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Silica sol–gel anchoring on aluminum pigments surface for corrosion resistance based on aluminum oxidized by hydrogen peroxide

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ABSTRACT

The waterborne aluminum pigments were prepared by sol–gel encapsulation method using tetraethoxysilane and γ-aminopropyl triethoxysilane as precursors with H_2O_2 as anchoring agent. Fourier transformation infrared and X-ray diffraction results indicated that the boehmite formed by H_2O_2 oxidizing aluminum can successfully reacted with silanol to make the silica sol–gel film anchored on the aluminum surface in the encapsulation process. The reaction conditions were optimized and the products were characterized by scanning electron microscopy, optical microscopy and stability test. It was found that when controlling the pH value of encapsulation media at about 9.5 and H_2O_2 concentration of 5.1×10^{-5} mol/m^2 of aluminum flake surfaces, the boehmite on aluminum flake surfaces carried a strong positive charge and the silica sol–gel film carried a negative charge, which conduct the most anchorage efficiency. A crack free, smooth and dense coating was formed and exhibited best corrosion resistance on the aluminum flake surfaces.

1. Introduction

Aluminum flakes (also called aluminum pigments) have been widely used in paint and coating industry to achieve a certain metallic appearance in combination with an angle-dependent color change, which was known as flip-flop effect. Recently, stricter legislation and growing environmental consideration have forced paint manufacturer to develop coating systems with reduced content of volatile organic compounds (VOC). This led to the development of waterborne coatings. However, finely dispersed, untreated aluminum flakes are unstable in combination with alkaline water and react to form aluminum hydroxide and hydrogen gas. This corrosion reaction results in undesirable color change and dangerous pressure buildup in container. Therefore, waterborne aluminum pigment (WBAP) is strongly favored. At present, intense investigation focus on inhibiting the corrosion reaction by surface modification of aluminum pigments. Compared with adsorption of corrosion inhibitors on pigment surface [1], encapsulation methods are more promising since either organic [2,3] or inorganic [4–6] protective layer can insulate the aluminum pigments from the corrosion medium. The silica sol–gel encapsulation process has been used for preventing corrosion by formation of silica film as a barrier layer on the aluminum flake surfaces [4]. The main work in the field involved the hydrolysis and condensation of the siloxane in the alcohol/water media under catalysis of the ammonia solution [4–7]. Although the silica film on aluminum flake surface has been reported, as to the important question "how the silica sol–gel film anchor to the aluminum flake surfaces", the study of this issue remains very limited. Karlsson [1] and Li [4] inferred that there is a layer of aluminum oxide on the surface of the aluminum flakes due to their exposure to the air, and the aluminum oxide in a humid or moist environment forms a significant population of hydroxyl groups. These surface hydroxyls can participate in the sol–gel condensation reaction to form a chemical linkage between the aluminum flake and the silica sol–gel film. Such speculation would be the truth in part. But there are hardly any surface hydroxyls in fresh prepared aluminum pigments and too much aluminum oxide on the long-term storage aluminum pigments surface would results in a deterioration of metallic luster. Moreover, since the anchoring points formed by natural corrosion are less quantifiable, the effective anchorage cannot be guaranteed. After careful analysis of the sol–gel process, two functions of ammonia solution can be found: the first one is to catalyze the hydrolysis and condensation of the siloxane; and the second one is to provide sufficient alkalinity to ensure aluminum reacting with water to form surface hydroxyls as anchor points. Since the strong

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exothermic reaction of aluminum with water is difficult to control especially in a high water ratio and high alkalinity system, most of the encapsulation processes choose low water ratio system. Here the amounts of water become the limiting factor, leading to insufficient hydrolysis and condensation reactions of siloxane. As a result, the coatings on aluminum flake surfaces are loose and cannot provide enough protection. Up to now, the long-term stability of aluminum pigments in acid or alkaline media has not been solved completely. Surface pretreatment methods are usually used in practice to strengthen the bonding between surface and adhesive. The sol–gel encapsulation process of aluminum pigments was widely conducted in weak basic medium [4–6], in which the H_2O_2 could oxidize metallic aluminum and form a significant population of hydroxyl groups as anchoring points on aluminum flake surfaces according to the following reaction:

$$3HO_2^- + 2Al + 3H_2O \rightarrow 2\left[Al(OH)_x\right]^{(3-x)+} + (9-2x)OH^-$$

Moreover, ammonia is very harmful to worker's health. Ammonia free Na_2CO_3–$NaHCO_3$ buffer as a weak basic medium is a good choice.

In this work, WBAP were prepared by tetraethoxysilane (TEOS) and γ-aminopropyl triethoxysilane (AMEO) as siloxane precursors with H_2O_2 as anchoring agent. The reaction conditions were optimized and the products were characterized by means of scanning electron microscopy (SEM), optical microscopy (OM) and hydrogen evolution test. Furthermore, the anchoring mode of silica film on aluminum flake surface is studied by Fourier transformation infrared (FTIR) and X-ray diffraction (XRD).

2. Experimental

2.1. Materials

The aluminum pigment pastes (aluminum flakes 74%) and acrylic resin emulsion were kindly provided by Baoding Ji-Nuo metal products Co. Ltd (China). Isopropanol (C3–OH), NaOH, H_2O_2 (30% water solution), Na_2CO_3, $NaHCO_3$ were all analytical reagents and used as received. Tetraethoxysilane (TEOS), γ-aminopropyl triethoxysilane (AMEO) and Propylene glycol monomethyl ether were market industrial products used as received without further purification.

2.2. Encapsulation process

The mixture of 50 g aluminum pigment paste and 125 ml C3–OH was put into a four-neck round bottom flask which was connected to a condenser and thermometer. The solution was stirred at 40 °C for 1 h. The mixture of H_2O_2 and 39 ml Na_2CO_3–$NaHCO_3$ buffer was added over a period of 10 min to the solution. Then the mixture of 10 ml TEOS and 7 ml AMEO diluted by 25 ml C3–OH was added drop by drop over a period of 2 h. The product was further stirred for 6 h, and then filtered. The resulting pigments were kneaded with 20% propylene glycol monomethyl ether and 1% dispersant to prepare WBAP. The specification of encapsulating conditions used in the experiment was listed in Table 1.

Table 1
The specification of encapsulating conditions.

Sample	H_2O_2/ml		pH
	V/ml	*n*/mmol	
A0	1.00	8.8	8.5
A1			9.0
A2			9.5
A3			10.0
A4			10.5
B0	0.00	0	9.5
B1	0.25	2.2	
B2	0.50	4.4	
B3	1.50	13.2	

2.3. Stability test

To evaluate the stability of aluminum flakes in the encapsulation media, 0.500 g aluminum flakes washed with C3–OH were put in 100 ml glass bottles and stored at the 40 °C. The volume of hydrogen varied with time was recorded after 10 ml C3–OH/W (40 °C) was added. To evaluate the corrosion inhibition of the encapsulation described in this paper, 1 g WBAP was dispersed in 40 ml 0.2% NaOH solutions. The hydrogen evolution to time was recorded.

2.4. Optical microscopy

According to the ratio of 100:7, the mixture of acrylic resin emulsion and the WBAP was coated evenly on the cover glass. The coating films were dried at 60 °C, and then observed under optical microscope (QImaging MicroPublisher 5.0 RTV) of 400 magnifications.

2.5. XRD and FTIR

1 g aluminum flakes washed with C3–OH were added to the solution of 1 ml H_2O_2 diluted with 20 ml, pH = 9.5 Na_2CO_3–$NaHCO_3$ buffer. After the mixture was stirred at 40 °C for 1 h, half of the product was filtered, washed with distilled water and anhydrous ethanol, successively. Then the sample was dried at 60 °C for the XRD and FTIR measurement as aluminum flakes that have surface with anchoring points (pretreated Al).

After 0.4 ml TEOS added, the remaining product was further stirred at 40 °C for 1 h, then filtered and washed with distilled water and anhydrous ethanol, successively. Finally the sample was dried at 60 °C for FTIR analysis as aluminum flakes that surface anchored silica films (silica coated A1).

FTIR spectra were obtained on a Nicolet 380 spectrometer (Thermos, America). The phase identification of the sample was performed using a Y-2000 X-ray diffraction meter (Dandon Aolong,

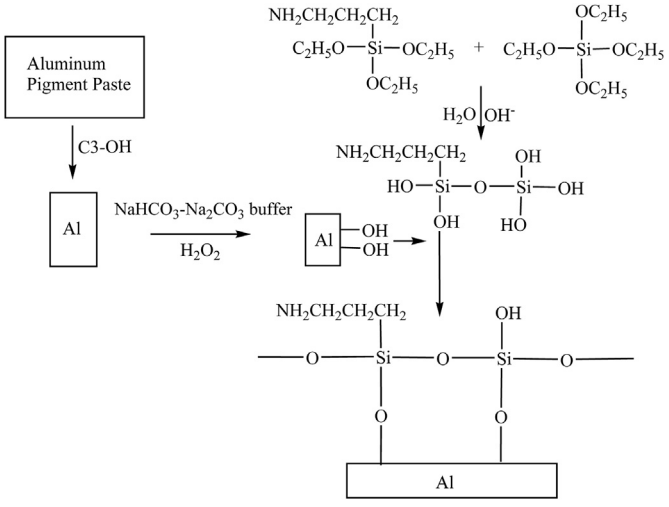

Fig. 1. Flowchart for encapsulation process of silica coated Al pigments.