

## Progress for Preparation and Application of Nano-aluminate phosphate

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**Abstract:** This paper reviews the main preparation methods of aluminum phosphate nanoparticles, briefly introduces the process of each method, and analyzes the advantages and disadvantages of these methods. The application of nano aluminum phosphate in coating adhesive, medicine and refractories is described. Finally, the development trend of aluminum phosphate coating is prospected, and it is pointed out that the development of formula and organic-inorganic composite coating will be the focus of future research.

**Keywords:** aluminum phosphate; inorganic coating; curing mechanism; preparation method;

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### I. INTRODUCTION

Aluminum phosphate nanoparticles are widely used materials and have good application prospects in building materials, refractories, medicine and chemical industry [1]. There are many methods for preparing aluminum phosphate, including liquid phase ion exchange (including three kinds of complex decomposition reactions), solid reaction and gas phase reaction. It is pointed out that the preparation mainly develops to optimize the synthesis process, reduce the production cost and be more green and environmentally friendly. The application of aluminum phosphate in coatings, adhesives, medicine and refractories is described in detail, and the mechanism and characteristics of its application as inorganic coatings, binders and molecular sieves are mainly excavated. Finally, the development trend is prospected.

#### 1. Preparation of nano-aluminum phosphate

##### 1.1 Liquid-phase ion exchange method (decomposition reaction method)

According to the different reactants, this method includes the following three kinds: the first is to use sodium phosphate and aluminum sulfate to react to form aluminum phosphate precipitation, while sodium sulfate remains [2] in solution. The typical preparation process is to dissolve sodium phosphate and aluminum sulfate in hot water to form a solution, filter and remove insoluble impurities, and then send the two solutions into the reactor at an appropriate concentration for re-decomposition to form white colloidal aluminum phosphate precipitation. if the  $\text{Na}_3\text{PO}_4$  in the system is slightly excessive, it is beneficial to  $\text{AlPO}_4$  precipitation and accelerate the reaction. After the reaction was finished, the solid-liquid separation was carried out directly by plate-frame filter press, and the solid phase was left in the filter press, washed with dilute hydrochloric acid and clear water, the entrained  $\text{SO}_4^{2-}$ , was removed, dried and crushed to obtain the finished product, and the filtered mother liquor was used to recover sodium sulfate.

The second is reaction with phosphoric acid and sodium aluminate, which needs to be heated to 230°C in autoclave to complete the [3]. The typical preparation process is to dissolve sodium aluminate in hot water and heat it to 80°C then add 83% phosphoric acid to react to form white precipitate, and the end point pH is controlled at about 4.3. and then the reaction slurry was transferred into the autoclave and heated at 230°C for 8 hours. Then the solid-liquid separation was carried out, and the solid substances were white crystal aluminum phosphate and a small amount of sodium dihydrogen phosphate and other salts. The solid matter is washed in the washing tank with dilute hydrochloric acid and clear water to remove water-soluble impurities, and the finished product is obtained after filtration and drying. The main component of mother liquor after liquid-solid separation is sodium dihydrogen phosphate, which can be used as raw material for the production of other phosphates after recovery and treatment.

The third is the neutralization reaction of phosphoric acid-aluminum hydroxide. The typical preparation process is 60% phosphoric acid added to the reactor, Heating to 88°C Adding aluminum hydroxide under stirring, Control endpoint pH values, Continue heating to make the reaction complete, Get a paste solution, 20~30 times more water injected into the solution, White aluminum phosphate precipitates. Solid-liquid separation of slurry, The separated solid phase is washed with water, Drying, And roasted over 800°C The hexagonal aluminum

phosphate is obtained. Finally, At room temperature, A uniform and viscous aluminum phosphate adhesive can be obtained. The study found, The content of phosphoric acid and aluminum hydroxide determines the composition of the synthesized aluminum phosphate binder, And then has a great influence on the properties of [4] cured coating. A major component of the synthesized binder was found to be  $\text{AlH}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  by Liping He et al Via controlling the molar mass ratio of the reactants aluminum hydroxide and phosphoric acid (Al/P)[5]. When the Al/P is below 1.3: 3, Unreacted phosphoric acid; When the Al/P is above 1.4: 3, There is aluminum hydroxide surplus. In addition, When the Al/P is above 1: 3, The dehydration and recrystallization reaction [6] of aluminum phosphate binder after long storage:  $\text{Al}(\text{H}_2\text{PO}_4)_3 \rightleftharpoons \text{AlPO}_4 \cdot \text{XH}_2\text{O} + 2\text{H}_3\text{PO}_4$ . The dehydration reaction reduces the properties of the binder, Therefore, a small amount of oxalic acid is often added as a stabilizer to inhibit the reaction. A series of phase transitions occur during heating and curing of aluminum phosphate binder, and the phase transition temperature is greatly affected by the Al/P molar ratio. Kingery research [7], When the Al/P is 1: 3, After heating, the main product is aluminum dihydrogen phosphate ( $\text{Al}(\text{H}_2\text{PO}_4)_3$ ), It is the best adhesive component in phosphate. Femando and other [8] believe that when the Al/P is 1.2: 3, binder synthesized at 150°C reaction has better performance. Yang Baoping [9] studied the effect of Al/P ratio and reaction temperature on the phase composition and bond properties of the product. When the Al/P is 1.4: 3, the reaction temperature is within 120~200°C  $\text{Al}(\text{H}_2\text{PO}_4)_3$ , And its bond performance is the best. And when the temperature exceeds 105°C Dehydration of the binder, By  $\text{AlH}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$  transformation into  $\text{Al}(\text{H}_2\text{PO}_4)_3$  and  $(\text{AlH}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O})$ ; At 200°C almost all converted to  $\text{Al}(\text{H}_2\text{PO}_4)_3$ ; When it was heated below 400°C Binder  $\text{AlH}_2\text{P}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$  and  $\text{AlPO}_4$  exist; After the temperature exceeding to 400°C The binder is no longer dehydrated and  $\text{AlPO}_4$  crystal transformation occurs.

### **1.2 Solid State Reaction Method**

The first is the reaction of ammonium dihydrogen phosphate with aluminum hydroxide, that is, alumina or aluminum hydroxide and ammonium dihydrogen phosphate are mixed according to the mass ratio of 1: 2. Preheat 30 min, then it was heat to 900°C in roasting furnace to synthesize aluminum phosphate, and then comminute the finished product with the required fineness. The second method is the reaction of phosphorus pentoxide with alumina, that is, the dry fluidity phosphorus pentoxide and alumina are mixed evenly in the mixer with the mass ratio of 1: 1, and the mixed materials are input into the kneading machine. After 800°C roasting, aluminum phosphate was crushed.

### **1.3 Gas Reaction Method**

In a special gas phase reactor, aluminum chloride and phosphorus trichloride were burned and gasified on a hydrogen-containing flame, which oxidized phosphorus trichloride to phosphorus oxychloride and hydrolyzed into gaseous phosphoric acid, gaseous phosphoric acid and gaseous aluminum chloride to form aluminum phosphate.

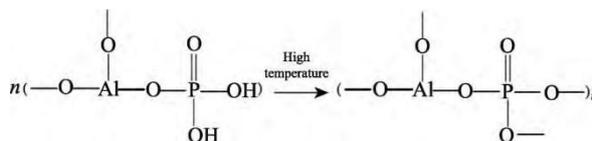
## **2. Application of nano-aluminum phosphate**

### **2.1 Serve as inorganic coatings**

Aluminum phosphate coating began in the 1950s, the former Soviet Union first applied it to high temperature permeable materials [10]. Subsequently, GE began to study this aspect, reducing the curing temperature of the coating to 315°C and obtaining the [11] of quartz fabric reinforced aluminum phosphate matrix composites. By the 1990s, the curing temperature of aluminum phosphate composite coatings had been reduced to 170°C [12].

Aluminum phosphate coating is a kind of waterborne inorganic coating. It is made of phosphate binder formed by chemical reaction of phosphoric acid with alkaline metal hydroxide as film forming material and metal oxide as filler aggregate [13]. Aluminum phosphate coating not only has excellent corrosion resistance, firm adhesion [14], but also has good high temperature resistance, friction and wear resistance, aging resistance and oil pollution resistance compared [15] organic coatings. In addition, aluminum phosphate coatings have been paid more and more attention to the characteristics of non-toxic, tasteless and environmentally friendly, and have been widely used in aerospace, petroleum pipelines, marine equipment and other fields.

Curing film forming theory of aluminum phosphate coating is mainly based on the "high temperature baking film forming" mechanism proposed by Japanese scholar [16] Youzhaoh Murata. Taking aluminum dihydrogen phosphate as an example, dehydration and condensation reaction occurred at high temperature to form a macromolecular network of aluminum phosphate as skeleton. The reaction is shown in figure 1 [17].



**Fig.1** High temperature curing mechanism of aluminum dihydrogen phosphate

This mechanism explains the film forming mechanism of aluminum phosphate coating under high temperature baking condition, which is recognized by researchers.

## 2.2 Serve as binder

Aluminum phosphate adhesive has excellent high temperature resistance and weathering resistance. It is not only a kind of binder used in refractories, but also an important component [18] in inorganic coating formula. Aluminum phosphate adhesive can be used in the production of silicon, high aluminum, magnesium, silicon carbide and oxide concrete. This inorganic polymer framework has high strength and elastic modulus. since the Al atomic radius is small and the Al<sub>3</sub> coordination number formed is low, the disordered solid can be produced, and finally the stress and strain are absorbed. the adhesive formed after the reaction with phosphoric acid has the optimal adhesion. Therefore, the current binder is the most widely used aluminum phosphate, and plays an important role in refractories, insulating materials, flame retardant materials, adhesive materials and other fields.

## 2.3 Serve as a molecular sieve

The aluminum phosphate (AlPO<sub>4</sub>)-n molecular sieve is a new kind of molecular sieve developed by American UCC Company in 1982. It has new crystal structure and unique properties. Its emergence has attracted the great attention of scientists all over the world, has carried out a large number of research, so far has developed more than 60 such microporous molecular sieve materials. Because the neutral skeleton structure of (AlPO<sub>4</sub>)-n has no ion exchange property and the surface acidity is weak, the modification has been studied. A large number of the same series of molecular sieves have been synthesized by homomorphic replacement of phosphorus and aluminum partially replaced by many elements. they include more than 30 structures similar to (AlPO<sub>4</sub>)-n, skeleton composition of 16 elements and more than 200 chemical compositions. Due to the introduction of heteroatoms into the skeleton of (AlPO<sub>4</sub>)-n, the ion exchange and catalytic properties of aluminum phosphate series molecular sieves are greatly improved. molecular sieves of each configuration show their unique properties in hydrocracking, isomeric alkylation, polymerization, reforming, hydrogenation, dehydrogenation, hydration, etc. Hydrothermal synthesis and solvothermal synthesis are the main synthesis methods of aluminum phosphate molecular sieves. With the development of synthetic chemistry, aluminum phosphate molecular sieves are developing towards high stability and high order. Some new modification techniques have emerged. Aluminum phosphate molecular sieve has a new skeleton structure and unique properties. As an adsorbent and catalyst material, it plays an important role in petroleum refining industry.

## 2.4 Serve as special cement

Aluminum phosphate cement is one of the main components of special cement, which is used as thermal equipment material in metallurgy and building materials industry. Aluminum phosphate cement is used in building materials industry for thermal units lining, metallurgical industry Martin furnace and capacitor furnace lining. It is characterized by high fire resistance, no shrinkage, high strength and wear resistance. The life of refractory masonry with aluminum phosphate cement is about 4 times larger than that of traditional masonry mortar and other masonry materials. In addition, aluminum phosphate cement can also be used in the manufacture of instruments, the instruments on large equipment can be used for thermal protection with aluminum phosphate insulation materials, and in the power industry to produce heat-resistant insulation products.

## 3. Prospects

At present, aluminum phosphate materials have played an important role in various sectors of the national economy. In order to expand its application, various efforts should be made: (1) For aluminum phosphate adhesives, it should be developed in the direction of environmental protection, functional and special type, develop adhesives used under extreme conditions, apply new technologies to adhesive production, and develop from two-dimensional bonding to three-dimensional technology. (2) Optimizing the synthesis process of aluminum phosphate molecular sieves, reducing the synthesis cost of aluminum phosphate molecular sieves and rationally modifying aluminum phosphate molecular sieves are the future research and development trends of aluminum phosphate molecular sieves. (3) Increasing bond strength and reducing brittleness should be the key points in the research of aluminum phosphate cement. (4) The structural and physicochemical properties of

aluminum phosphate make it a promising coating material in the field of high temperature and anti-oxidation.

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