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Silica sol–gel anchoring on aluminum pigments surface for corrosion protection based on aluminum oxidized by copper ammonia complex ion

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ABSTRACT

To reduce the volatile organic compounds emission led to the development of waterborne coatings. Correspondingly, waterborne aluminum pigment is desirable to develop. Here, the waterborne aluminum pigments were prepared by sol–gel encapsulation method using tetraethoxysilane and γ-aminopropyl triethoxysilane as precursors with $[Cu(NH_3)_4]^{2+}$ as anchoring agent. Fourier transformation infrared and X-ray diffraction results showed that the boehmite formed by $[Cu(NH_3)_4]^{2+}$ oxidizing aluminum can successfully react 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 control the pH of encapsulated media between 8.77 and 10.10, 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, and the waterborne aluminum pigment exhibit best stability.

1. Introduction

As one of the most important metallic pigments, lamellar aluminum pigment (aluminum flakes) has been used in solvent borne metallic paints or inks for many years because of its shiny appearance, “flop-effect” and cheap price. Recently, waterborne base-coats are used to reduce the emission of organic solvents. However, replacing the organic solvent by water in coatings based on aluminum pigments is not trivial, because the aluminum flakes react with alkaline water and then 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 desirable to develop. The pigment industry has worked on this issue for a long time. The organic [1,2] or inorganic [3–5] films encapsulation method are very promising since the 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 [3]. 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 [3–6]. Although the silica films on aluminum flake surfaces have been reported, the study of this issue still remains very limited. Accurate understanding of aluminum flakes in encapsulation media is essential for the encapsulation process. Furthermore, as to the important question “how the silica sol–gel layer anchor to the aluminum flake surfaces”, very few reports can be found till now. Li [3] and Karlsson [7] inferred that there is a layer of aluminum oxide on the surface of the aluminum flakes due to their exposure to the air. The surface of the aluminum oxide layer in a humid or moist environment has a significant population of hydroxyl groups. These surface hydroxyls would participate in the silica 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 fresh prepared aluminum flakes hardly have any surface hydroxyls, and the long-term storage aluminum pigments have excess aluminum oxide on the aluminum flakes surfaces which result 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 catalyzes the hydrolysis and condensation of the siloxane; and the second one provides sufficient alkalinity to ensure aluminum reacting with water to form surface hydroxyls as anchor points. Since the strong exothermic reaction of aluminum with

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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 [8]. Here the amounts of water become the limiting factor, leading to inefficient 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 such as sulfuric, phosphoric or chromic acid anodizing, conversion coatings and chromic-sulfuric acid etch are usually used in practice to create a surface that can marry with the adhesive. The sol–gel encapsulation processes of aluminum pigments were widely conducted in weak basic ammonia medium [3–5], in which the Cu^{2+} could exist in the form of $[Cu(NH_3)_4]^{2+}$. The $[Cu(NH_3)_4]^{2+}$ as the pretreating agent is expected to oxidize metallic aluminum and form a significant population of hydroxyl groups as anchoring points on aluminum flake surfaces according to the following reaction:

$$3\left[Cu(NH_3)_4\right]^{2+} + 2Al + 12H_2O = 2\left[Al(OH)_x\right]^{3-x} + 3Cu + 12NH_4^+ + (12-2x)OH^-$$

Tetraethoxysilane (TEOS) and silane coupling agents are typical precursors in silica sol–gel encapsulation process. One of the well-known silane coupling agents is γ-aminopropyl triethoxysilane (AMEO), which can readily react with TEOS and can be incorporated into the silica sol–gel network to form hybrid inorganic/organic polymers. Increasing the relative amounts of organic components can enhance the hydrophobicity of the film and lead to an improvement of the corrosion resistance of aluminum pigments in acid or alkaline media, and at the same time, enhance the compatibility between aluminum surfaces and other organic compounds contained in waterborne coatings. It was reported that when the volume ratio of organic/inorganic was 2/3, the dense barrier layer formed on the aluminum pigments surfaces [3]. Hence, the AMEO/TEOS volume ratio was 2/3 used as the precursors of silica films.

In this work, WBAP were prepared with $CuSO_4 \cdot 5H_2O$ as anchoring agent in ammonia medium. 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, $CuSO_4 \cdot 5H_2O$, NH_4Cl were all analytical reagents and used as received. Tetraethoxysilane (TEOS), γ-aminopropyl triethoxysilane (AMEO), Propylene glycol monomethyl ether and ammonia solution were commercial industrial products used as received without further purification.

2.2. Encapsulation process

50 g aluminum pigment pastes and 100 ml of C3–OH were put into a four-neck round bottom flask connected to a condenser and thermometer. The mixture was stirred at 40 °C for 1 h. The solution of $CuSO_4 \cdot 5H_2O$ dissolved in 30 ml of NH_3–NH_4Cl buffer was added over a period of 10 min. Then the mixture of 9 ml TEOS and 6 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.

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 bottle 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 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 (OM)

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 0.5 g $CuSO_4 \cdot 5H_2O$ dissolved in 20 ml, pH = 9.55 NH_3–NH_4Cl 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 surface with anchoring points (pretreated Al).

After 0.4 ml TEOS was 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 Al).

FTIR measurements were carried out by using a Nicolet 380 spectrometer (Thermos, America). The phase identification of the sample was performed with a Y-2000 X-ray diffraction meter (Dandon Aolong, China) equipped with Cu Ka radiation (30 kV × 20 mA), and with a scanning speed of 0.06°/s.

2.6. BET and SEM

Aluminum pigment paste was wrapped in a filter paper, extracted with acetone in a Soxhlet apparatus for 72 h and finally dried at 60 °C for specific surface area measurement and SEM

Table 1
The specification of encapsulating conditions.

Sample	$[Cu(NH_3)_4]^{2+}$/mol	pH
A	0	9.55
B	2×10^{-4}	9.55
C	4×10^{-4}	9.55
D	6×10^{-4}	9.55
E	8×10^{-4}	9.55
F	4×10^{-4}	8.55
G	4×10^{-4}	8.77
H	4×10^{-4}	9.77
I	4×10^{-4}	10.00
J	4×10^{-4}	10.68