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PREPARATION OF OXIDE DISPERSIONS WHICH ARE STABILIZED BOTH STERICALLY AND ELECTROSTATICALLY.

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ABSTRACT

TiO₂ dispersions prepared in the presence of polyacrylic acid (PAA) may be sterically stabilized, electrostatically stabilized, or stabilized by both mechanisms simultaneously, depending on PAA and electrolyte concentrations. Very stable suspensions are obtained when both steric and electrostatic stabilizations occur.

PAA adsorption is especially pronounced at low pH, when TiO₂ and PAA are oppositely charged. Larger amounts of PAA are effectively adsorbed as neutral molecules since the large concentration of anionic groups near the TiO₂ surface cause a large negative electrical potential which exerts a strong attraction on H⁺ ions.

The thickness of the PAA layer was found to be about 3 nm at pH=6 in 0.01 M KNO₃ solutions. The results of the experiments suggests that both mechanisms are important and that there is a positive influence of the thin polymer layer on the electrostatic stabilization.

KEYWORDS

TiO₂ dispersions; polyacrylic acid; stabilization by polyacrylic acid adsorption.

INTRODUCTION

In order to improve the quality of water based paints, so called dispersing agents are used to optimize the dispersion process of the oxide pigments in water. As dispersing agents polyacrylic acid (= PAA) has proved to enhance the gloss and the opacity of the dry paint film. Polyacrylic acid is a water soluble polymer with carboxylic acid groups. The polymer is therefore negatively charged depending on the pH. With adsorbed charged polymers in theory two stabilization mechanism are possible: First, steric stabilization caused by the steric hindering of the loops and tails of the polymers adsorbed on the oxide surface; second, enhanced electrostatic stabilization due to increase of negative charge on the surface as a result of the adsorption of the charged polymer. The aim of our research was to investigate the relative importance of both mechanisms for the dispersion process of oxide pigments in water.

EXPERIMENTAL

Materials

TiO₂: prepared by hydrolysis of TiCl₄ (Bérubé et al., 1968).

Polyacrylic acid: a. ex Jansen Chimica (M.W. 2000); b. ex Servo FX 508 (M.W. 11000).

Methods

pH titrations were performed using a Philips PHM 84 Research pH meter, and an ABU 80 autoburette with conventional glass and calomel electrodes. Zeta potentials were measured by electrophoresis using a Malvern Zetasizer 3. PAA equilibrium concentrations in solution were calculated from total organic carbon content measurements.

Adsorption of the polyacrylic acid on the titanium dioxide surface.

For both stabilization mechanisms it is important to investigate the amount adsorbed of the polymer as a function of pH and electrolyte concentration. The pH is a very important parameter in the adsorption process because the charge of both the oxide as well as the polymer vary with the pH. The concentration of the indifferent electrolyte is important because it is of influence on the mutual repulsion of the charged groups on the polymer chain and on the Coulomb interaction of the charged groups on the surface and the charged groups of the polymer.

Fig. 1. Titration curves of polyacrylic acid and titanium dioxide

- charge of polyacrylic acid in 0,01 M KNO₃
- △ charge of titanium dioxide in 0,001 M KNO₃
- charge of titanium dioxide in 0,01 M KNO₃
- ▽ charge of titanium dioxide in 0,1 M KNO₃

1. The influence of the pH:

The adsorption of the polymer is stimulated when charges on the TiO_2 -surface and on the PAA are of opposite sign whereas the adsorption is limited when both charges become negative. In figure 1 the charges of separate titanium dioxide and polyacrylic acid are plotted as a function of the pH. The charges are measured by comparing an acid/base titration of the species with a titration of an electrolyte solution. The charge of polyacrylic acid varies from almost zero at pH 3 to about 90% of the theoretical maximum charge at pH 11. The hydroxyl groups on the titanium dioxide surface can be either negatively charged at a high pH or positively charged at a low pH. At pH 5.7 the oxide surface is not charged (point of zero charge, PZC). As expected from these considerations the amount adsorbed at a low pH is larger than at a higher pH (see figure 2). The isotherm at pH=6.5 illustrates that a negative polyelectrolyte can adsorb on a negative surface, indicating that the adsorption is not due to electrostatic forces only, but that chemisorption is involved.

2. The influence of the electrolyte concentration:

According to Lyklema (1987) the increase of indifferent electrolyte can either increase or decrease the amount adsorbed of the charged polymer. There are two opposing influences: First the mutual repulsion of the charges on the chain is decreased, so the polymer behaves at high salt concentrations as an uncharged polymer rather than as a charged polymer. Uncharged polymers adsorb in larger amounts compared to charged polymers, so the adsorption is increased. The second effect of the electrolyte concentration is the effect on the interaction between surface groups and negative carboxylic acid groups: the coulombic attraction between positive and negative groups decreases with increasing electrolyte concentration and as a consequence the amount adsorbed is decreasing at higher salt concentrations. In our case the influence on the mutual repulsion of the carboxylic acid groups is the most important effect of the electrolyte concentration because the amount adsorbed is increasing with the salt concentration (see figure 3).

Fig. 2. Adsorption isotherms of polyacrylic acid on titanium dioxide, in 0.01 M KNO_3 solutions

■ pH 6.5; ▽ pH 5.3; ● pH 4.2;

Fig. 3. The influence of the electrolyte concentration on the adsorption of PAA, pH=5.3. The lines represent the same experiments as shown in more detail in fig. 2, for comparison.

○ 10^{-1} M KNO_3 ○ 10^{-3} M KNO_3

Fig. 4. Stability of TiO_2 -dispersions as a function of the electrolyte concentration at different polyacrylic acid concentrations at pH=6.0 (g/m^2).

● 0; ▲ $3.5 \cdot 10^{-4}$;
 △ $2.8 \cdot 10^{-5}$; ● $4.9 \cdot 10^{-4}$;
 ▼ $2.2 \cdot 10^{-4}$; ◇ $5.9 \cdot 10^{-4}$

3. Stability measurements:

The stability of an oxide dispersion can be followed by measuring light-transmission as a function of time. It should be noted that light transmission is a function not only of the total effective particle size of the aggregates, but also of their compactness. However, in the initial stage of the coagulation, aggregates are small, for the most part confined to pairs of particles. In this stage no significant influence of aggregate compactness is expected. The light transmission therefore can be used as an indication of average aggregate size, and its time dependence can be used for measuring coagulation rates. From these measurements we can calculate a stability factor W , which is defined as: the coagulation rate in the absence of any kind of stabilization, divided by the experimentally observed coagulation rate.

Fig. 5 Stability of TiO_2 -dispersions as a function of the electrolyte concentration at different concentrations SERVO FX 508 (g/m^2) at $\text{pH}=6.0$.
 ∇ 0; $\diamond$ $1.2 \cdot 10^{-4}$; Δ $2.4 \cdot 10^{-4}$;
 $\blacktriangle$ $3.2 \cdot 10^{-4}$; $\bullet$ $4.7 \cdot 10^{-4}$.

If the stability factor W is measured as a function of the electrolyte concentration we find for low polyacrylic acid concentrations a graph typical (Lyklema et al., 1987) for electrostatic stabilization: At electrolyte concentration above 0.15 M KNO_3 the stability factor indicates that at these concentrations there is no stabilization at all. At lower electrolyte concentrations the stability is increasing (W higher) as a result of the increasing electrostatic repulsion. With increasing polyacrylic acid concentrations, stability factors significantly larger than 1 are obtained even at electrolyte concentrations of 0.4 M. But even in this polyacrylic acid concentration range, the $\log(W)$ versus $\log(c)$ graph turns upwards with decreasing c values (figure 4). Under these circumstances, the stability significantly surpasses the values found for electrostatic stabilization. This indicates that under these circumstances,

both sterical and electrostatic stabilization occur simultaneously, and act synergistically. Almost the same results are obtained with a polyacrylic acid copolymer used in the paint industry to stabilize pigment dispersions for water based paints (figure 5). The concentration mentioned is the initial concentration calculated per square meter of specific surface of the oxide. In this experiment it is not possible to give an equilibrium concentration because the amount adsorbed is changing with the electrolyte concentration. We did not find a difference in stability using the two polymers of different molecular weight. This indicates that polyacrylic acid is adsorbed lying flat on the TiO_2 surface.

4. Electrostatic stabilization:

For the electrostatic stabilization the zeta potential is a better parameter than the surface charge because the surface charge is by definition only the charge of the surface groups and does not include the charge of the adsorbed species. In our case it is possible that at a low pH the surface charge of the oxide is positive whereas the overall charge of the particle is negative as a consequence of the adsorption of the charged polyacrylic acid. The zeta potential is an overall parameter and is therefore directly related to the stability of the particle (Horn et al., 1990). In figure 6 the zeta potential is plotted as a function of the pH at different polyacrylic acid concentrations. The zeta potential is measured in the suspension used to measure the adsorption isotherms of figure 2. Because the equilibrium concentrations are measured, the zeta potential can in this case directly be compared with the amount adsorbed. Comparing these two measurements a striking difference is observed between the shape of the adsorption isotherm and the shape of the zeta potential vs. equilibrium concentration curve: the zeta potential reaches a constant value at low concentrations whereas the amount adsorbed is still increasing at higher concentrations. In order to explain these differences we calculated the total charge on the surface by adding together the surface charge and the charge of the adsorbed polymer. Because of electroneutrality this charge should be equal to the charge in the diffuse layer surrounding the particles:

$$\sigma_{\text{diff}}^0 = -\sigma_{\text{TiO}_2} - \sigma_{\text{PAA}}$$

σ_{diff}^0 then is the charge in the diffuse layer if the charges on TiO_2 and PAA would not change on adsorption.

We compared this calculated charge in the diffuse layer with the charge behind the electrokinetic slipping plane (calculated from the zeta potential). As expected we observe a large difference between the two calculated charges: σ_{diff}^0 is still increasing while the charge calculated from the zeta potential reaches a constant value (figure 7). The discrepancy between the two calculated charges is a consequence of the assumption that the charge of the polymer as well as the charge of the oxide does not change during the adsorption process. This is in fact not true. We can measure the change in charge caused by the adsorption by measuring the acid consumption after addition of the polyacrylic acid and keeping the pH constant (pH-stat experiment).

$$\sigma_{\text{diff}} = -\sigma_{\text{TiO}_2} - \sigma_{\text{PAA}} + \sigma_{\text{pHstat}}$$

Fig. 6 Zeta potential of TiO_2 versus equilibrium PAA concentration in 0.01 M KNO_3 solutions at
 ▲ pH=4.2; ▼ pH=5.3; ■ pH=6.5.

Fig. 7 Charges behind the electrokinetic slipping plane. pH=5.3;
 $[\text{KNO}_3] = 0.01\text{ M}$.

σ_{diff}^0 calculated on the assumption of absence of
 charge changes during adsorption.
 σ_{diff}^0 calculated from the zeta potential.

If we use the result of the pH-stat measurements in the calculations of the diffuse charge, the calculated charge is of the same magnitude as the charge calculated from the zeta potential (figure 8). The conclusion of these measurements is that although the amount adsorbed is increasing at higher equilibrium polymer concentrations the net charge of the particle reaches a maximum value and is not changing any more. The additional amount of polymer is therefore effectively adsorbed as a neutral polymer. This can be effected either by adsorption of undissociated PAA, or by simultaneous adsorption of PAA anions and an equivalent amount of H^+ ions. The latter alternative is the most likely one: a large amount of adsorbed PAA anions would lead to a large negative potential near the surface, which exerts a strong attraction on H^+ ions.

5. Sterical stabilization:

The hydrodynamic layer thickness of an adsorbed polymer gives an indication of the extension of the loops and the tails of the polymer and is therefore an indication for the steric stabilization of a dispersion. The hydrodynamic layer thickness can be obtained from measurements of a parameter which is dependent on the total volume of the solid fraction of the dispersion. With oxide particles the viscosity of the dispersion or the sedimentation velocity of the particles may be suitable measurements. But in our case the expected hydrodynamic layer thickness is small compared to the size of the oxide particles and the particles are not spherical. Therefore we measured the thickness of the adsorbed layer by measuring the hydrodynamic permeability of a column packed with titanium dioxide as a function of the electrolyte concentration (figure 9). The porous plug was previously flushed with 0.5 g/l polyacrylic acid solution until the permeability became constant. The amount adsorbed resembles the amount adsorbed at an equilibrium concentration of 0.5 g/l PAA. Using the Blake-Kozeny equation (Bird et al., 1960) we calculated a hydrodynamic layer thickness of 3 nm in 0.01 M KNO_3 and at pH=6. This is a thin layer compared to layers of adsorbed uncharged polymers on oxides (Pandoe et al., 1987).

Fig. 8. Charges behind the electrokinetic slipping plane.
pH=5.3; [KNO₃]=0.01 M.

- ◆ σ_{diff}^0 taking into account charge changes during adsorption.
- σ_{diff}^0 calculated from the zeta potential

Fig. 9 Hydrodynamic permeability of a packed bed of titanium dioxide as a function of the electrolyte concentration
pH=5.5, PAA: 0.5 g/l.

CONCLUSIONS

The electrostatic stabilization is enhanced by the adsorption of charged polyacrylic acid molecules on the oxide surface. But at rather low polymer concentrations the zeta potential reaches a constant value and the total charge of the particle is not changing anymore. As the amount adsorbed is still increasing the polymer is adsorbed as an uncharged molecule and is not increasing the electrostatic stabilization. The polymer molecules form a hydrodynamic layer on the oxide surface of about 3 nm at pH 6 and 0.01 M KNO_3 . But this rather thin layer increases the stability of the dispersion significantly.

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