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Corrosion Protection on the Surface of Waterborne Aluminum Pigments by Sol-Gel Method

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The aluminum pigments were coated with SiO_2 by sol-gel method using tetraethoxysilane as precursors to improve their stability. The effects of formulation factors, such as dosage of tetraethoxysilane, water and ammonia solution, reaction temperature and reaction time on the corrosion protection efficiency and coater gloss were investigated. The results showed that under the optimum conditions, the corrosion protection efficiencies reach 98.9 % and 99.1 % in acid media of pH 1 and alkaline media of pH 11, respectively and the coater gloss is 86.5. By the characterization of scanning electron microscopy, Fourier transformation infrared spectroscopy and X-ray diffraction, SiO_2 was proved to be coated on the surface of the as-prepared waterborne aluminum pigments and the reaction conditions were optimized.

Key Words: Aluminum pigment, Sol-gel method, Acid and alkaline corrosion, Tetraethoxysilane.

INTRODUCTION

Aluminum pigments are a kind of ultrathin flaky aluminum powders and have been widely used as a metallic pigments in automotive paint, industrial paint, printing inks and plastic materials for their protective and decorative functions during the last two decades[1]. Recently, growing importance of environmental aspects has led the paint and coatings industry to the development of coating systems with a reduced content of volatile organic compounds[2,3]. Waterborne coatings are the favoured way to solve the problem. However, ordinary aluminum pigments cannot meet the requirements of the waterborne paint, because they may be corroded in the waterborne paint to emit hydrogen gas according to the following reaction, resulting in a dangerous pressure buildup in container and the degradation of metallic luster.

In neutral or acid media:

$$Al + H_2O \rightarrow Al_2O_3 + H_2\uparrow \quad (1)$$

In neutral or alkaline media:

$$Al + H_2O \rightarrow Al(OH)_3 + H_2\uparrow \quad (2)$$

These results in severe deterioration of metallic luster and dangerous pressure build up in the storage vessels[1-7]. The methods adopted for aluminum pigments stabilization in aqueous media can be divided into two principal categories:[8] the adsorption of corrosion inhibitors on the pigment surface[1,3-7,9-18] and the encapsulation of the pigment with a protective coating[2,8,19-22]. The encapsulation method is more promising since the protective layer can insulate the aluminum pigments from the corrosion medium. Inorganic coatings, such as SiO_2, show excellent mechanical strength, but poor compatibility with resins and other organic compounds contained in waterborne coatings. In regard to organic coatings, the poor adhesion of the coating material to the aluminum surface greatly limits their application. The combination of inorganic and organic compounds for the encapsulation of the aluminum pigments may be more effective and promising, but few reports can be found in this field till now. Furthermore, up to now, the long-term stability of aluminum pigments in acid or alkaline media has not been solved completely.

The sol-gel process, involving the hydrolysis and condensation of the alkoxides [typically tetraethoxysilane (TEOS)], has been used for corrosion protection of aluminum by the formation of the sol-gel film as a barrier layer on the aluminum surface[3,8]. In this paper, aluminum pigments encapsulated by TEOS in sol-gel process were reported. Reaction conditions were analyzed and optimized to obtain the encapsulated aluminum pigments with excellent coating gloss and stability in acid and alkaline media.

EXPERIMENTAL

Raw materials used are listed in Table-1. Aluminum pigments (median particle size of 30 μm) were washed with ethanol and distilled water before encapsulation, then dried under vacuum at 50 ºC. Tetraethoxysilane was purified by distillation prior to use. Absolute ethanol and ammonia solution were used as received without further purification.

Encapsulation: Two grams of aluminum pigments and 50 mL of ethanol were put into a four-neck round bottom flask connected to a condenser, thermometer and nitrogen gas inlet/outlet. The solution was stirred at room temperature for 1 h and then heated to a certain temperature (30-70 ºC). Ammonia (1-9 mL) and distilled water (2.5-12.5 mL) were diluted with 30 mL ethanol; tetraethoxysilane (2-3 mL) was also diluted with 30 mL ethanol and then were added drop-by-drop over a period of 1 h to the solution simultaneously. The solution was further stirred for 6 h and then filtered and the residue washed with ethanol. The resulting pigments were dried under vacuum at 60 ºC for 5 h.

TABLE-1
RAW MATERIALS

Materials	Grade	Manufacturer
Aluminum pigments	≥ 99 %, -30 μm	Huicai Trade Co. Ltd.
Absolute ethanol	≥ 99.7 %	Fuyu Fine Chemical Industry Co. Ltd.
Ammonia solution	25-28 %[a]	Dongda Chemical Co. Ltd.
Tetraethoxysilane	≥ 28 %[b]	Jizhun Chemical Reagent Co. Ltd.
Distilled water	Home made	-

[a]NH_3 content; [b]SiO_2 content

Corrosion protection efficiency: To evaluate the effect of the encapsulation described in this paper, the stability test was carried out. 0.1 g of the encapsulated or unencapsulated aluminum pigments were dispersed in H_2SO_4 solutions of pH 1 for stability test in acid media and in NaOH solutions of pH 11 for stability test in alkaline media respectively. The suspension was put in 60 mL glass bottles and stored at room temperature for 24 h. The hydrogen evolved was collected to estimate the effect of the encapsulation. The corrosion protection efficiency (η, %) was calculated using the following equation:

$$\eta = \frac{V_0 - V}{V_0} \times 100\% \quad (3)$$

where the V_0 and V are the evolved hydrogen volume of the unencapsulated and encapsulated aluminum pigments in the stability tests, respectively.

Coating gloss: The encapsulated aluminum pigments, thinners and resins were stirred as the mass ratio is 1:2:3, then coated on the glass slide by the QGX type bar, natural drying. The coating gloss measurements were carried out by using KGZ-1C type glossmeter to characterize the coating gloss of the pigments.

Surface morphology: Fourier transformation infrared measurements were carried out by using a Bruker Vector 33 spectrometer to characterize the functional groups of the pigments. The samples were ground with dried potassium bromide (KBr) powder and compressed into a disc. The KBr disc was subjected to analysis by an IR spectrophotometer. The scanning electron microscopy (SEM) investigations were performed with a JSM-6700F. X-ray diffraction (XRD) spectra were obtained on XRD-7000.

RESULTS AND DISCUSSION

Effect of the ratio of TEOS: When the mass ratio of water, ammonia solution and naked aluminum pigments is 28:0.85:1, the reaction temperature is 50 ºC and the reaction time is 8 h, the effect of the ratio of TEOS (m_{TEOS}/m_{Al}) was inspected on waterborne aluminum pigments corrosion protection efficiency (Fig. 1) and coating gloss (Fig. 2).

It can be seen in Fig. 1 that when TEOS dosage is only 1, the hydrogen evolution and corrosion protection efficiency is the lowest. This is because hydrolysis-condensation of SiO_2 generated amount is too small so that the surface of the aluminum pigments are not fully covered and only a loose SiO_2 films can not play a better protective effect of pigments. It can be seen that when the TEOS dosage increasing, corrosion protection efficiency also increase. However, when the TEOS dosage is 1.3, the corrosion protection efficiency is increasing marginally. This may result from hydrophobicity and compactness of the sol-gel SiO_2 films, less effect on the corrosion protection efficiency.

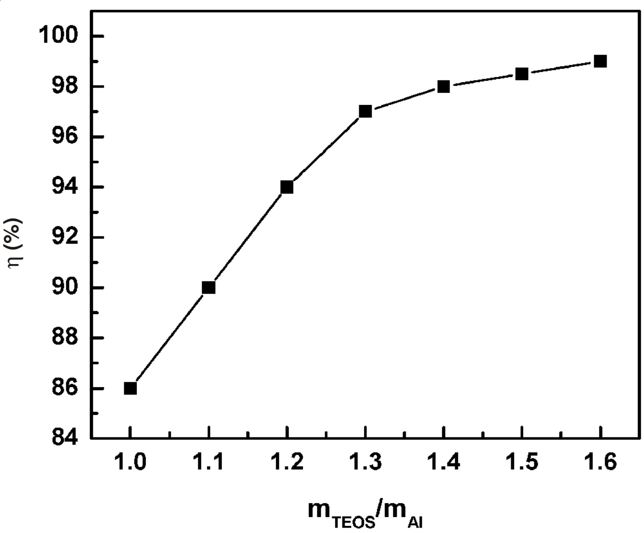

Fig. 1. Effect of TEOS dosage on corrosion protection efficiency

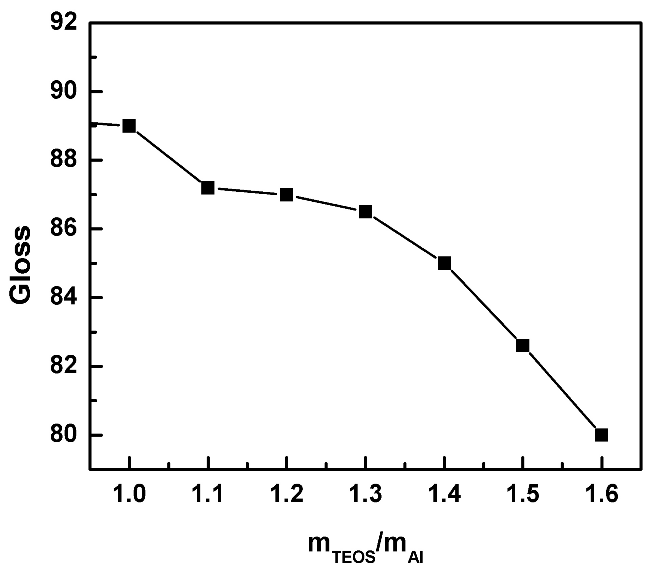

Fig. 2. Effect of TEOS dosage on coating gloss

As showed in Fig. 2, with the amount of TEOS increasing, coating gloss almost linear decline. This is due to SiO_2 as a milky white translucent material. When SiO_2 coating thickness increases, the absorption of light, refraction and scattering enhance.

Considering the corrosion protection efficiency of waterborne aluminum pigments and coating gloss, comparing of different samples has been showed in Figs. 1 and 2, aluminum pigments encapsulated at the ratio of $m_{TEOS}/m_{Al} = 1.3$ show best stability, which corrosion inhibition efficiency of waterborne aluminum is 97 % and coating gloss is 86.5.

Effect of water: As known of TEOS hydrolysis - condensation reaction, water is both a reactant and resultant in the reaction system, which has a very important influence on the chemical balance of the whole reaction.

In the hydrolysis reaction, water is a reactant:

$$Si(OC_2H_5)_4 + H_2O \rightarrow Si(OH)_4 + C_2H_5OH \quad (4)$$

In the condensation reaction, water is the resultant:

$$Si(OH)_4 + Si(OH)_4 \rightarrow (HO)_3Si\text{-}O\text{-}Si(OH)_3 + H_2O \quad (5)$$

When the amount of silane and ammonia is kept constant, increasing the amounts of water will greatly promote the rate of hydrolysis[23].

When the mass ratio of TEOS, ammonia solution and naked aluminum pigments is 1.3:0.85:1, the reaction temperature is 50 ºC and the reaction time is 8 h, the effect of the ratio of water (m_{H_2O}/m_{Al}) was inspected on waterborne aluminum pigments corrosion protection efficiency (Fig. 3). When water dosage is 20 mL, the corrosion protection efficiency is low. This is because that the amount of water is not enough to make TEOS fully hydrolyzed and the product of high activity $Si(OH)_4$ generates less difficult to form a uniform and dense coating. From Fig. 3, we can find that when the water dosage is 28, the encapsulated aluminum pigments display best stability. At this point, the concentration of active product $Si(OH)_4$ keeps at relatively high level. Si-OH in the surface of the aluminum pigments is fully adsorption and polymerization to form three-dimensional short key cross-linked structure, the gel is uniform and compact coated on the aluminum surface. However, water dosage is too large so that it will be diluted to generate a single silicate concentration and lead to the formation of silicon - oxygen bond to hydrolysis, indirectly lead to the extension of the gel time, thus affecting the coating effect. Therefore, water dosage should be controlled at about 28 mL.

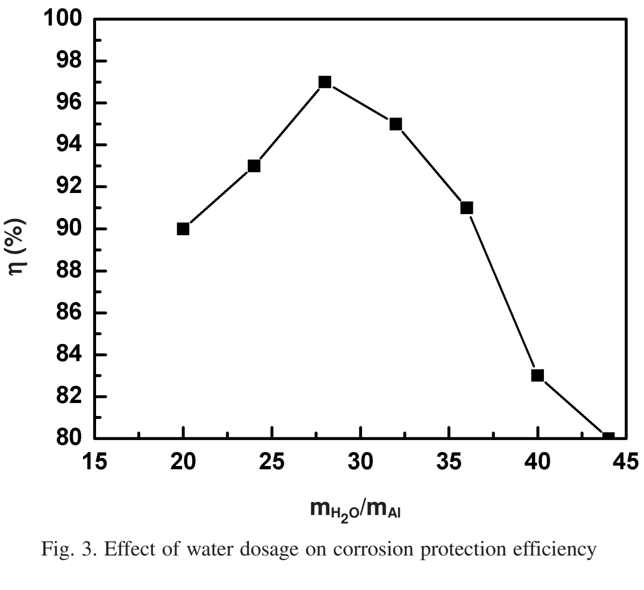

Fig. 3. Effect of water dosage on corrosion protection efficiency

Effect of ammonia: When the mass ratio of TEOS, water and naked aluminum pigments is 1.3:28:1, the reaction temperature is 50 ºC and the reaction time is 8 h, the effect of the ratio of ammonia (m_{NH_3}/m_{Al}) was inspected on waterborne aluminum pigments corrosion protection efficiency (Fig. 4). When ammonia dosage is 0.25, the corrosion protection efficiency is low. This is because the ammonia concentration is too low, affecting the rate of TEOS hydrolysis and condensation, the activity of SiO_2 concentration decreases, thereby affecting the aluminum flake coating. Increase the ammonia dosage and the corrosion protection efficiency can be improved significantly. However, ammonia dosage should not exceed 0.85, otherwise the pH value increased and exacerbated by the hydrogen evolution reaction, which affects the coating effect.

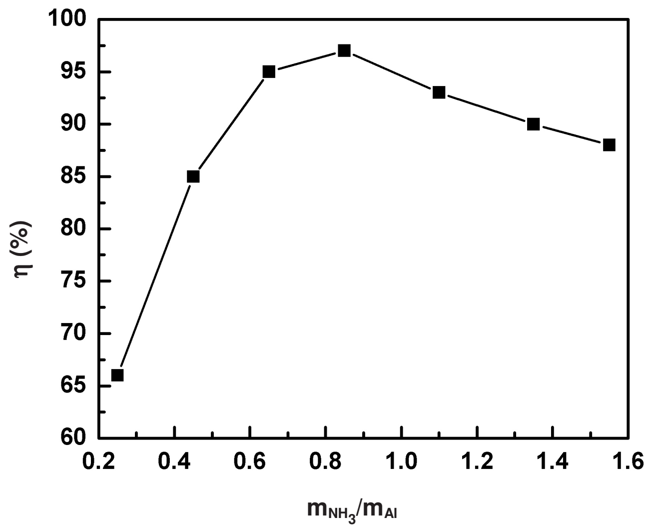

Fig. 4. Effect of ammonia dosage on corrosion protection efficiency

Effect of reaction temperature: When the mass ratio of TEOS, water, ammonia solution and naked aluminum pigments is 1.3:28:0.85:1 and the reaction time is 8 h, the effect of reaction temperature was inspected on waterborne aluminum pigments corrosion protection efficiency (Fig. 5). Fig. 5 shows that at low temperature the corrosion protection efficiency of encapsulated aluminum pigments are poor. It is because the rates of hydrolysis and condensation of silane depend on reaction temperature. It was reported that under basic condition, the condensation of siloxane is much faster than the hydrolysis and the condensation species participate in nucleation at once and retain a very low concentration[24]. When the reaction temperature is low, the rate of hydrolysis is much slower than that of condensation, which indicates that the condensation species participate in nucleation as soon as silanol comes into being. As a result, particles in stead of uniform films are formed on the surface of aluminum pigments, which induces unfavourable barrier layer. On the contrary, the high reaction temperature will result in high nucleation rate. Consequently, the barrier layer is not compact because the amount of silanol absorbed on the aluminum surface decreases. In our experiment, 50 ºC is the optimum temperature for encapsulation of aluminum pigments.

Effect of reaction time: When the mass ratio of TEOS, water, ammonia solution and naked aluminum pigments is

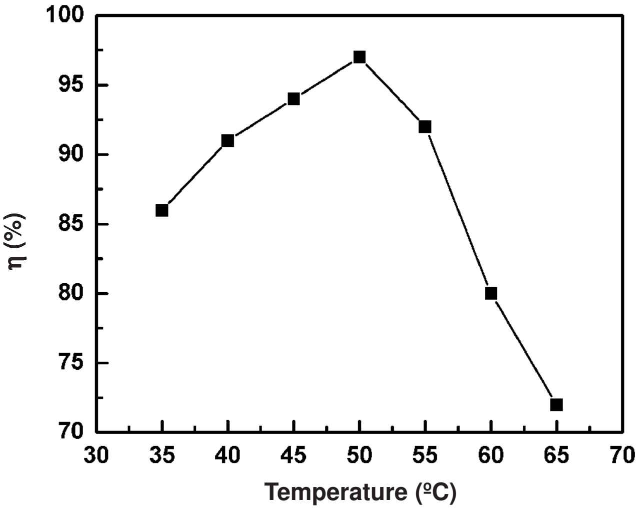

Fig. 5. Effect of reaction temperature on corrosion protection efficiency

1.3:28:0.85:1 and the reaction temperature is 50 ºC, the effect of reaction temperature was inspected on waterborne aluminum pigments corrosion protection efficiency (Fig. 6). When the reaction time is 4 h, due to the TEOS hydrolysis-condensation reaction is not sufficient, the corrosion protection efficiency is low. To extend the reaction time appropriately can promote the activity silicon full condensation and dense SiO_2 coating layer to be generated. Reaction time should not be more than 8 h, if not the coated silicon layer on the aluminum pigments surface is partially hydrolyzed and impacting the coating effect.

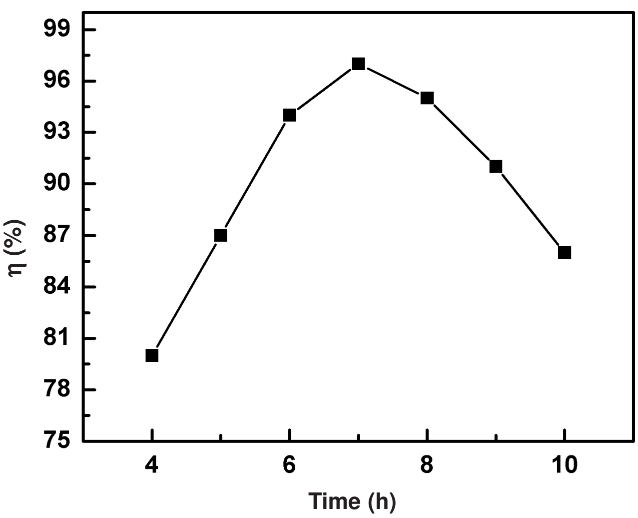

Fig. 6. Effect of reaction time on corrosion protection efficiency

Characterization of waterborne aluminum pigments: The specification of preparing conditions used in our experiment was listed in Table-2.

SEM micrographs of waterborne aluminum pigments and unencapsulated aluminum pigments have been showed in Fig. 7. Fig. 7 indicate that the films formed on the surface of 2# sample aluminum pigments, which surface are attached by the translucent film, are much denser than 1#, 3# and 4# samples. For direct and clear comparison, the stability of uncoated aluminum pigments is also given. From Fig. 7, it

TABLE-2
SPECIFICATION OF PREPARING CONDITIONS IN THE EXPERIMENT

Reaction temp. (ºC)	Reaction time (h)	Mass of aluminum pigments (g)	Mass of TEOS (g)	Mass of water (g)	Mass of ammonia (g)
-	0	1	0	0	0
50	8	1	1.3	28	0.85
65	8	1	1.3	28	0.85
50	10	1	1.3	28	0.85

can be found that the aluminum pigments prepared under optimized conditions exhibit excellent stability both in acid and alkaline media. The corrosion protection efficiency of 2# sample reaches 98.9 %, respectively in acid media of pH 1. In alkaline media of pH 11, the corrosion protection efficiency of 2# sample is 99.1 % respectively. The results of stability test reveal that using TEOS as precursors in the sol-gel process can provide aluminum pigments sufficient protection in acid and alkaline media.

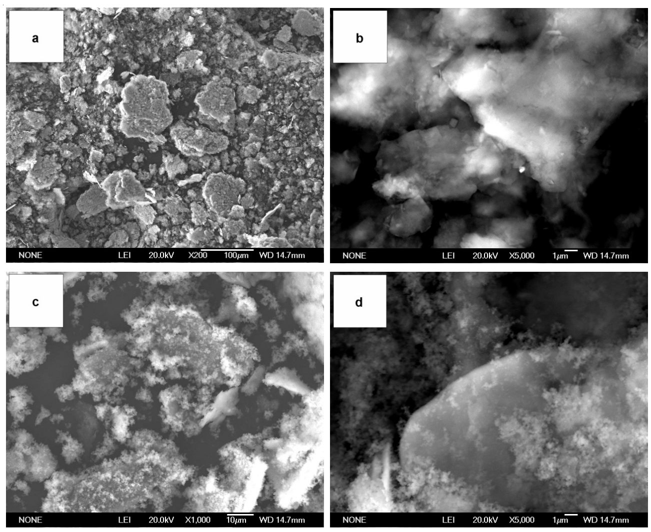

Fig. 7. SEM micrographs of aluminum pigments: (a) 1#; (b) 2#; (c) 3#; (d) 4#

The FTIR spectra of waterborne aluminum pigments and unencapsulated aluminum pigments have been shown in Fig. 8. Comparing Fig. 8a and b, both the waterborne aluminum pigments and unencapsulated aluminum pigments in the 3400 cm^{-1} have appeared in the vicinity of a broad peak, which is the absorption peak of the structure of water. Comparing the unencapsulated aluminum pigments the new characteristic peaks of the Si-O-Si asymmetric stretch are assigned to the waterborne aluminum pigments. In addition, the strong absorption peak near 1087 cm^{-1} is assigned to the Si-O-Si asymmetric stretch; the bands near 1120, 950, 799 and 625 cm^{-1} are assigned to the vibration of Si-O-Si, indicating that the Si-OH or Si-OC_2H_5 further condensed in the sol-gel reaction. This further illustrates the waterborne aluminum pigments were coated by SiO_2 on the surface.

Fig. 9 presents the results of XRD measurements for further quantitative analysis of the elements on the surface of aluminum flakes. Comparing Fig. 9a and b, the weak absorption peaks of SiO_2 can also be found in the spectrum of waterborne aluminum pigments at around 2θ = 23º, which means

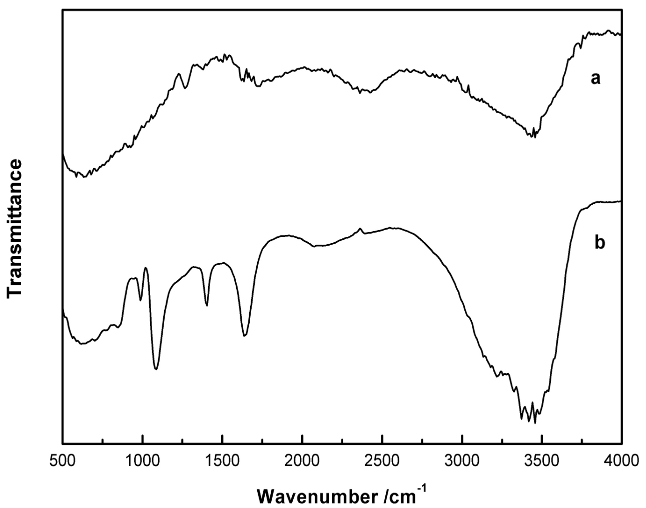

Fig. 8. FTIR spectra of (a) unencapsulated aluminum pigments; (b) waterborne aluminum pigments

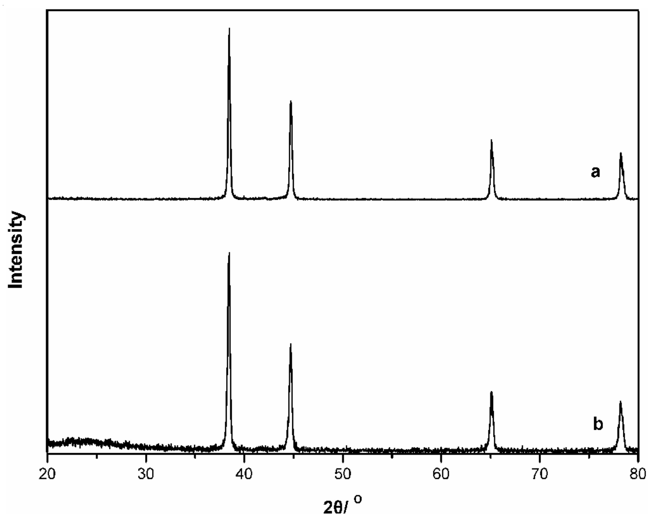

Fig. 9. XRD spectra of (a) unencapsulated aluminum pigments; (b) waterborne aluminum pigments

that the SiO_2 exists on the Al surface. Combined with the front of the FTIR spectra analysis, the peaks are characteristic absorption peaks of SiO_2. Further the coated SiO_2 on the aluminum pigments content is less, so the absorption peak intensity is weak. In addition, the locations of characteristic absorption peaks of coated and uncoated aluminum have not changed. The resulting analysis shows that waterborne aluminum pigments are coated by SiO_2 and SiO_2 on the surface of the aluminum pigment is not only exist in crystal forms, but also exist in amorphous forms. In addition, the aluminum pigment is coated by SiO_2, but its crystal structure has not changed.

Film-forming mechanism of TEOS on aluminum pigments surface: The film-forming mechanism of TEOS in the aluminum pigments surface is shown in Fig. 10. Firstly, in alkaline conditions TEOS occurred of the hydrolysis reaction to generate silanol and then the hydrogen bonds were formed between hydrogen bonds of silanol and aluminum surface. Finally, under heated conditions the silanol hydroxyl and aluminum surface hydroxyl occurred to condensation reaction from Si-O-Al.

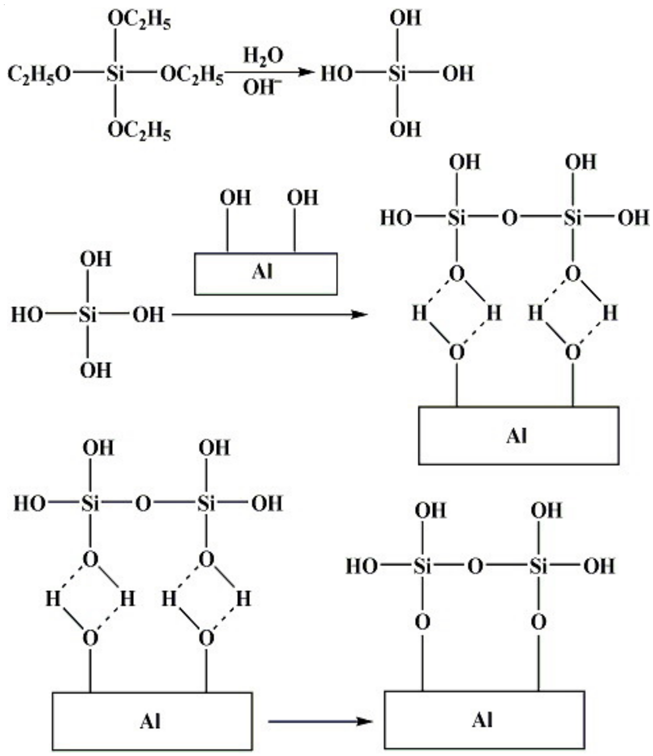

Fig. 10. Film-forming mechanism of TEOS on aluminum pigments surface

Conclusion

In order to improve the corrosion resistance and thermal stability, lamellar aluminum pigments were successfully coated with SiO_2 by sol-gel method. It has been found that ratio of TEOS/Al, reaction temperature, contents of ammonia and water have a crucial influence on the sol-gel film forming on the surface of aluminum pigments and thus on the stability of the encapsulated pigments in corrosion media. The results show that when the mass ratio of TEOS, water, ammonia solution and naked aluminum pigments is 1.3:28:0.85:1, the reaction temperature is 50 ºC and the reaction time is 8 h, the corrosion protection efficiencies under the optimum experimental conditions reach 98.9 % and 99.1 % in acid media of pH 1 and alkaline media of pH 11, respectively and the coater gloss is 86.5. It is found from SEM analysis that the TEOS formed a dense netlike layer on the aluminum surface. The FTIR analysis indicates that TEOS hydrolyzed and consequently condensed in the sol-gel reaction. The shift of Si-O-Si absorption band in the FTIR measurements suggests that TEOS reacted in the sol-gel process. The XRD result indicates that SiO_2 on the surface of the aluminum pigment is not only exist in crystal forms, but also exist in amorphous forms.

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