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Aluminum pigment encapsulated by in situ copolymerization of styrene and maleic acid

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Abstract

To improve its anticorrosion property, aluminum pigment was encapsulated by in situ copolymerization of styrene (St) and maleic acid (MA). It was found that the conversion of monomers (C), the percentage of grafting (PG) and the grafting efficiency (GE) could attain 92%, 12%, 25%, respectively, when m(BPO)/m(St + MA) = 10% and m(St + MA)/m(Al) = 10%. The optimum condition for protection factor was studied according to an orthogonal testing. When m(St + MA)/m(Al) was 20%, the encapsulated aluminum pigment simultaneously showed good anticorrosion property and luster. FTIR, SEM and particle size analysis indicated that aluminum pigment had been successfully encapsulated with styrene–maleic acid copolymer by in situ copolymerization, which remarkably improved its anticorrosion property and the chelate complex formed between SMA and Al(III) was possibly the actual corrosion inhibitor. \bigcirc 2007 Elsevier B.V. All rights reserved.

Keywords: Aluminum pigment; Encapsulate; In situ copolymerization; Styrene; Maleic acid

1. Introduction

It was well known that metallic pigments had been increasingly used in various kinds of application fields. As one of the important metallic pigments, aluminum pigment had been widely used in plastic, printing, inks, and painting industries for many years because of its shiny appearance, excellent properties, and cheap price [1–3]. Flaky aluminum pigment acted as tiny mirrors and selectively reflected light close to special angle, which was known as flip-flop effect, so it had been gradually applied in automotive, mobile and computer industries in the recent 5 years. However, a severe problem is the corrosion reaction of aluminum pigment in aqueous acidic or alkali painting media, which causes the evolution of hydrogen. The corrosion reactions are listed in following [4,5]:

 $2Al\,+\,3H_2O\rightarrow Al_2O_3+3H_2\uparrow$

 $2A1 + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2 \uparrow$

$$2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2$$

A disadvantageous consequence of the corrosion reaction is that the color of aluminum pigment changes from silver to grey. Furthermore, it may lead to a dangerous pressure buildup in container [6]. Therefore, corrosion inhibition is necessary. Many methods have been considered to improve its anticorrosion property in aqueous painting media. All of them can be divided into two principal categories: the adsorption of corrosion inhibitors on the pigment surface and the encapsulation of the pigment with a protective coating. Müller described that nitro- and aminophenols could be effective inhibitors for aluminum and zinc pigments [7,8]. El-Etre reported that anticorrosion property of aluminum pigment could be improved by using opuntia extract [9]. Karlsson et al. [6] reviewed the surface modification of aluminum pigment inhibition, and listed many inhibitors, such as fatty acids, polyelectrolyte, and chromate. Silica-coated aluminum pigment with excellent weather fastness was prepared by Kiehl and Greiwe through sol-gel method [3]. Colored aluminum pigment coated with either single layer (Fe₂O₃) or double layer (Fe₂O₃ on SiO₂) were synthesized and characterized by Smith et al. [10].

In accordance, in situ polymerization had been of interest as a powerful technique for preparing polymer/inorganic particle composite, and many efforts had been made to synthesize

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composite particles. Liu et al. prepared silica composite particles by in situ chemical graft polymerization [11] and twosteps UV induced reaction [12]. Bourgeat-Lami and Lang made use of dispersion polymerization to encapsulate inorganic particles with polymer [13,14]. Esumi had studied the interactions between surfactants and particles on the basis of conventional measurements such as particle size and zeta potential [15].

In the present work, in order to improve its anticorrosion property, aluminum pigment was encapsulated with styrene– maleic acid copolymer (SMA) by in situ copolymerization.

2. Experimental

2.1. Materials

Aluminum pigment (from Changsha Aote Metallic Pigment Co. Ltd., China) was dried in vacuum at 100 °C for 24 h before use. Styrene (St, from Guangzhou Chemical factory, China) was washed with dilute alkali solution and deionized water, dried over calcium chloride, and distilled under reduced pressure. Maleic acid (MA, from Shanghai Chemical Reagent Plant, China) and initiator, benzoyl peroxide (BPO, from Tianjin Chemicals Co. Ltd., China), were recrystallized before use. All other reagents were of analytical grade and used as received.

2.2. Experimental process and characterization

Into a four-necked round-bottomed flask equipped with a stirrer, a thermometer, a reflux condenser and a guttate funnel, MA and toluene were first added. When MA dissolved completely, St and aluminum pigment were added. When the mixture was stirred to give a homogenous solution, toluene solution of BPO was added into flask by guttate funnel at 50 °C under nitrogen flowing. Then the temperature of the reactant was slowly increased to 80 °C and reacted for several hours. After the reaction, the mixture was precipitated with methanol and filtered. The cake was dried in vacuum for 24 h and encapsulated aluminum pigment was obtained.

In order to determine the quantitative grafted and nongrafted SMA in encapsulated samples, a certain amount of encapsulated aluminum pigment was dispersed in acetone, and centrifuged (10,000 rpm) for 1 h. The filtrate was precipitated with methanol again and non-grafted SMA was obtained. The cake was then extracted with acetone for 24 h, and SMAgrafted aluminum was obtained. The evolved hydrogen detection in the reaction between aqua regia and aluminum was employed to measure the content of aluminum in SMAgrafted aluminum. Therefore, the conversion of monomers (C), percentage of grafting (PG) and grafting efficiency (GE) were calculated according to the following equations [16]:

$$C = \frac{\text{total SMA}(g)}{\text{monomer used}(g)} \times 100\%$$
$$PG = \frac{\text{grafted SMA}(g)}{\text{aluminum pigment used}(g)} \times 100\%$$

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$$GE = \frac{\text{grafted SMA}(g)}{\text{total SMA}(g)} \times 100\%$$

The corrosion reaction of aluminum pigment in 0.1 M HCl solution was determined hourly by volumetric measurement of the evolved hydrogen over a period of 3 days at room temperature, and protection factor (J) was calculated according to the following relationship [17]:

$$I = \frac{V_0 - V}{V_0} \times 100\%$$

where V_0 and V were the hydrogen volume evolved from the unencapsulated and encapsulated sample immersed in 0.1 M HCl solution after 3 days, respectively.

AVATAR infrared spectrometer was used for the Fourier transform (FTIR) spectroscopy analysis of aluminum pigments. The morphology of encapsulated samples was characterized with a JEM-1200EX/S scanning electron microscope (SEM). The average particle size of aluminum pigment was determined by a Zetasizer 3000 HSA analyzer (MALVERN).

3. Results and discussion

3.1. Investigations of C, PG and GE

Fig. 1 shows the effect of initiator amount on the C, PG and GE. As can be seen, C, PG and GE increases to 92%, 12% and 25%, respectively, with the increasing m(BPO)/m(St + MA). In addition, when m(BPO)/m(St + MA) reaches 10%, all three values are becoming nearly "saturated". In fact, too much initiator may lead to formation of SMA with low molecular weight and self-polymerization of St, which is unfavorable to in situ copolymerization of St and MA onto the surface of aluminum pigment. Furthermore, based on the kinetic theory that initiator amount has an important influence on the copolymerization rate, BPO concentration could not be too low. So 10% of m(BPO)/m(St + MA) is selected for the further experiments.

At the same time, the amount of monomer is one of the important impacting factors on in situ polymerization. Fig. 2



Fig. 1. The effect of m(BPO)/m(St + MA) on C, PG and GE.

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Fig. 2. The effect of m(St + MA)/m(Al) on C, PG and GE.

demonstrates the effect of monomer amount on C, PG and GE. It is found that C is not dependent of m(St + MA)/m(Al), because it mainly depends on initiator amount, reaction temperature, and time. However, PG increases and GE decreases, with increasing m(St + MA)/m(Al). It can be interpreted that, under the same conversion of monomers, higher m(St + MA)/m(Al) may result in more total SMA (including grafted and non-grafted SMA). PG mainly depends on grafted SMA, yet GE is relevant to grafted SMA and non-grafted SMA. In short, when m(St + MA)/m(Al) is 10%, both PG and GE reach a satisfactory result.

3.2. The analysis of orthogonal test according to J

In order to obtain the optimum condition according to *J*, an orthogonal test $(L(9)_3^4)$ with four affecting factors and three levels was designed in Table 1. And the analysis of orthogonal test was listed in Table 2. As can be seen, the *J* of all the encapsulated aluminum pigments is above 70%. That is to say, the anticorrosion property of samples encapsulated with SMA has been remarkably improved. In addition, it is concluded that the sequence of affecting extent is A (reaction temperature), C (n(St)/n(MA)), B (reaction time), and D (adding mode). The optimum condition is $A_2B_3C_3D_2$, namely, reaction temperature is 80 °C; reaction time is 4 h; n(St)/n(MA) is 1:0.9; feeding mode is only BPO dropped.

Firstly, temperature is the most remarkable factor that affects the encapsulation. Low temperature may lead to slow initiating rate and incomplete conversion, which results in formation of SMA with wide molecular distribution. On the contrary, since copolymerization between St and MA is of exothermic reaction type, increasing temperature will prevent the equilibrium of

Table 1				
The confirmation	of affecti	ng factors	and	levels

Table 2	
The orthogonal analysis according to protection factor	

Sample number	А	В	С	D	J (%)
1	1	1	1	1	72.0
2	1	2	2	2	80.0
3	1	3	3	3	85.0
4	2	1	2	3	90.5
5	2	2	3	1	92.4
6	2	3	1	2	96.8
7	3	1	3	2	85
8	3	2	1	3	73.9
9	3	3	2	1	82
Ι	79.0	82.5	80.9	82.1	
II	92.2	82.1	84.2	87.3	
III	80.3	87.9	87.5	83.1	
R	14.2	5.8	6.6	5.1	

chemical reaction. Furthermore, too high temperature may lead to the agglomeration of aluminum pigment, which is detrimental to in situ copolymerization of St and MA. Secondly, if the reaction time is too short, the reaction is not complete and the conversion of monomers is low. So long polymerizing time is preferred. Thirdly, as far as radical copolymerization is concerned, the proportion of two monomers plays an important role in molecular weight and molecular structure. According to the reactivity ratios for MA-St copolymerization ($r_1 = 0.018$ and $r_2 = 0.074$) [18], the resulting copolymer has an alternating structure. Although MA does not polymerize homogenously, St has the tendency to polymerize homogenously. So a little excess of St is advantageous to the in situ copolymerization between St and MA. Finally, feeding mode is of importance to encapsulation. When aluminum pigment and monomer are first added to the reaction system, the adsorption of monomer onto the surface of aluminum powder bears high probability, which is beneficial to in situ copolymerization of St and MA from aluminum pigment. In addition, gradually dropped initiator may result in high conversion of monomers.

3.3. Effect of m(St + MA)/m(Al) on J and luster

Anticorrosion property and luster are two important attributes of aluminum pigment. Fig. 3 demonstrates the effect of m(St + MA)/m(Al) on J and luster. It is found that, with increasing m(St + MA)/m(Al), protection factor increases and luster decreases. That is to say, the higher the monomers concentration, the better anticorrosion property, and the darker the luster. So finding out the equilibrium point of anticorrosion property and luster is the key of in situ copolymerization from

Levels	Affecting factors	Affecting factors					
	Reaction temperature A (°C)	Reaction time B (h)	n(St)/n(MA) C	Feeding mode D			
1	70	2	0.9:1	All reactant dropped together			
2	80	3	1:1	BPO dropped only			
3	90	4	1:0.9	Monomer dropped only			

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Fig. 3. Effect of m(St + MA)/m(Al) on J and luster.

aluminum pigment. When m(St + MA)/m(Al) is 20%, the encapsulated samples simultaneously show good anticorrosion property and luster.

3.4. Characterizations and analysis

The FTIR spectra of unencapsulated and encapsulated aluminum pigment are illustrated in Fig. 4. As can be seen, there are only a few absorption peaks in the unencapsulated sample, whereas the vibration bands corresponding to SMA (C-H stretching vibration at 2843, 2951, 1243, 1271, 1387 and 1484 cm⁻¹, the stretching bands of C=C of benzene at 1650, 1495 and 1454 cm^{-1} , bending bands of C-H of benzene at 763 and 704 cm⁻¹, the characteristic absorption bands of the five-circle-structure of acid at 1860, 1780 and 1230 cm⁻¹) are all found in the FTIR of the encapsulated aluminum pigment. Moreover, the chemical shift of C=O from 1720 cm⁻¹ of pure SMA (without aluminum pigment) in literature [19] to 1760 cm^{-1} in the curve of encapsulated aluminum pigment is possibly due to chemical bonding between SMA and aluminum. It indicates that SMA has been successfully grafted onto the surface of aluminum pigment. So it may be speculated that the simplified presentation of



Fig. 4. FTIR spectra of (a) unencapsulated and (b) encapsulated aluminum pigment.

the possible chemical reaction mechanism of anticorrosion of aluminum pigment can be described as Fig. 5. Because it may prevent aluminum pigment from reacting with hydrochloric acid solution, the chelate complex formed between SMA and Al(III) is possibly the actual corrosion inhibitor.

The SEM images of samples 6 and 7 (see Table 2) are demonstrated in Fig. 6a and b, respectively. As can be seen, compared to sample 7, sample 6 is evenly encapsulated, which is consistent with the protection factor. Furthermore, the agglomeration of aluminum pigment occurs in sample 7, which may be attributed to its higher reaction temperature. It can also be estimated from Fig. 6 that average particle size of the sample is about $10-15 \mu m$.

Fig. 7 illustrates the particle size distribution curves of unencapsulated and encapsulated aluminum pigment. It can be found that the particle size distribution shape and region of the two samples are alike, but that the average size is a little different. The size of the latter is a litter bigger than that of the former, which is attributed to the fact that the latter is



Fig. 5. The simplified presentation of the possible chemical reaction mechanism of anticorrosion.

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Fig. 6. SEM images of sample 6 (a) and sample 7 (b).



Fig. 7. Particle size distribution curves of unencapsulated and encapsulated aluminum pigment.

encapsulated with a layer of SMA. At the same time, the result of particle size analysis is consistent with the SEM analysis.

4. Conclusion

To improve its anticorrosion property, aluminum pigment has been encapsulated by in situ copolymerization of styrene (St) and maleic acid (MA). It is found that the conversion of monomers (C), the percentage of grafting (PG) and the grafting efficiency (GE) could attain 92%, 12% and 25%, respectively, when m(BPO)/m(St + MA) = 10% and m(St + MA)/m(Al) = 10%. According to protection factor, the optimum encapsulation conditions are as follows: reaction temperature is 80 °C; reaction time is 4 h; n(St)/n(MA) is 1:0.9; adding mode is BPO dropped only. When m(St + MA)/m(Al) is 20%, the encapsulated samples simultaneously show good anticorrosion property and luster. FTIR analysis indicates that styrene-maleic acid copolymer (SMA) has been successfully grafted onto the surface of aluminum pigment and the chelate complex formed between SMA and Al(III) is possibly the actual corrosion inhibitor. In addition, the encapsulated aluminum pigments were analyzed and characterized by SEM and granularity analysis. Based on above evidences, it is concluded that the anticorrosion property of aluminum pigment has been remarkably improved by in situ copolymerization of St and MA.

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