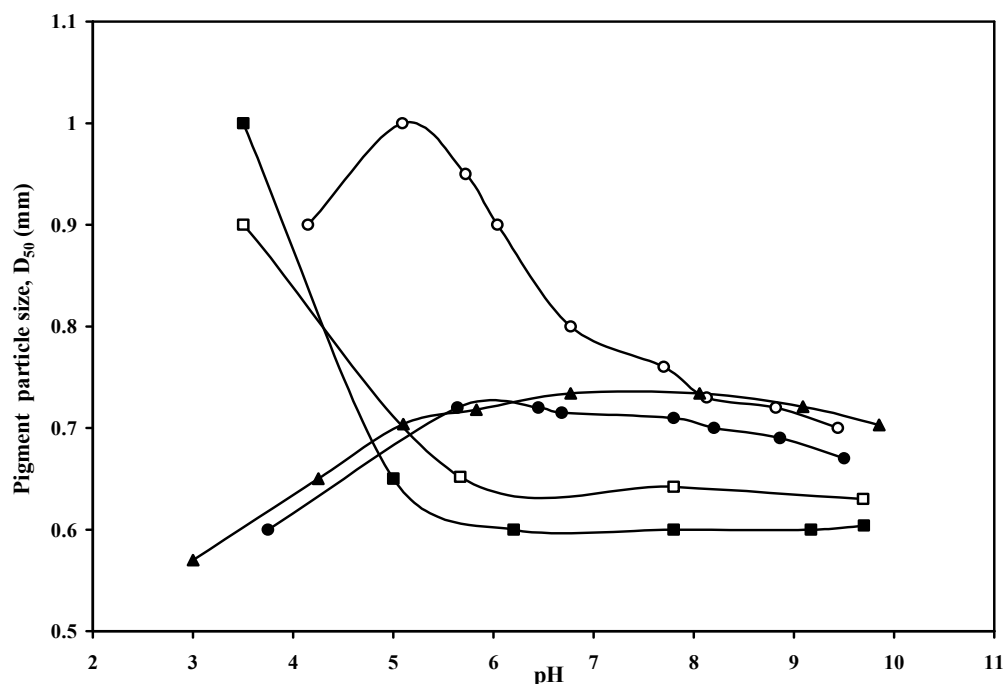

Figure 7: TiO₂ pigment particle size as a function of pH in the absence of dispersant (▲) and presence of 20 mg/g Polymer-A (■), Polymer-C (□), Polymer-H (●) and Polymer-N (○) in 0.01 M KCl (pigment concentration 2.5 wt%; d_{50} is 50% of the cumulative particle size distribution).

However, at pH values below the iep, the pigment particles aggregated upon Polymer-N addition due to reduction in the pigment zeta potential. The presence of hydroxyl functional groups, attached to the polyacrylamide backbone in Polymer-H, decreased the suspension yield stress and the mean pigment particle size by steric stabilisation.

5. References

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