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ENCAPSULATION OF ALUMINIUM PIGMENTS

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This contribution presents the results of encapsulation experiments aiming to provide aluminium pigments with enhanced stability, to be used in water-borne painting systems. Aluminium pigments milled with fatty acids, milled with Coatosil, washed and dried were encapsulated in SiO_2 matrix using tetraethoxysilane as precursor. Best results were obtained when the pigment was washed and dried, before the encapsulation process.

Keywords: encapsulation, industrial aluminium pigments, tetraethoxysilane

1. Introduction

Aluminium pigments (AP) are widely used in automotive industry, industrial and decorative coatings and printing inks. AP are obtained by milling aluminium flakes with fatty acids and white spirit. AP are traditionally incorporated into solvent-borne formulations. For reasons related to environmental protection, the industry aims to replace the organic solvents with water-borne systems and powder coatings. The main problem is that aluminium easily reacts with water. As a result of this reaction, a large amount of hydrogen is released and the metallic appearance of AP is degraded [1]. Thus, for safety and esthetical reasons, the aluminium surface has to be protected. In aqueous media, AP can be protected by adding chromium-based inhibitors or by encapsulation of the pigment in a protective layer. The later method is less toxic and therefore is preferred by industry [1], [2]. The encapsulation can be done using inorganic polymers (by sol-gel process), organic polymers (by in-situ polymerization) or composite polymers.

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Various organosilanes are widely used as precursors for obtaining (functionalized) inorganic polymers. The general formula of organosilanes involves two classes of functionalities attached to a silicon atom: $R_nSiX_{(4-n)}$. X is a hydrolysable group such as alkoxy, aciloxy, amine, while R is a non hydrolizable organic radical [3]. The simplest alkoxysilane is tetraetoxysilane (also known as tetraethyl ortosilicate, TEOS), with four hydrolysable groups. Other organosilanes used for encapsulation purposes have one organic substituent and three hydrolizable substituents [4].

Many works are based on the sol-gel process involving the hydrolysis and condensation of alkoxides [3], [5-8]. Witucki [9] describes the reaction between silane and the metallic substrate. The mechanism involves the hydrolization of the X group generating silanols groups, condensation of the silanols, hydrogen bonding with substrate and the bond formation with substrate. The encapsulation process is influenced by several parameters, such as concentration of alkoxysilane, catalyst, water, solvent, temperature and pH.

It should be remarked that previously reported experiments used aluminium pigments that were thoroughly conditioned before the encapsulation was performed. Such conditioning requires a long processing time and use of important amounts of solvent, which contribute negatively to the economy of an industrial process. In this work, we present results of aluminium pigments encapsulation, using TEOS as inorganic precursor. In contrast with experiments reported elsewhere, we use industrial-grade aluminium pigments and investigate the effect of pre-treatment on the encapsulation efficiency. The raw materials and the encapsulated pigments were characterized by FTIR and SEM.

2. Encapsulation mechanism

The encapsulation of aluminium pigments with inorganic polymers involves organosilanes, especially alcoxysilanes which have three hydrolizable alcoxy groups and one organic group. The hydrolizable groups lead to Si-O-Si (siloxane) and Si-O-Al bonds. The organic group bond the inorganic part (aluminium pigment) with the organic components of the water-based paint (the resine) [10]. However, TEOS is widely used as precursor in exploratory encapsulation experiments, because it is cheaper and more reactive.

The mechanism of encapsulation using organosilane precursors is described below. When the hydrolysis of the hydrolizable groups takes place, very reactive silanol groups (Si-OH) are formed. The silanol groups condense with other silanol groups to form siloxane bonds (Si-O-Si). Moreover, hydroxyl groups exist on the surface of the aluminium pigment. Therefore, the silanol groups also react with OH radicals from the aluminium surface to form Si-O-Al bonds [4].

Equation (1), (2) and (3) represents the hydrolysis and condensation of the alcoxysilane.

Hydrolysis

$$\mathrm{Si - OR + H_2O \leftrightarrow Si - OH + ROH} \quad (1)$$

Si-bonding, water-forming condensation

$$\mathrm{Si - OH + Si - OH \leftrightarrow Si - O - Si + H_2O} \quad (2)$$

Si-bonding, alcohol-forming condensation

$$\mathrm{Si - OR + Si - OH \leftrightarrow Si - O - Si + ROH} \quad (3)$$

Equation (4) and (5) are the reaction between the hydrolysed /non-hydrolized silane and metal.

Al-bonding, water-forming condensation

$$\mathrm{Si - OH + Al - OH \leftrightarrow Si - O - Al + H_2O} \quad (4)$$

Al-bonding, alcohol-forming condensation

$$\mathrm{Si - OR + Al - OH \leftrightarrow Si - O - Al + ROH} \quad (5)$$

Fig.1 illustrates the formation of an inorganic, protective layer around the aluminium pigment, as result of successive hydrolysis / condensation reactions.

The rate of the hydrolysis reactions should by higher than the rate of condensation reactions. However, it should be emphasized that an encapsulation experiment must achieve the proper ratio between the Si-bonding and Al-bonding condensation, such that a uniform layer of inorganic polymer is formed around the Al pigment. The rate of hydrolysis and condensation reactions are determined by the temperature, the pH, type of alcoxysilane, and reactants ratio [2], [4].

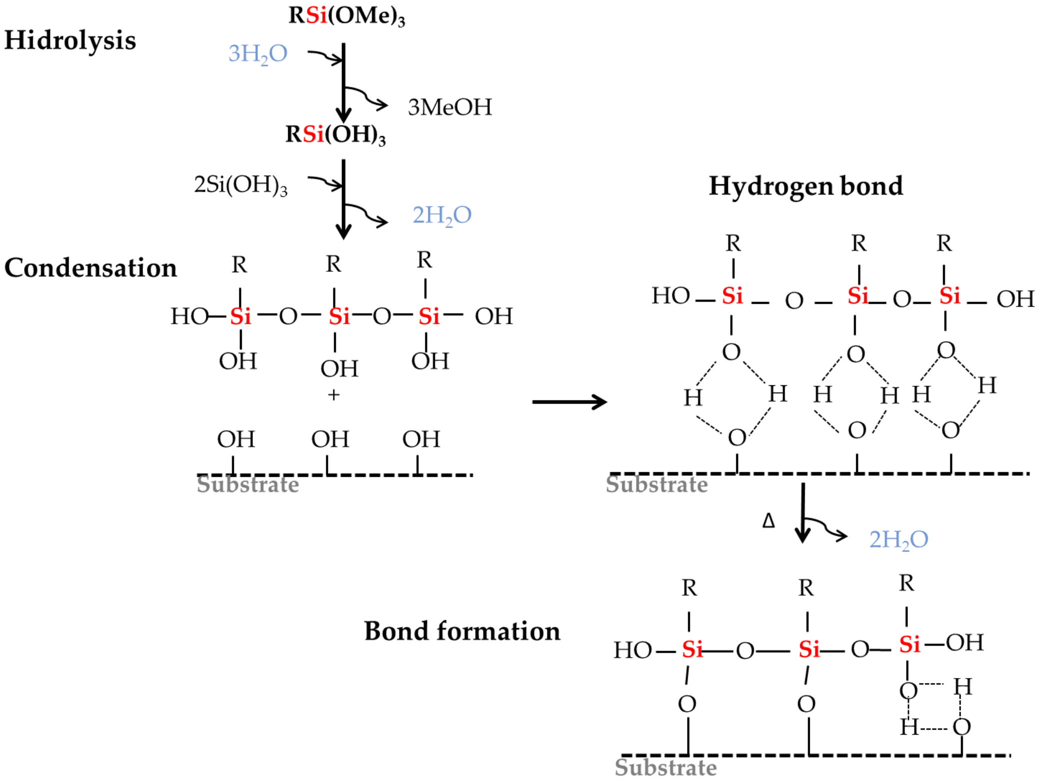

Fig.1. Hydrolysis and condensation reactions occurring during the encapsulation of aluminium pigments

2. Experimental

2.1. Materials

Aluminium pigments (AP) produced by Alba Aluminiu Ltd were used. The particle size distribution of aluminium pigment was determined by CILAS 1064 liquid apparatus. The distribution of AP size is: D_{10}=2.89, D_{50}=11.02, D_{90}=29.38.

In the first set of experiments, AP as obtained in the industrial process (milling with fatty acids, 0.56% grease content) were used. It was expected that the fatty acids might block the access of silanol groups to the aluminium surface, hindering therefore the formation of Si – O – Al bonds. Thus, in a second set of experiments, the aluminium pigments were obtained by milling with Coatosil (an epoxysilane with lubricant properties, produced by Momentive), instead of the usual fatty acids. The grease content of AP obtained in this way was 0.16%.

Finally, the AP were washed with acetone and ethanol and dried for 10 h at 80˚C, before being used in the encapsulation process. The washed-and-dried AP had 0.12% grease content.

Tetraethoxysilane (TEOS), ethanol 99.8% purity, acetone 99% purity, and sodium hydroxide anhydrous pellets 97% purity from Sigma Aldrich were used as received.

2.2. Methods

In order to determine the grease content, which is an important characteristic of aluminium pigments, a pigment mass (M_p) of 5 g is dispersed with 200 mL of acetone. The mixture is heated to boiling temperature, for 2-3 minutes, when the organics (grease) dissolve in acetone. After cooling to room temperature, the mixture is filtered. From the filtrate, acetone is evaporated on sand bath. The residue is kept at 150°C for 15 minutes, and the amount of dry material (M) is determined. The grease content is calculated as $M / M_p \times 100\%$.

5 grams of aluminium pigment (normal pigment / Coatosil-milled pigment / washed-and-dried pigment) was dispersed in 75 ml ethanol (solution 1). Then solution 2 (TEOS in 25 ml ethanol) and solution 3 (NaOH in 5 ml water) were prepared. Solution 1 and 2 were mixed in a flask, stirred and heated. Then, solution 3 was added to initiate the coating reaction. The mixture was stirred for 3-7 h, then washed with ethanol and dried at vacuum and 80˚ C.

The temperature, the volume of TEOS and the amount of basic catalyst were varied, following a 2^3 factorial design of experiments. The ranges of operating parameters are presented in Table 1.

Table 1

Operating conditions

Parameter	Range	
	Minimum	Maximum
Volume of TEOS, ml	2.5	8
Mass of NaOH, g	0.5	2
Temperature, ˚C	30	60
Reaction time, h	3	7
Al / TEOS ratio	0.6	2

The coated aluminium pigments were analyses by Fourier transform infrared spectroscopy (FTIR) and their morphology was determined by scanning electron microscopy (SEM). The stability of the encapsulated aluminium pigments was determined according to industrial standards, by measuring the volume of hydrogen released after contacting AP with boiling water. The stability test indicated that the washed-and-dried encapsulated AP have the best stability.

The scanning electron microscope (SEM) analysis is a method used for characterization of coated AP [1-3], [11]. SEM uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid samples. The signals that derive from electron-sample interactions reveal information about the sample: morphology, chemical composition, crystalline structure and orientation of materials making up the sample. The analyses were performed on a fully PC controlled Tescan - Vega 3 LMH scanning electron microscope, with conventional tungsten heated cathode working in high vacuum. The microscope is equipped with SE and BSE detectors, and EDX spectrometer.

The FTIR analyses were performed on a Thermo Scientific spectrometer, Nicolet iS50 model. The following instrument setup was used: diamond crystal ATR, DTGS-KBr detector, with KBr beamsplitter. The measuring range of this setup is 400 - 4000 cm^{-1}. The number of scans used was 32, with a resolution of 4. The background was collected before each sample.

3. Results

3.1. SEM analysis

The morphology of uncoated and coated normal aluminium pigment is shown in Fig. 2 and Fig. 3. Fig. 4 and Fig. 5 show the uncoated and coated Coatosil-milled aluminium pigments, respectively.

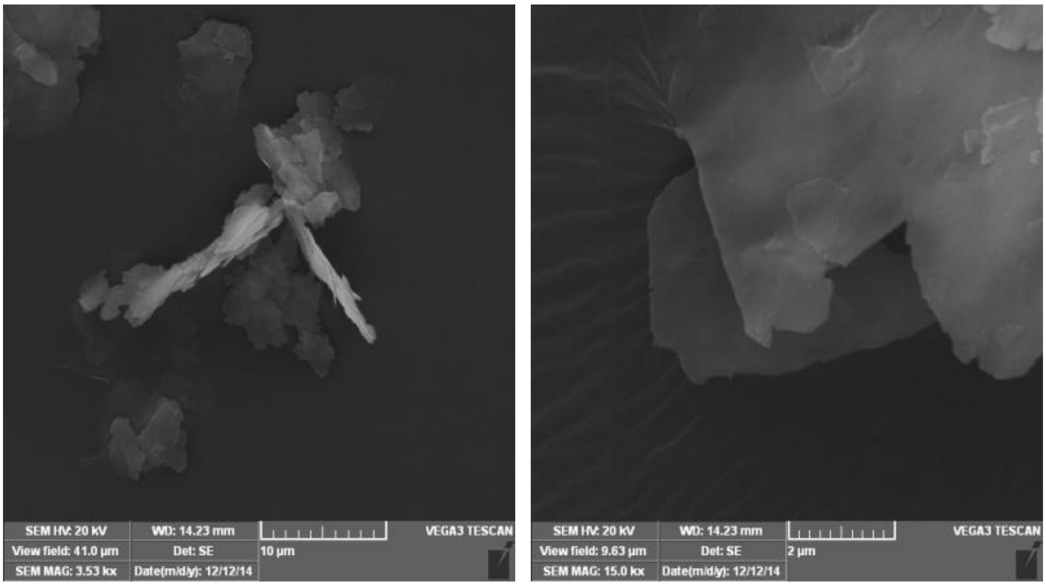

Fig. 2. Morphology of uncoated normal aluminium pigments: left-10µm, right-2µm

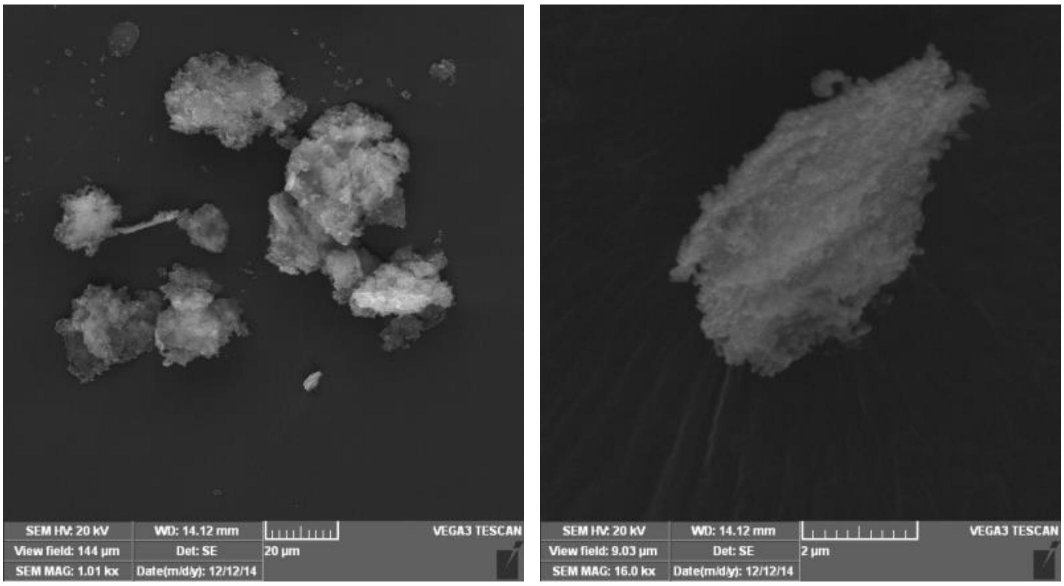

Fig. 3. Morphology of coated normal aluminium pigment: left-20µm, right-2µm

The SEM micrographs of aluminium pigments clearly show morphological differences between the coated and uncoated aluminium pigments: at the same particle dimension, the uncoated AP looks like a flake and the coated AP looks like a cloud, which indicates the formation of an inorganic SiO_2 polymeric layer around the aluminium substrate.

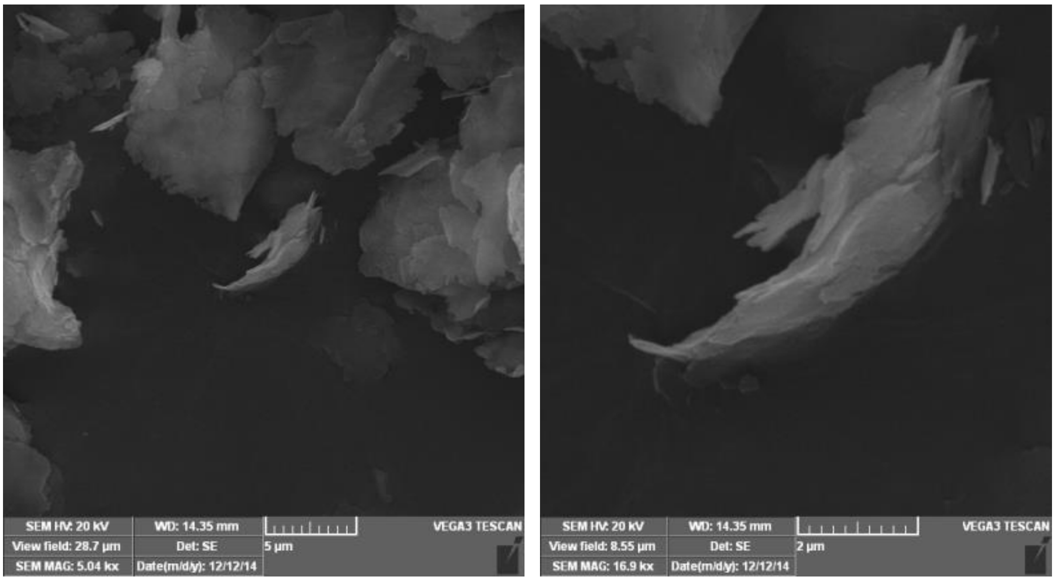

Fig.4. Morphology of uncoated Coatosil-milled aluminium pigment: left-5µm, right-2µm

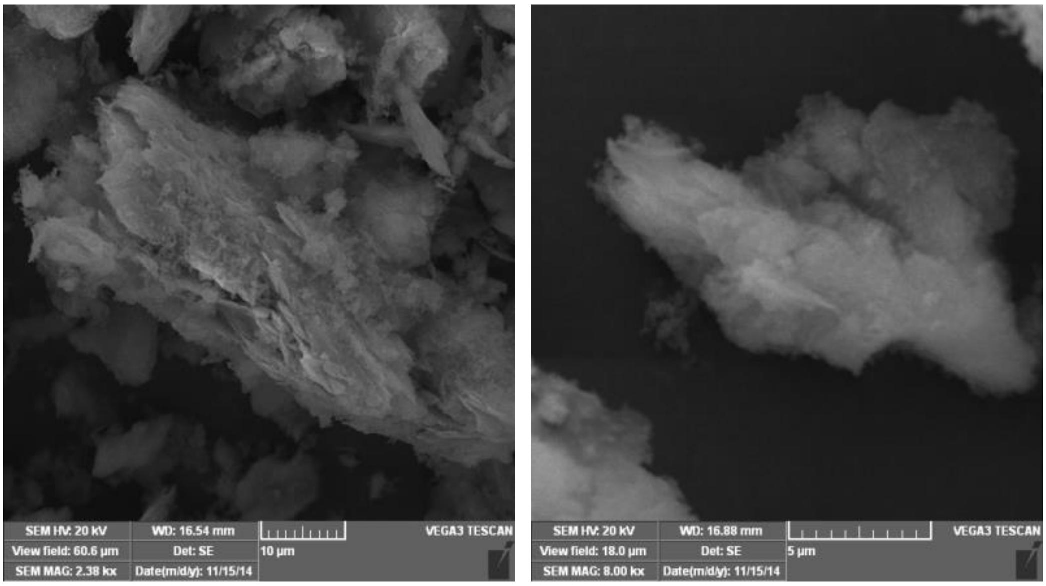

Fig.5. Morphology of coated Coatosil-milled aluminium pigment: left-10µm, right-5µm

3.3. FTIR analysis

FTIR spectra of several samples are presented in Fig. 6. FTIR absorption spectra of encapsulated aluminium pigment described in the literature [11], [12] contain a peak at 1100 cm^{-1}, which is a fingerprint of Si-O-Si bondsvibration. This peak does not appear in the FTIR spectra of the uncoated sample (line 1).

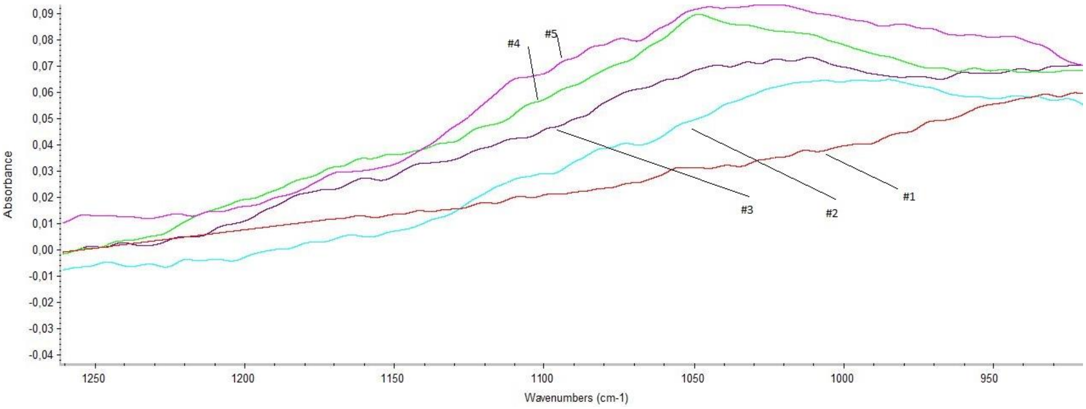

Fig. 6. FTIR spectra for several coated samples of AP and for uncoated AP

Lines 2 – 5 show the spectra of aluminium pigments encapsulated in different conditions. The band near 1100 cm^{-1}, assigned to Si-O-Si bond, indicates pigment encapsulation in a silica matrix. The best encapsulation was achieved in experiment “4”, which shows the biggest Si-O-Si peak (line #4). The conditions of experiment “4” are: reaction temperature 60°C; pH=8.5; 5 grams of Al dispersed in 75 ml ethanol; 7.5 ml of TEOS in 25 ml ethanol.

4. Conclusions

The encapsulation process was applied for aluminium pigment (AP) milled with fatty acids (0.56% grease content), AP milled with Coatosil (0.16% grease content) and AP washed and dried (0.12% grease content). Although the SEM micrographs show encapsulation of normal AP, the stability of the product in water is low. Replacement of fatty acids with Coatosil as lubricant agent did not improve the stability of the coated AP. Best results were obtained when the AP was washed and dried, before the encapsulation process.

Acknowledgement

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