



Coating organic pigment particles with hydrous alumina through direct precipitation

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ABSTRACT

A novel coating process of hydrous alumina on organic pigment particles through direct precipitation in aqueous solution was developed in this work. The aqueous suspensions of organic pigment particles were prepared using cetyltrimethylammonium bromide (CTAB) and sodium dodecylbenzene sulfonate (SDBS) as additives before the coating. The organic pigment particles were then coated with hydrous alumina using $Al_2(SO_4)_3$ as precursor. The morphology and surface states of as-coated organic pigment particles were analyzed by high-resolution transmission electron microscopy (HRTEM) and zeta-potential. TEM images showed that a uniform hydrous alumina film could be formed on the organic pigment particle surface with anion surfactant SDBS. However, with cation surfactant CTAB, no alumina coating film was generated on the organic pigment particle surface.

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1. Introduction

Inorganic pigments based on heavy metal oxides, such as cadmium and lead oxides, are environmentally toxic, therefore, a complete phase-out of heavy metal oxide pigments is imminent [1]. Organic pigments have been used in coatings, inks and plastics industries or even in color filters for electronics and communication apparatus since they have many advantages, for instance, good photosensitivity, brilliance, transparency and so on [2]. However, the limited power hiding, poor dispersion ability, and, especially, the poor weathering durability are the real drawbacks for organic pigments in many applications [1]. Thus, the surface treatment of organic pigment particles is necessary to make them be practically useful.

Several methods for coating the organic pigment particles have been developed, including mainly the surface polymerization (polymer adsorption [3], polymer grafting [4,5], polymer encapsulation [6]), and inorganic coatings [2]. In practice, the uniform surface treatment on organic pigment particles was performed usually in well dispersed pigment particle suspensions [1], in which surfactants were often utilized as additives [3]. Surfactants are organic compounds consisting of both hydrophilic

and hydrophobic portions, and have been widely used in improvement of the wetting ability, emulsifying, and the inhibiting properties of electrodeposition process, etc [7]. Nsib et al. [8] evaluated three carboxylic dispersants for the dispersion of C.I. pigment Violet 23 in organic medium, he found that the copolymer dispersant adsorbed strongly onto the pigment surface, which reduced the suspension viscosity, and increased the pigment loading by 50%, but kept the rheological properties. Wijting et al. [3] coated organic pigment particle through polymer adsorption, they studied the coating of anionic polyacrylic acid sodium salt (PNa), and non-ionic block copolymer of polystyrene oxide (SO) and polyethylene oxide (EO) (SO–EO) on organic pigment particle surface, and found that adhesion affinity of SO–EO to the organic pigment surface is much stronger than that of the PNa. The physical adsorption of polymer on the organic pigment surface may generate a coating layer, but it is not strong enough for many applications. Hence, some researchers [4,5], explored the chemical graft of polymers on the organic pigment surface in which the polymer molecules are bonded chemically on the organic pigment surface forming stable coating layer [9]. To get chemically grafted polymeric coating layer, laborious work is required to create specific functional groups on the organic pigment particle surface to bind the external polymer molecules. The encapsulation procedure has also been employed for organic pigment particle surface modification. For example, Nguyen et al. [6] developed a method for the encapsulation of both hydrophilic inorganic (c.a. zirconia

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and alumina-coated titanium dioxide) and hydrophobic organic (c.a. phthalocyanine blue) pigment particle with poly (methyl-methacrylate-co-butyl acrylate) through living amphiphatic random macro-reversible addition fragmentation chain transfer (RAFT) copolymers to both stabilize the initial particle dispersion and to facilitate the uniform growth of polymer on the pigment particle surface. Encapsulated composite particles were formed that have core (pigment particles) – shell (polymer) morphology. The difficulty of this process is the particles must be correctly dispersed in the continuous phase to avoid the presence of large aggregates in the encapsulated materials. In comparison with conventional emulsion polymerization, the miniemulsions are sufficiently small, thus the polymerization predominantly within the preexisting miniemulsion droplets [10,11], which was found to be attractive for particle surface coating. Steiert and Landfester [11] encapsulated different organic yellow, magenta, and blue pigment nanoparticles by cosonicating pigment dispersions and monomer miniemulsions followed by polymerization. Lelu et al. [10] encapsulated an organic phthalocyanine blue pigment into polystyrene latex particles using a miniemulsion polymerization process.

It was a long standing dream for pigment researchers to coat a thin layer of inorganic material on the surface of an organic pigment particle to improve the stability of the organic pigments against light, heat or chemical aggressions [2]. General, the inorganic chemical modification of organic pigment particles can be approached in two ways. One is to coat the inorganic material on organic pigment surface. For example, Yuan et al. [2] coated organic pigment particles with nanoscale silica particles via layer-by-layer self-assembly technique. The results revealed that the coating layer of nano-silica on the surface of pigment particles could improve the thermal stability, wettability, acid and alkali resistances, and weathering durability of the organic pigments. The other is to immobilize the organic pigment on the inorganic core materials, which was used long ago since the ancient maya [13]. Fei et al. [14] modified a Naphthol red pigment (known in China as 808 Scarlet) by coupling aniline with Naphthol on the surface of inorganic cores. Jesionowski et al. [15] modified spherical silica particles with N-2-(aminoethyl)-3-aminopropyltrimethoxy silane, and onto the aminosilane-treated silica surface. Additionally, Hayashi et al. [12] produced recently nano-sized core–shell pigments by dry milling of organic pigments together with nano-sized surface-modified silica powder, and the as-coated organic pigment particles had uniform spherical shape with narrow size distributions and enhanced color density.

Herein we describe a novel coating process of hydrous alumina on organic pigment particle surface through direct precipitation with surfactant as additive, which holds great promise for scaling up industrially. The effects of two surfactants, cationic cetyltrimethylammonium bromide (CTAB) and anionic sodium dodecylbenzene sulfonate (SDBS), have been investigated. The coating film morphology, and electrokinetic's behavior of pigment particle were analyzed using high-resolution transmission electron microscopy (HRTEM), and zeta-potential analyzer, respectively.

2. Experimental

2.1. Materials

Surfactants, cetyltrimethylammonium bromide (CTAB) and sodium dodecylbenzene sulfonate (SDBS), were purchased from Aldrich (USA) and used as received. Deionized water was generated with Millipore Water Puring System. Organic pigment, C.I. Pigment Yellow 3 ($C_{16}H_{12}Cl_2N_4O_4$), was supplied by Zhejiang Ever Joint Chemicals Co., Ltd. Other chemicals used in the experiments were all analytical reagent (AR) grade.

2.2. Coating process

The coating experiments were carried out in a flask with the temperature and pH measured on time. Typically, 20 g of organic pigment particles were dispersed in deionized water, at a concentration of 200 g/L, by continuous ultrasonication for 30 min before the coating. The concentration of the surfactant in the suspension was maintained to 2% in weight. The $Al_2(SO_4)_3$ (0.3 mol/L, 20 mL), and NaOH (1 mol/L) aqueous solutions were titrated into the organic particles suspension simultaneously. The mixture was stirred vigorously, and the pH of the reaction system was kept about 6 by controlling the titrating speed of the NaOH solution, while the titrating speed of the $Al_2(SO_4)_3$ solution was kept constant. The temperature, 20 °C, was controlled by a thermostatic water-bath. Then, the suspension was aged for 2 h under stirring. Finally, the coated organic pigment particles were filtered and washed repeatedly until SO_4^{2-} was no longer detected using a $BaCl_2$ solution, and dried at 70 °C for 12 h.

2.3. Preparation of $Al(OH)_3$

The $Al_2(SO_4)_3$ (0.3 mol/L, 20 mL), and NaOH (1 mol/L), were titrated simultaneously into 100 mL of deionized water with peristaltic pumps at the pH of 6, and temperature of 20 °C, the same as coating process. After 2 h of aging, the $Al(OH)_3$ gel was filtered and washed repeatedly using pure water until SO_4^{2-} was no longer detected using a $BaCl_2$ solution, and dried at 70 °C for 12 h.

2.4. Characterization

The size and shape of the organic pigment particles were characterized using scanning electron microscopy (SEM, Ultra 55, Zeiss, Germany). The morphology and structure of the hydrous alumina coating on the organic pigment particles were examined by high-resolution transmission electron microscopy (HRTEM, JEM-2011, Japan). Samples for HRTEM inspection were prepared by dropping the ethanol dispersion of the particles on the TEM grids, and dried in air.

A particle sizer (MasterSizer, MICRO-PLUS, Malvern Instruments, England) was used to measure the obstruction of the solution online, which reflects the concentration of the precipitated particles.

The zeta-potential of the particles was measured using a zeta-potential analyzer (Nicomp 380/ZLS, Particle Sizing Systems, USA). The temperature during measurements was kept at 25 °C. The particle was dispersed in water by ultrasonication. The diluted HCl and NaOH solutions were used for pH adjustment. The pH of each sample was measured rapidly with a pH meter before the zeta-potential measurement. The cell and pH electrode were carefully cleaned to avoid any possible contamination in each measurement. The final zeta-potential was the mean value averaged from three measurements.

3. Results and discussion

3.1. Characterization of the pigment particles

Organic pigment particles were characterized by SEM, TEM and electrophoretic mobility (zeta-potential) measurements. Fig. 1a shows the SEM image of the organic pigment particles. The size of the particles ranges in 200–500 nm in diameter, and their surface was smooth, which was illustrated in the TEM image (Fig. 1b), too. The zeta-potential of the pigment particles is plotted as a function of the pH in Fig. 2. It implies that the organic pigment particle surface was negatively charged when pH ranged from 3–12.

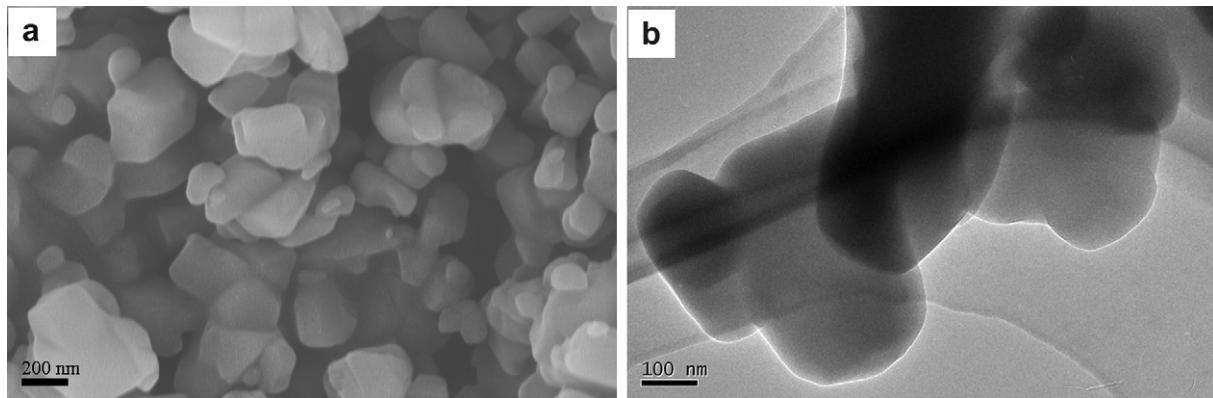


Fig. 1. Typical SEM (a) and TEM (b) images of organic pigment particles.

However, the surface potential of the organic pigment particles should be varied with coating processing. Additionally, the surfactants used as additives affect also their surface charging properties. On the other hand, the zeta-potential of the organic pigment particles plays an important role in the particle-coating process, especially for the organic particles coated with inorganic materials [16]. Therefore, the change of zeta-potential during the coating processes with anion and cation surfactant as additives were investigated.

3.2. Effect of surfactant on the zeta-potential

The organic pigment particles were first dispersed in the anionic SDBS or the cationic CTAB surfactant with ultrasonication. The organic pigment particles were dispersed with different amount of anionic SDBS and cationic CTAB surfactant in deionized water, and the zeta-potentials were measured (Fig. 3). The organic pigment particles originally assume positive charge, as shown in Fig. 2, with pH ranged in 3–12, but, when the anionic SDBS surfactant was added in the suspension, the zeta-potential decreased with the increment of anionic SDBS first, and became stable when the ratio of SDBS/pigment reached 1%. However, when cationic CTAB surfactant was added in the organic pigment suspension, the zeta-potential of the suspension was reversed first, then increased, and finally became stable when the CTAB/pigment reached 2%. Therefore, the effect of the surfactant on the zeta-potential of the organic

pigment particles under different pH was investigated at the surfactant/pigment equals 2%, and was shown in Fig. 4. It illustrated that no matter how much the pH (3–12) was, the organic pigment particles were positive charged with the cationic CTAB surfactant, but negative charged with the anionic SDBS surfactant.

3.3. Effect of surfactant on coating process

Organic pigment particles were coated using $\text{Al}_2(\text{SO}_4)_3$ solutions as the precursor reagent at pH 6 and temperature 20 °C with CTAB and SDBS, which was demonstrated as a suitable procedure for coating the TiO_2 particle surface with a thin hydrous alumina film previously [17]. The HRTEM images of the hydrous alumina-coated organic particles are depicted in Fig. 5. It shows that, Fig. 5a, there is a uniform thin film that was generated on the organic pigment particles when SDBS was used. While isolated nanoparticles of $\text{Al}(\text{OH})_3$ (due to homogeneous nucleation) were observed when the CTAB was used, as shown in Fig. 5b.

Fig. 6 shows the electrokinetic's behavior of the organic particles coated under different surfactant. The zeta-potential versus pH curve and isoelectric points (IEPs) for the organic particles coated with hydrous alumina under SDBS are similar to those of pure $\text{Al}(\text{OH})_3$ gel, which means that the organic particles have the same surface charge and surface groups as $\text{Al}(\text{OH})_3$ gel. Combined with the TEM images, we believe that there is a uniform hydrous

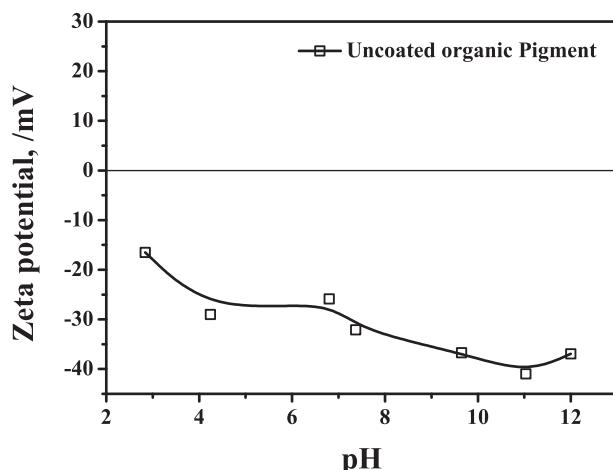


Fig. 2. Zeta-potentials of organic pigment particles versus pH.

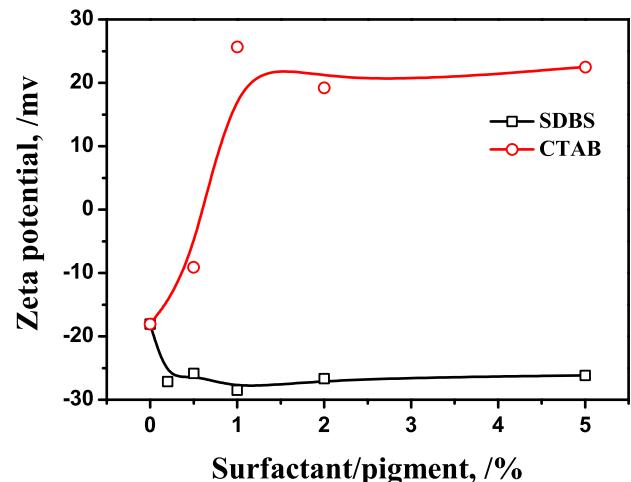


Fig. 3. Zeta-potentials of organic pigment particles changed with the amount of surfactant.

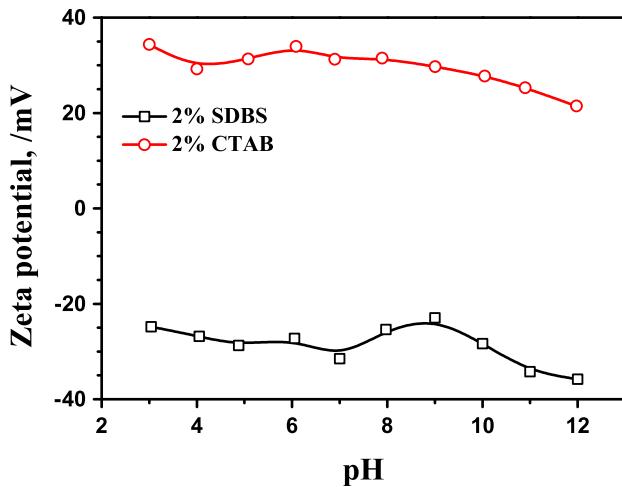


Fig. 4. Zeta-potentials of organic pigment particles versus pH.

alumina film formed on the organic particle surface when SDBS was used as additive. Whereas the zeta-potential of the organic particles coated with as CTAB additive is similar to that of pure organic particles (Fig. 2), implying that the coating process with the anionic surfactant CTAB was defeated. This leads us to believe unambiguously that the SDBS surfactants do play an important role in the hydrous alumina coating layer formation on the organic pigment particle surface.

3.4. The coating layer formation mechanisms with different surfactants as additives

In order to understand the coating process, the precipitations of Al^{3+} in different surfactant suspensions were investigated using NaOH and $\text{Al}_2(\text{SO}_4)_3$ as precursors. In a typical experiment, the NaOH was titrated into Al^{3+} solution containing different surfactants, and the obstruction changes with $\text{OH}^-/\text{Al}^{3+}$ ratio (mol/mol) were varied accordingly. The obstruction value reflects usually the particle concentration in the aqueous solution. Fig. 7 shows the situation of NaOH titration into the solutions of $\text{Al}_2(\text{SO}_4)_3$, $\text{Al}_2(\text{SO}_4)_3 + \text{SDBS}$ and $\text{Al}_2(\text{SO}_4)_3 + \text{CTAB}$, respectively.

Comparing the obstruction versus $\text{OH}^-/\text{Al}^{3+}$ ratio curves in Fig. 7, it was found that the precipitation of Al^{3+} increased gradually

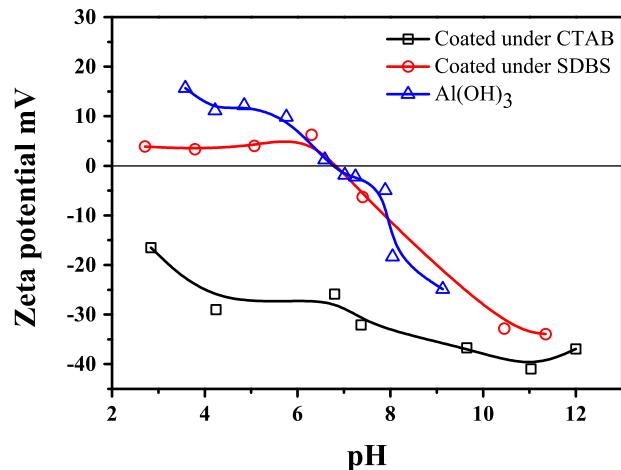


Fig. 6. Zeta-potentials of organic pigment particles coated using (a) SDBS and (b) CTAB as additives.

when NaOH was titrated into the solution of $\text{Al}_2(\text{SO}_4)_3$ and $\text{Al}_2(\text{SO}_4)_3 + \text{CTAB}$, reached a maximum value and then decreased gradually. However, when anion surfactant SDBS was used, in the initial stage of the NaOH titration, the obstruction was almost zero, which indicates that there was no precipitant or particle formed in the aqueous solution. When the mole ratio of $\text{OH}^-/\text{Al}^{3+}$ approached to 2.5, the slope of the obstruction increased sharply, which indicated that a large amount of precipitant or particles was formed, after that the obstruction decreased gradually, which implied that the OH^- from NaOH titration was mainly consumed in dissolving the $\text{Al}(\text{OH})_3$ gels indicating that the anion surfactant can change the precipitation behavior of the Al^{3+} notably, due might to that the anion surfactant adsorbs the Al^{3+} .

The effect of surfactant on the coating process under anion surfactant SDBS was further examined through the zeta-potential analysis performed during the coating processing. The zeta-potentials versus time curve with anion surfactant SDBS as additive was shown in Fig. 8. It demonstrates that the charge carried by the organic particles changed immediately from negative to positive when $\text{Al}_2(\text{SO}_4)_3$ solution was added. This can be inferred that the positive charge carried by the organic particles resulted from the absorption of $\text{Al}-\text{OH}$ species, and the zeta-potential changed little afterward. Therefore, the negative

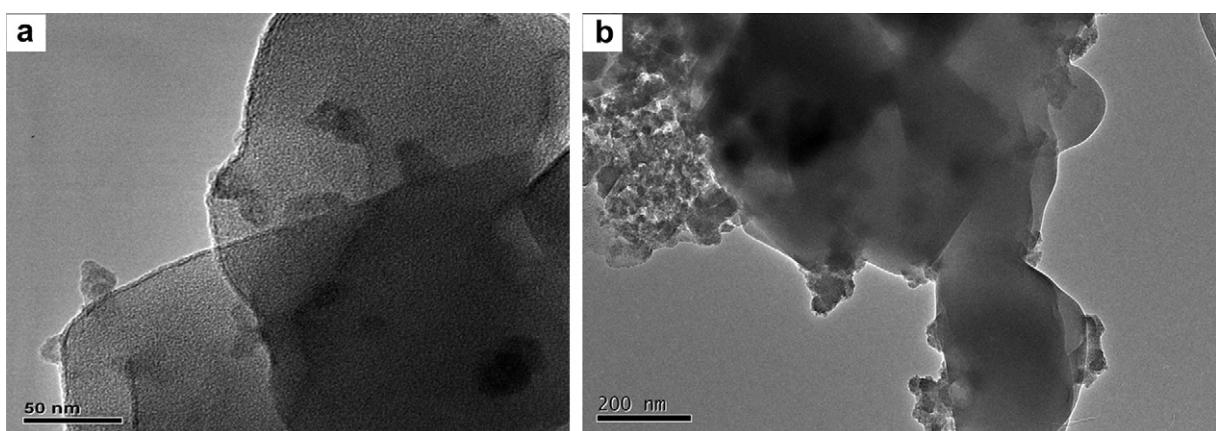


Fig. 5. Typical morphology of the as-coated organic pigment particles using (a) SDBS and (b) CTAB as additives.

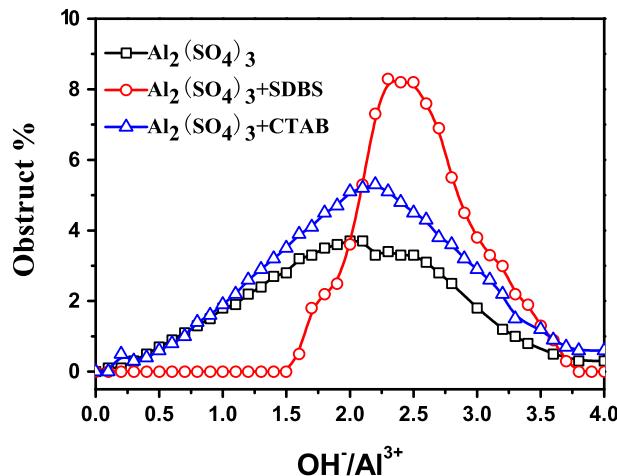


Fig. 7. NaOH titration into Al^{3+} solution. 20 mL of 0.1 mol/L NaOH solution was titrated into 500 mL of 0.001 mol/L $\text{Al}_2(\text{SO}_4)_3$, $\text{Al}_2(\text{SO}_4)_3 + \text{SDBS}$ and $\text{Al}_2(\text{SO}_4)_3 + \text{CTAB}$ by a peristaltic pump at the titration speed 0.5 mL/min.

organic particles first adsorb the positive $\text{Al}-\text{OH}$ species through the static attraction, and the anion surfactant SDBS served as a linker. When the charge on the organic particle surface was reversed, the repulsion between the $\text{Al}-\text{OH}$ species and the organic particles dominated the slurry system, and the coating should occur through the random collision of $\text{Al}-\text{OH}$ species with organic particles, which may adsorbed a layer of $\text{Al}-\text{OH}$ species, and whenever the $\text{Al}-\text{OH}$ species or the particles have enough energy to cross the repulsion threshold, the $\text{Al}-\text{OH}$ species in the adsorbed layer on the organic particles surface will be condensed, resulting in the film coating of the $\text{Al}-\text{OH}$ species on the organic particle surfaces (Fig. 5a).

However, when CTAB was used, the organic particles were positive charged (Fig. 4). It is known that CTAB in aqueous may be dissociated into $\text{R}(\text{CH}_3)_3-\text{N}^+$ cations. The $\text{R}(\text{CH}_3)_3-\text{N}^+$ cations are easily adsorbed onto the surface of organic particle and the long alkyl chains extend outward reducing the original negative charge character of the organic pigment particles (Fig. 4). As a result, the introduction of CTAB would inhibit the agglomeration and adsorption of the positive charged $\text{Al}-\text{OH}$ species on the organic pigment particles, but can promote the adsorption of the SO_4^{2-}

anions. With the titration of $\text{Al}_2(\text{SO}_4)_3$ solution, more and more SO_4^{2-} anions were accumulated, causing the desorption of CTAB. After filtration and washing, CTAB and SO_4^{2-} anions were all get rid of and leaving the uncovered organic particles. Therefore, the zeta-potential of the organic particles coated under CTAB (Fig. 6) was much similar to the pure particles (Fig. 2), but not the particles dispersed in CTAB (Fig. 4). Because completely inelastic collisions also occur between the $\text{Al}-\text{OH}$ species, the formation of a small amount of isolated particles of hydrated alumina is unavoidable as shown in Fig. 5b. This might be the reason for anion surfactant SDBS played a positive role in the uniform coating layer formation, while the cation surfactant CTAB blocked the formation of hydrous alumina thin film on the organic pigment particles.

4. Conclusions

A simple direct precipitation route for coating of organic pigment particles with inorganic hydrous alumina in the presence of surfactant has been developed. We demonstrated that the coating process was highly depended on the surfactants. The anion surfactant can play as a bridge when the hydrous alumina coat on the organic pigment particle surface initially, then the random collision makes the coating process go on, while the cation surfactant did not show a positive role during the precipitation coating process. Given the pigment particle concentration in the aqueous coating suspension can reach 200 g/L, and the coating condition (pH 6, 20 °C) was moderate, this process should be easily scaled up, and may be developed as a general coating procedure.

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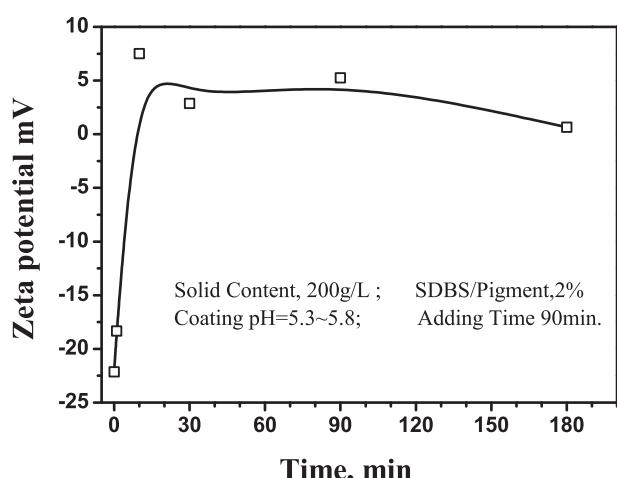


Fig. 8. Zeta-potentials of organic pigment particles during the coating process.

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