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Synthesis of aluminum tri-polyphosphate anticorrosion pigment from bauxite tailings

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Abstract: Aluminum tri-polyphosphate was synthesized from bauxite tailings and phosphoric acid with a P/Al molar ratio of 3. This is highly advantageous from a waste recycling perspective as bauxite tailings are generally regarded as unusable waste. The acidity, whiteness and mean particle size of prepared aluminum tri-polyphosphate are all improved after modification. The possibility of using modified aluminum tri-polyphosphate as an anticorrosive pigment was also investigated by electrochemical impedance spectroscopy. The resistance of the coatings with modified aluminum tri-polyphosphate is 7×10^7 Ω for 40 d of immersion, which is superior or at least comparable to that of coatings containing APW−2, which exhibits a resistance of 5.7×10^7 Ω.

Key words: aluminum tri-polyphosphate; waste processing; electrochemical impedance spectroscopy

1 Introduction

Classical anticorrosive paints normally contain inhibitors based on hexavalent chromium or lead compounds. The incorporation of these compounds is being restricted because they contaminate the environment and cause health problems to humans. Regulations in various countries led to an intense research effort to find alternative pigments of low toxicity without compromising performance. A new generation of pigment, layer-structured aluminum tri-polyphosphate ($AlH_2P_3O_{10}\cdot 2H_2O$: abbreviated as ALP) has been developed and used widely as an anticorrosion pigment due to its low toxicity to humans and the environment [1].

The synthesis, structure, thermal changes and ion-exchange properties of acidic aluminum tri-polyphosphate were first reported in 1960 before its industrial production methods were established in 1970. The industrial production method was based on their patent of producing ALP by means of the substance containing aluminum and phosphoric acid or phosphate [2]. This maintains the current industrial preparation method of ALP [2]. The development and application of ALP in the paint industry was achieved by the Imperial Japanese Corporation until the 1970s. Since then, many studies have been carried out on its synthesis and application. TSUHAKO et al [3] found that the formation of ALP is greatly dependent on the water content of the primary product and on the vapor pressure in the secondary treatment. They also showed that $AlH_2P_3O_{10}\cdot 2H_2O$ dehydrates at 150 °C to form $AlH_2P_3O_{10}$ which decomposes to form $Al_4(P_4O_{12})_3$ at 500 °C. SHI and LIN [4] showed that the optimum parameters for maximizing ALP yield was when a P to Al molar ratio of 3:1 was used, coupled with a condensation temperature in the range of 200−320 °C and condensation time of about 10 h.

Bauxite tailings are the aluminosilicate-waste generated during the process of improving the molar ratio of aluminum to silicon in bauxite by beneficiation methods. It was reported that 0.2 t of aluminosilicate tailings were generated from every ton of bauxite ores processed by flotation. In China, a large quantity of bauxite tailings are stored in the tailing dam after flotation [5]. The main minerals in bauxite tailings are diaspore, kaolinite, illite and pyrophyllite. Some investigations and trials for the utilization of bauxite tailings in building materials [6], fillers [7] and refractory materials [8] have been carried out in recent years. However, because of the high iron content in the waste,

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its large-scale application has been rendered infeasible. In order to expand the application volume of bauxite tailings, researchers attempted to remove iron from bauxite tailings by magnetic separation, acid pickling, reduction and other methods, but failed. This is due to the iron in the bauxite tailings distributed between numerous minerals that are mutually embed with complicated relationships and fine particles.

With industrial development, low-cost production for a variety of materials is required. Much industrial waste has been studied and recycled [9−11]. ALP was generally prepared using chemicals. Till now, there are no reports on preparation of ALP from industrial waste. Aluminum oxide content in bauxite tailings is generally more than 50%. Therefore, we attempted to prepare ALP using bauxite tailings and phosphoric acid. In addition, we believe that it is possible to prepare a white anti-corrosive pigment by means of the reactions between iron and phosphoric acid, which not only reduces the production cost of ALP, but also recycles the bauxite tailings.

2 Experimental

2.1 Bauxite tailings

The bauxite tailings were obtained from Zhongzhou bauxite flotation plant in China. The chemical compositions were 57.6% Al_2O_3, 19.8% SiO_2, 2.18% TiO_2, 1.6% MgO, 1.08% CaO, 4.84% TFe, 0.69% K_2O and 0.82% Na_2O. Diaspore, kaolinite, illite, anatase, hematite and quartz were determined as the main minerals in bauxite tailings by X-ray powder diffractometry. The bauxite tailings were milled for 5 h with a planet-ball mill. The average diameter of milled tailings measured with a laser diffraction analyzer was 3.8 μm.

2.2 Synthesis of white anti-corrosion pigments

The milled bauxite tailings were calcined at 600 °C for 2 h in order to eliminate organic matter and to increase its reactivity. The aluminum tri-polyphosphate was prepared via two heat treatments. The specific process for preparation is as follows.

First, tailings and phosphoric acid were mixed in a porcelain crucible with P to Al molar ratios of 2.0, 2.5 and 3.0. The quantity of used phosphoric acid is equal to the sum of the stoichiometric phosphoric acid of the following each reaction due to the fact that the calcium, magnesium, iron and other metal elements except silicon for tailings likely react with the phosphoric acid.

$$Al_2O_3+H_3PO_4 \longrightarrow AlH_2P_3O_{10}\cdot 2H_2O$$

$$Fe_2O_3+H_3PO_4 \longrightarrow Fe\,(PO_3)_3+H_2O$$

$$CaO+H_3PO_4 \longrightarrow Ca_3\,(PO_4)_2+H_2O$$

$$MgO+H_3PO_4 \longrightarrow Mg_3\,(PO_4)_2+H_2O$$

$$TiO_2+H_3PO_4 \longrightarrow Ti_3\,(PO_4)_4+H_2O$$

Second, the mixture was then dehydrated by heating over a weak flame with vigorous agitation to obtain a white, highly viscous product in each case. This is designated as the primary heat treatment, giving the primary products.

Third, the primary product was heated at 300 °C for 10 h in a sealed tube. This is designated as the secondary heat treatment, giving the secondary products. The secondary product was washed, milled and dried, eventually a white powder was obtained.

Fourth, the aluminum tri-polyphosphate prepared and zinc oxide (ZnO) were mixed with the mass ratio of 17:3. The resultant mixture was milled for 8 h by wet process, then reacted for 3 h at 120 °C in a reactor, dried, pulverize, a modified aluminum tri-polyphosphate was obtained.

2.3 Test and characterization

X-ray diffraction (XRD) patterns were recorded on a RIGAKU D/max−2550VB+18 kW powder diffractometer with Cu K_α-radiation (λ=1.541806 Å). The thermal stability of the samples was measured in air with a heating rate of 10 °C/min in the range of 35−800 °C on a STA449C and simultaneously on a DSC−TG instrument. The morphology of the sample was examined by scanning electron microscopy (SEM, Sirion 200 field emission, FEI Company). The whiteness samples were determined according to the criterion of GB/T 5950—2008 of the National Standards of China. The pH value of aqueous suspension of sample was determined by the criterion of GB−T 1717—1986. The average diameter of the particle was measured on a MS2000 laser diffraction size analyzer.

2.4 Evaluation of anticorrosive properties of pigments

2.4.1 Method

Electrochemical impedance spectroscopy (EIS) was employed to assess the anticorrosive properties of the pigments. EIS measurements were performed using a PAR 2273 potentiostat. The coated samples were immersed in a 3.5% NaCl solution. A three-electrode system comprising of a saturated calomel electrode as a reference electrode, the coated sample as a working electrode and platinum as a counter electrode was employed (Fig. 1). A sine wave of 10 mV was applied across the cell. The measurements were made in the frequency range of 50 kHz−0.01 Hz.

2.4.2 Preparation of coated samples

The pigment powder was added to an epoxy resin solution (Epikote1001 solution 70% in toluene) and mechanically dispersed. The liquid substance with dispersed pigment powder was mixed with a curing agent (polyamide, Crayamid 115) at stoichiometric ratio. The pigment content in the paint was 15%. The paint was coated on one surface of steel panels with dimensions of 140 mm×100 mm×4 mm by brushing to a thickness of (80±5) μm, and cured at room temperature for 7 d. The surfaces of panels were polished, degreased with acetone and ethanol, and dried in air before painting. In addition, the coatings with no pigment (blank coating) and with zinc aluminium phosphate ($ZnAlPO_4$) under the trade mark APW−2 were employed as references.

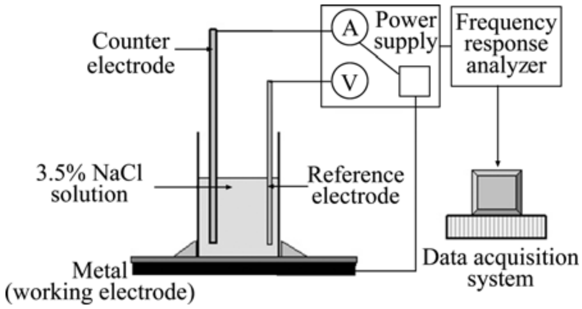

Fig. 1 Sketch of EIS experimental set-up

3 Results and discussion

3.1 XRD analysis

The phases present in each prepared sample were determined via XRD analysis. Figure 2 shows the XRD patterns of the samples. There are some peaks that cannot be discerned, in addition to aluminum phosphate and aluminum tri-polyphosphate peaks in patterns of $n(P)/n(Al)=2.0$ and $n(P)/n(Al)=3.0$. We denoted the unidentifiable diffraction peaks as "Unknown". It is apparent that phases of samples depend on the amount of phosphoric acid. Sample of $n(P)/n(Al)=2.0$ contains aluminum phosphate, a small amount of aluminum tri-polyphosphate and other unidentifiable crystalline phases. Compared with sample of $n(P)/n(Al)=2.0$, sample of $n(P)/n(Al)=3.0$ showed an increase of aluminum tri-polyphosphate, a decrease in unidentifiable crystalline phases, and a disappearance of aluminum phosphate. Among all samples, sample of $n(P)/n(Al)=2.5$ exhibited the highest intensity peak of aluminum tri-polyphosphate, which was the only crystalline phase present in it, and the pattern of sample of $n(P)/n(Al)=2.5$ also exhibited the minimum baseline noise, which indicates that sample of $n(P)/n(Al)=2.5$ is more crystalline with a maximum yield.

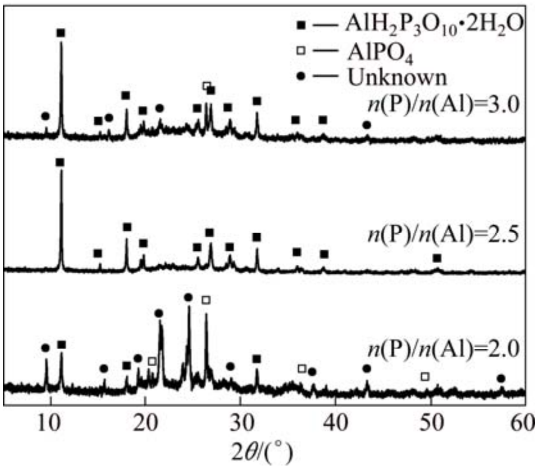

Fig. 2 XRD patterns of prepared samples of $n(P)/n(Al)=2.0$, 2.5 and 3.0

3.2 DSC−TG analysis

Figure 3 shows the DSC−TG curves of sample of $n(P)/n(Al)=2.5$. The curves reveal a two-stage dehydration process. The dehydration of the first stage occurred in the range of 120−260 °C, the mass loss of 6.48% was the loss of two molecules of water in the crystalline structure. The second stage occurred in the range of 430−570 °C, the mass loss of 4.21% was indicative of a further loss of one water molecule [12]. The mass losses in the two stages are different from the theoretical loss of 11.32% and 5.66%, which resulted from impurities in the sample. Simultaneously, formation of new phases also occurred in the course of dehydration. The process is expressed as follows:

$$AlH_2P_3O_{10}\cdot 2H_2O \xrightarrow{-2H_2O} AlH_2P_3O_{10} \xrightarrow{-H_2O} Al(PO_3)_3$$

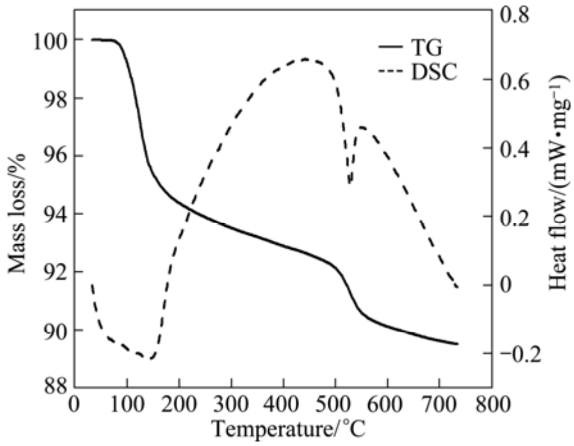

Fig. 3 DSC−TG curves of sample at $n(P)/n(Al)=2.5$

3.3 Morphology of sample

SEM morphology of sample of $n(P)/n(Al)=2.5$ is shown in Fig. 4. The particles have a layered structure and irregular shape, but most of the particles are flaky. The grain sizes range from 0.1 to 5 μm. There are a few agglomerations between grains. Flaky particles are better than granular particles in obstructing air and water whose penetration is the main cause of steel corrosion.

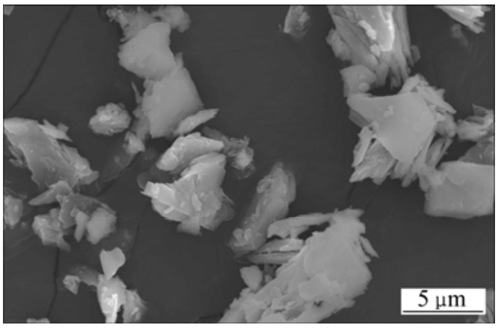

Fig. 4 SEM image of sample with $n(P)/n(Al)$=2.5

3.4 pH value and whiteness

The physical parameters for pigment of APW−2 and the samples of $n(P)/n(Al)$=2.5 before and after modification are shown in Table 1. The pH value for APW−2 is 6.8. The unmodified sample has only pH value of 5.8, which is too low to be anticorrosive, so it is indispensable to improve its pH via modification.

Table 1 Chemical compositions and physical parameters of samples of $n(P)/n(Al)$=2.5, modified samples of $n(P)/n(Al)$=2.5 and APW−2

Sample	pH	Whiteness/%	Mean particle size/μm	Mass fraction/%			
				Al_2O_3	SiO_2	P_2O_5	ZnO
ATP	5.8	84.6	5.3	19.2	6.6	66.7	−
ZATP	7.2	85.4	4.8	15.9	5.5	55.2	13
APW−2	6.8	87.3	4.3	11.4	12.6	41.0	29.3

ATP: Sample of $n(P)/n(Al)$=2.0; ZATP: Sample of $n(P)/n(Al)$=2.0 modified by ZnO

People think that protection depends more on the high pH provided by the pigment than on other of its properties [13, 14]. The pH value increases to 7.2, the whiteness and the mean particle size are all improved after the sample modification.

3.5 Electrochemical impedance spectroscopy

EIS is a well established quantitative method for examining protective properties, such as anticorrosion performance of organic coatings. This technique is widely used with good results for the electrochemical characterization of protective organic coatings on metal [15]. Impedance can reflect the degree of difficulty of an electrolyte passing through the coating, and is a valid method to extrapolate the long-term anti-corrosion effect of coatings. Greater impedance indicates a better anticorrosion effect [16].

In this study, the anticorrosive behaviors of coatings containing modified aluminum tri-polyphosphate pigment, APW−2 pigment, and no pigment were investigated by means of electrochemical impedance method. The coating resistance as a function of time during the immersion in 3.5% NaCl solution is shown in Fig. 5.

It is clear from Fig. 5(a) that the resistance of the coatings with modified aluminum tri-polyphosphate pigment at 0.01 Hz was higher than 10^8 Ω at the beginning of exposure and it decreased to 6.5×10^7 Ω after 20 d of exposure. After that it showed a small increase to 7×10^7 Ω until 40 d. The decrease in resistance at the initial stage of exposure may be due to the

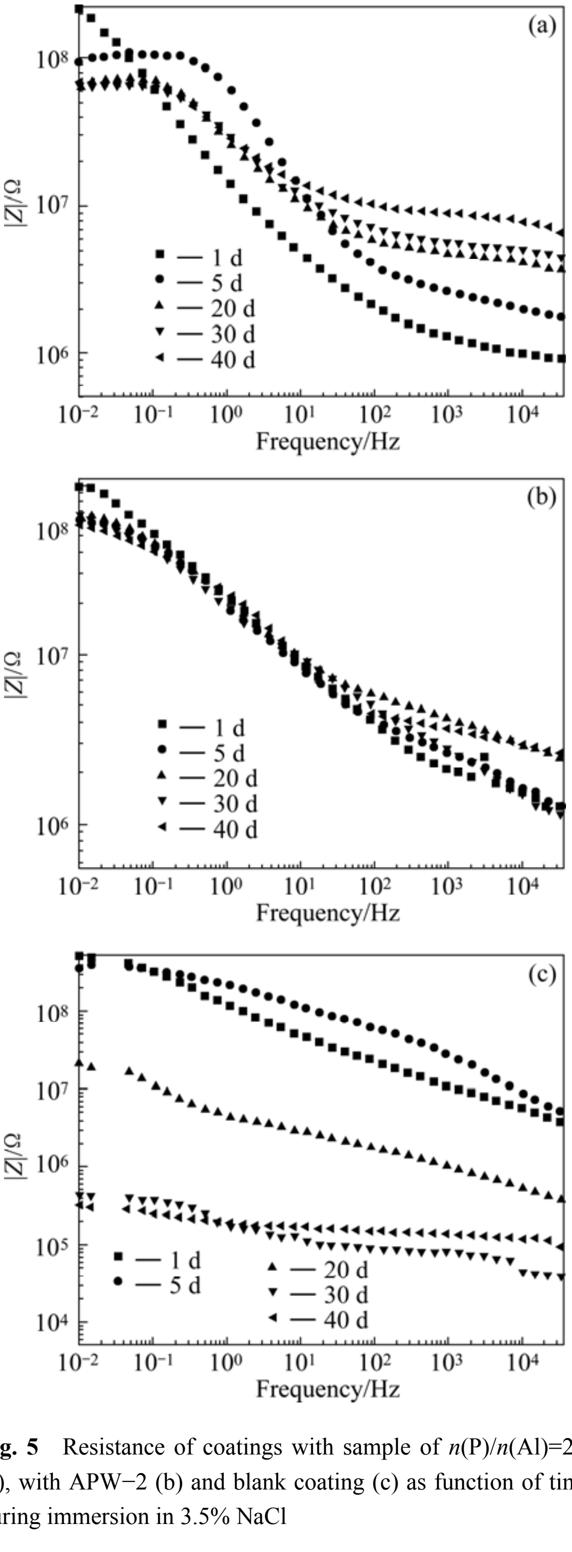

Fig. 5 Resistance of coatings with sample of $n(P)/n(Al)$=2.5 (a), with APW−2 (b) and blank coating (c) as function of time during immersion in 3.5% NaCl

permeation of water and ions into the film. The increase after 40 d of exposure seems to be attributed to the formation of passive states, such as iron phosphate and $Fe_3(PO_4)_2\cdot nH_2O$ [17].

Figure 5(b) presents the change of impedance with exposure time for an APW−2 pigmented film. At the beginning of exposure, the resistance at 0.01 Hz was around 9.8×10^7 Ω and it decreased continuously to 5.7×10^7 Ω until 40 d of exposure. The range of decrease also decreased after 5 d of exposure.

In the case of the blank coating, as shown in Fig. 5(c), the resistance at 0.01 Hz was higher than 10^8 Ω up to the first 5 d of exposure. However, it decreased quickly to 1×10^7 Ω at 20 d. After 40 d of exposure, a few blisters were found on the specimen and the resistance was 3×10^5 Ω. It is generally known that the coating films with a resistance higher than 10^8 Ω reveals good anticorrosive performance, while that with the resistance lower than 10^6 Ω has poor anticorrosive properties. So the blank coating lost its anticorrosive properties within the first 5 d of exposure.

From the comparison of results for the modified aluminum tri-polyphosphate, APW−2 and blank coating films, it can be seen that the anticorrosive performance of the modified aluminum tri-polyphosphate is superior or at least comparable to that of the APW−2, which has been used as anticorrosive pigments.

4 Conclusions

1) Aluminum tri-polyphosphate was successfully synthesized from bauxite tailings and phosphoric acid via two heat treatments, giving a molar ratio of P to Al of 2.5, a condensation temperature of 300 °C and condensation time of 10 h.

2) The acidity, whiteness and mean particle size for prepared aluminum tri-polyphosphate were all improved after modification. The possibility of using modified aluminum tri-polyphosphate as an anticorrosive pigment was investigated using electrochemical impedance spectroscopy.

3) The resistance of the coatings with modified aluminum tri-polyphosphate was 7×10^7 Ω, while that of coatings with APW−2 was 5.7×10^7 Ω after 40 d of immersion, which showed the superior anticorrosive performance of modified aluminum tri-polyphosphate, or at least comparable to that of APW−2. The whiteness of modified aluminum tri-polyphosphate is 85.4%, which meets the industrial requirements.

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运用铝土矿选矿尾矿制备三聚磷酸铝防腐颜料

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摘 要：将铝土矿选矿尾矿与磷酸以 P 与 Al 摩尔比等于 3 的比例混合，制备了三聚磷酸铝，并用氧化锌对所制备的三聚磷酸铝进行改性处理，得到三聚磷酸铝防腐颜料。改性的三聚磷酸铝的酸度、白度及粒度均得到了改善。运用电化学阻抗方法测试了所制备的三聚磷酸铝防腐颜料的防腐性能。结果表明：含有改性三聚磷酸铝防腐颜料的涂层在电解质中浸泡 40 d 后的阻抗为 $7\times10^7\,\Omega$，含商品三聚磷酸铝防腐颜料 APW−2 的涂层浸泡 40 d 后的阻抗为 $5.7\times10^7\,\Omega$，这表明所制备的三聚磷酸铝防腐颜料具有优于或相当于商品防腐颜料的防腐性能。

关键词：三聚磷酸铝；废物处理；电化学阻抗谱

(Edited by LI Xiang-qun)