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Preparation and characterisation of water-based aluminium pigments modified with SiO_2 and polymer brushes

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ABSTRACT

In order to improve the corrosion resistance and dispersiveness of aluminium pigments in aqueous media, SiO_2-coated aluminium was prepared and polyacrylic acid brushes were grafted on its surface. A decrease in hydrogen generation indicated that the corrosion resistance was improved by the SiO_2 coating, while the polyacrylic acid brushes improved dispersiveness. The $d(0.5)$ (particle size of 50% volume fraction) values of the SiO_2-coated aluminium sample and that of the sample with the polyacrylic acid brushes grafted on it were 41 μm and 29 μm, respectively. We believe that thus modified aluminium will find use in water-based paints and printing inks.

1. Introduction

Aluminium pigments have been widely used in oily paints and printing inks for many years. Recently, increasing concerns about protecting the environment have led the paint industry to develop water-based paints with reduced contents of volatile organic compounds. However, the use of flaky aluminium pigments in water-based media is restricted owing to the fact that they react with the media and release H_2 [1,2]. This corrosion reaction not only affects the metallic lustre but can also bring insecurity during production and conservation. In addition, aluminium pigments show poor dispersiveness in water-based media, owing to their poor compatibility.

Various methods have been developed to enhance the anticorrosion properties of aluminium pigments [3,4]. One method is to use low-molecular-weight inhibitors such as sodium dodecyl sulphate, sodium dodecyl phosphate [5], aromatic 2-hydroxy-oximes [6], *sansevieria trifasciata* [7], vanillin [8], surfactants [9], nitro- and aminophenols [10], citric acid [11], saccharides [12], and phosphate esters [13]. However, these inhibitors cannot form a dense protective layer, as they become unstable under certain conditions. Another method is to modify the pigments using macromolecular inhibitors such as polyacrylic acid (PAA) [14,15], poly(methyl methacrylate) [16], poly(trimethylolpropane triacrylate) [17], and SiO_2 [18–27]. The in-situ polymerisation of these macromolecular inhibitors can result in the formation of a dense layer on the surface of aluminium. However, the adhesion of these polymers is not strong enough for them to be immobilised on the aluminium sample. For instance, while a dense layer of SiO_2 prepared by the sol-gel method can improve the corrosion resistance of aluminium, even, a single SiO_2 layer has an adverse effect on the compatibility of aluminium in water-based media. Though the effects of a protective SiO_2 layer on aluminium have been studied widely, there have been few reports on the dispersiveness of thus-coated alumiuium.

In this paper, we propose a strategy for preparing water-based aluminium pigments (PAA/SiO_2@ In this paper, we propose a strategy for preparing water-based aluminium pigments (PAA/SiO_2@Al), that is, aluminium pigments modified with SiO_2 and PAA, in order to improve both their corrosion resistance and their dispersiveness. As shown in Fig. 1, flaky aluminium was first coated in a layer of SiO_2 by the sol-gel process. Then, self-made azo initiator [28] was attached to the surface of the coated aluminium. Acrylic acid (AA) monomers were polymerised on the surface of the coated aluminium under the effects of the azo initiator. The effects

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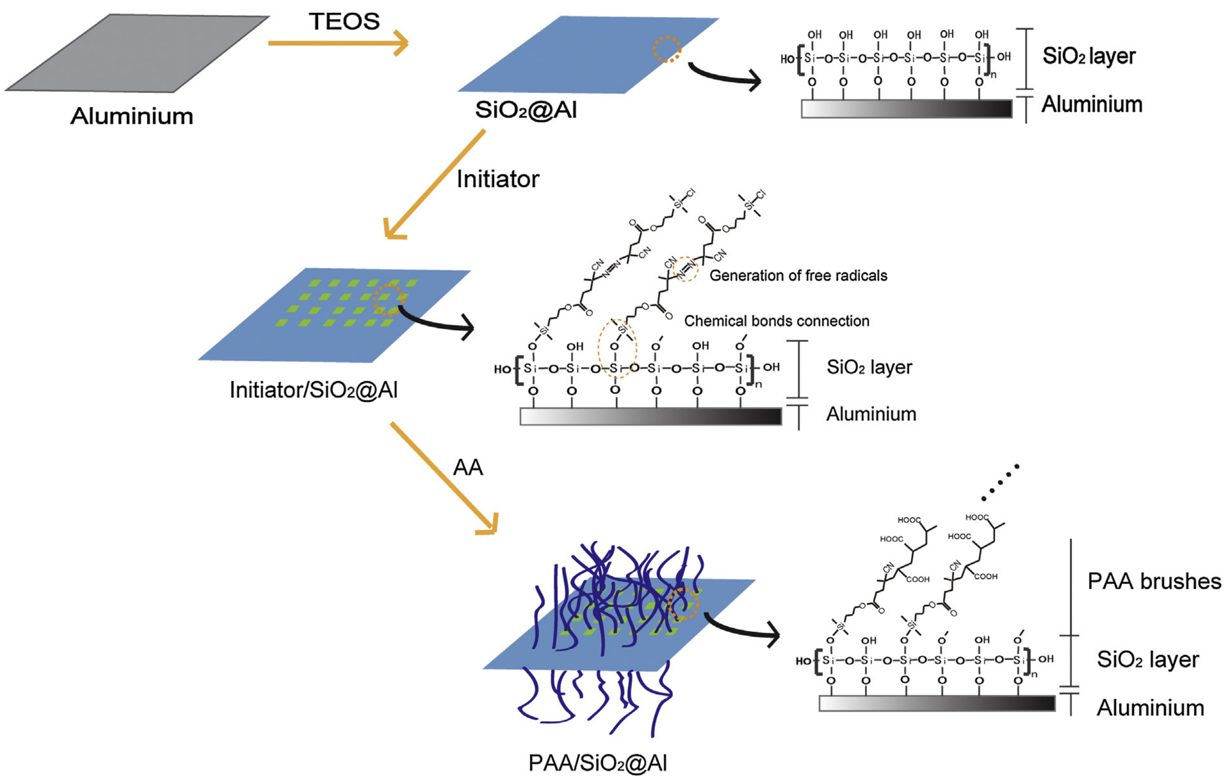

Fig. 1. Process of modifying aluminium to form PAA/SiO_2@Al.

of the modifications on the anticorrosion properties and dispersiveness of aluminium in water-based media were studied. The particle sizes of the SiO_2-coated aluminium (SiO_2@Al) and PAA/SiO_2@Al samples were also determined. The significance of this work is that the proposed modification method could enhance both the anticorrosion properties and the dispersiveness of aluminium pigments. We believe that this modification process will help increase the use of aluminium in environmentally benign pigments. Al), that is, aluminium pigments modified with SiO_2 and PAA, in order to improve both their corrosion resistance and their dispersiveness. As shown in Fig. 1, flaky aluminium was first coated with a layer of SiO_2 by the sol-gel process. Then, self-made azo initiator [28] was attached to the surface of the coated aluminium. Acrylic acid (AA) monomers were polymerised on the surface of the coated aluminium under the effects of the azo initiator.

The effects of the modifications on the anticorrosion properties and dispersiveness of aluminium in water-based media were studied. The particle sizes of the SiO_2-coated aluminium (SiO_2@Al) and PAA/SiO_2@Al samples were also determined. The significance of this work is that the proposed modification method could enhance both the anticorrosion properties and the dispersiveness of aluminium pigments. We believe that this modification process will help increase the use of aluminium in environmentally benign pigments.

2. Materials and methods

2.1. Materials and reagents used

Tetraethoxysilane (TEOS), 4,4′-azobis (4-cyanopentanoic acid) (Aladdin Company, Shanghai, China), AA, dichloromethane, hexane, ethanol, toluene, triethylamine, allyl alcohol, chloroplatinic acid, distilled water, and phosphorus pentachloride were used in this study. All the chemicals and solvents used were of the analytical grade. Flaky aluminium (median size 25 μm; 92.2% solid content and 7% of fatty acid) was obtained from Zuxing Corporation, China.

2.2. Methods employed

2.2.1. Preparation of SiO_2@Al particles by sol-gel process

The SiO_2@Al particles were prepared by the sol-gel method as follows. In brief, flaky aluminium was washed with acetone to remove the volatile organic compounds. Then, 1 g of the washed aluminium pigment and 30 mL of ethanol were placed in a three-neck bottom flask. Next, 1.8 g of TEOS, 6 g of distilled water, 30 mL of ethanol, and 1.3 g of triethylamine were mixed; this solution was labelled as solution A. Solution A was added to the flask containing the aluminium sample in a drop-by-drop manner at 40 °C under stirring. After a reaction time of 10 h, the product was filtered and washed with ethanol. The resulting wet cake was dried in a freeze dryer for 20 h.

2.2.2. Immobilisation of self-made initiator on surface of SiO_2@Al

The initiator, 4, 4′-azobis (4-cyanopentanoic acid-(3′chlorodimethylsilyl) propyl ester), was synthesised as per a previously reported method [28]. Approximately 1 g of the SiO_2@Al particles was placed in 50 mL of anhydrous toluene; 2 mL of triethylamine was added as a catalyst. 0.5 g of the azo initiator was dissolved in 10 mL of anhydrous toluene. Then, the initiator solution was added drop by drop to the reaction mixture, and the mixture was stirred at room temperature in a N_2 atmosphere for 24 h. After the completion of the reaction, the crude product was washed with toluene and dried under vacuum for 24 h at 25 °C to This yielded SiO_2@Al particles covered with the initiator (initiator/SiO_2@Al).

2.2.3. Surface-initiated polymerisation

Next, 1 g of initiator/SiO_2@Al and 0.4 g of AA were put in a flask with 18 g of distilled water and 0.5 g of ethanol as solvent. This mixture was carefully degassed to remove the oxygen. Then, polymerisation was performed at 60 °C in a N_2 atmosphere for 2 h. After the reaction, the product was filtered and washed with distilled