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The preparation and characteristics of pigments based on mica coated with metal oxides

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Abstract

Intensively coloured mica pigments based on mica flakes covered with surface oxide–hydroxide layer of different metals, such as Ti, Cr, Fe, Al, Co, Ni, Zn and Cu were prepared by homogeneous precipitation of metal sulphates with urea in the presence of mica flakes. The final colour was obtained by thermal annealing of precipitates at temperature 150–800 °C.

Keywords: Mica; Urea; Pigment; Homogeneous hydrolysis; Barrier effect

1. Introduction

Mica is a general name for a group of complex hydrous potassium–aluminum silicate minerals that differ in chemical composition; examples are biotite, lepidolite, muscovite, phlogopite and vermiculite. Mica has a low coefficient of expansion, high dielectric strength, good electrical resistance, a uniform dielectric constant and high capacitance stability; at one time it was one the of best electrical and thermal insulators known. The iron content determines its colour. Muscovite is generally grey, green, or brown; biotite is brown or black, lepidolite is pink or green, phlogopite is light brown to yellow and vermiculite is brown. Among mica varieties, muscovite has the greatest commercial value and is the mica that is ground and pulverized into pigment grade.

One of the most important applications of mica is pearlescent (luster, nacreous) pigments [1–3], which consist of transparent mica flakes coated on all sides with a thin layer of metal oxide, mostly titanium dioxide. The presence of a highly refractive and reflective surface layer covering the less refractive support material results in a significant pearlescent effect and provides colours resulting from light interference.

Intensively coloured pigments based on mica particles coated with colour oxides of metals other

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than Ti have been much less studied. Junru [4] prepared cobalt blue mica coated titania pearlescent pigment from solution $Co(NO_3)_2.6H_2O$, $Al(NO_3)_3.9H_2O$, Na_2SO_4 and urea. However, intensively coloured mica pigments and pigments with particle size above 100 μm (for special decorative applications) cannot be prepared using the method described.

In this paper, a method of preparation of intensively coloured lamellar mica particles is described based on the homogeneous hydrolysis of metal sulphates in aqueous media in the presence of mica particles [5]. Besides other applications, the pigments were tested in barrier type corrosion protective coatings.

2. Experimental

2.1. Synthesis of coloured mica pigment

The preparation of surface-treated muscovite was performed using controlled homogeneous hydrolysis, in which a mixture of metal oxides-hydroxides is precipitated onto the lamellar particle surface. Mica fractions of particle size in the ranges 125–250, 250–400 a 400–800 μm were used in this study. 100 g of mica was suspended in 4 l of water, metal sulphates, and urea were added to the mixture which was heated to boiling. The change in pH was continuously followed. The synthesis was complete after reaching pH = 8, which corresponds to a reaction time of 8 h. Completion of reaction was shown by the escape of ammonia developed in the reactor. The mixture was then kept in the reactor under continuous stirring without heating and left to cool to room temperature. The product was obtained by decantation, filtration and drying at 110 °C. The pigment, the dry pigment was annealed at a temperature of 150–800 °C for 2 h.

For the preparation of modified micas commercially available sieved fractions supplied by Garmica Měděnec Ltd. and Elektroisola Ltd. were used. These commercially available micas have a lower delamination degree (thickness above 1 μm) in comparison to perlescent pigment grades and the pigments derived from them were glossy or matt depending on the thickness of the oxide layer and subsequent thermal treatment.

2.2. Characterization methods

The spectral reflectance of the coloured mica was measured using a ColorQuest XE spectrophotometer. The TEM photomicrographs were obtained using a Philips 201 Transmission Electron Microscope and SEM studies were performed using a XL30 Philips CP microscope equipped with EDAX (to determine chemical composition of the observed objects), SE (secondary electron) detector and back scattered (BS) Robinson and solid state BSE detectors (to display the chemical contrast in the observed objects). X-ray powder diffraction was carried out using a Siemens D5005 employing CuK_α radiation (40 kV, 30 mA) and diffracted beam monochromator.

3. Results and discussion

It is known [6] that on heating to 80–100 °C in water, urea decomposes and produces ammonia and carbon dioxide as follows:

$$CO(NH_2)_2 + H_2O = CO_2 + 2NH_3 \quad (1)$$

Free ammonia reacts with metal sulphate on formation hydrolytic product:

$$3NH_3 + Me_2(SO_4)_3 + 3H_2O \rightarrow 2Me(OH)_3 + 3(NH_4)_2SO_4 \quad (2)$$

In the context of the mica pigment preparation used here, due to the action of the urea decomposition products, the pH of the solution increases slowly and homogeneously throughout the whole solution and causes hydrolysis of the metal ion present. In comparison with heterogeneous precipitation, when the neutralizing agent and metal ions solution are mixed and the hydrolysis process is rapid, the process of homogeneous hydrolysis is several orders slower. As such, the formed particles of the hydrolysis products can better develop a crystal structure. The gradual rise in pH results in the nucleation and growth of nanosize particles

of the solid hydrolysis products. Depending on the reaction conditions, these nanoparticles either agglomerate into spherical clusters or can be deposited onto the surface of a suitable substrate present in the reaction mixture [6,7].

The layer of nanoparticles on the mica surface colours the mica particles in various shades depending on the chemical composition of the oxide layer, the crystal structure of the particles, the layer thickness and the annealing temperature. Using various metals for the chemical modification, varied colours have been obtained, namely white, yellow, green, blue, red, black, and a wide variety of golden or bronze shades (Table 1).

The conditions of synthesis and the properties of the prepared pigments are summarized in Table 1. The XRD data show that the samples annealed at temperatures above 700 °C are contain crystalline metal oxide layers (hematite, chromite, spinels, anatase, etc.) whereas samples annealed at lower temperatures were amorphous. The colour scheme for the prepared mica pigments is shown in Table 2.

No destruction or sintering of the mica particles was observed during the annealing process, but only changes of colour, resulting from the crystallization of the layer, occured. Altering the temperature of annealing changed the colour of the pigment. The properties of the final pigment depended on the granularity, mica particle thickness, thickness of the metal oxide deposit and on chemical composition.

Fig. 1 shows a TEM micrograph of a mica particle covered with a layer of α-Fe_2O_3 and Fig. 2 is similar micrograph showing a surface covered with a layer of TiO_2. It can be seen that the layer of hematite (Fig. 1) or anatase (Fig. 2) consists of well distinguishable nanoparticles covering the surface of the muscovite mica. The layer is homogeneous and shows no signs of peeling.

Figs. 3 and 4 show the element mapping of the section of surface-treated Fe-muscovite, obtained by X-ray microanalysis (EDAX detector). Clearly, the muscovite particle bears a uniform oxide layer and the haematite surface layer can be distinguished from the lamellar particle carrier. The thickness of the precipitated Fe_2O_3 layer on the muscovite surface was ~1 μm. No significant amounts of metal oxides precipitated outside the mica surface were observed.

Oxides α-Fe_2O_3 and TiO_2 were seen in the XRD pattern of the metal oxide coated mica pigments. The X-ray diffraction lines corresponding to hematite (PDF 33-0664) and anatase (PDF 21-1272) modification are given in Figs. 5 and 6 respectively. It can be observed that, with the exception of strong muscovite mica diffraction

Table 1
Characteristics of coloured mica samples

Sample	Metal	Metal sulphate (g/l)	Urea (g/l)	Annealing temperature (°C)	Structure of the deposit (XRD)	Pigment colour
1	Fe	1	8	150	Not identified	Light gold
2	Fe	2	10	200	Not identified	Gold
3	Fe	4	12	300	Not identified	Bronze
4	Fe	8	20	400	Not identified	Dark bronze
5	Fe	16	36	800	Haematite	Red
6	Fe, Cu	8; 4	28	800	Cuprospinel	Black
7	Cr	8	20	700	Cr_2O_3	Green
8	Cr, Co	8; 4	28	700	Cochromite	Blue-green
9	Al, Ni	8; 4	28	800	$NiAl_2O_4 + Al_2O_3$	Green
10	Al, Co	8; 4	28	800	$CoAl_2O_4$	Blue
11	Al, Co	8; 2	24	800	$CoAl_2O_4 + Al_2O_3$	Aquamarine blue
12	Ti	16	36	800	Anatase	White
13	Ti, Fe	8; 8	32	800	$TiO_2 + FeTiO_5$	Gold
14	Ti, Co	8; 8	32	800	$TiO_2 + CoTiO_3$	Dark green
15	Ti, Ni	8; 8	32	800	$TiO_2 + NiTiO_3$	Yellow
16	Al, Co Cr	8; 8; 8	52	800	Not identified	Green-blue

pattern, a significantly weaker diffraction pattern of well crystalline haematite (Fig. 5) or anatase (Fig. 6) was also present.

The pigments can be used in various applications. As they are chemically stable and, depending on the composition of the metal oxide layer, they are also ecologically friendly. We successfully tested their use in various applications, such as organic coatings, plastics, glass and ceramics and paper. The pigments based on mica coated with α-Fe_2O_3 exhibited similar properties to the MIOX pigments based on mineral specularite (lamellar form of α-Fe_2O_3) used for barrier type corrosion protection of metal surfaces [8].

Samples on a binder base of epoxyester resin were prepared. A concentration range of 5–30 vol.% coated mica and muscovite in the binder was prepared. The pigment component was replenished by titanium dioxide to an overall pigment volume concentration (PVC) of 60%. In addition the formulation of model coating contains bentonite to improve the rheological properties, and organic and inorganic corrosion inhibitors.

The lamellar mica particles positively affect the coating adhesion to the substrate metal. The adhesion of coating to the substrate, is such that the adhesion of individual layers one to another is tightly connected with phenomena such as the

Table 2
Colour scheme for prepared mica pigments (in system CIE L^*a^*b)

Sample	L^*	a^*	b^*
1	64.37	3.89	13.45
2	56.10	7.99	16.60
3	46.68	9.40	13.09
4	62.01	11.18	10.44
5	39.39	7.11	3.83
6	39.24	1.62	0.62
7	55.91	−5.33	0.50
8	45.40	−5.33	0.50
10	59.90	−7.32	−12.26
11	49.27	−3.80	7.61
13	62.31	15.62	28.22
16	59.29	−7.89	−2.82

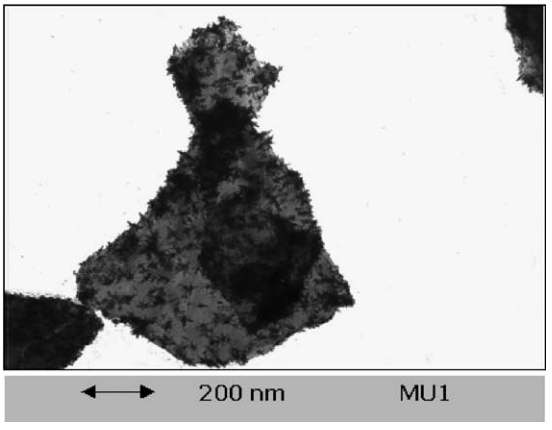

Fig. 1. Muscovite with layer of Fe_2O_3.

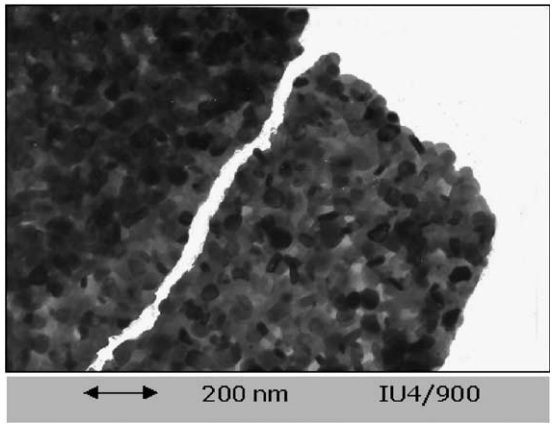

Fig. 2. Muscovite with layer of TiO_2.

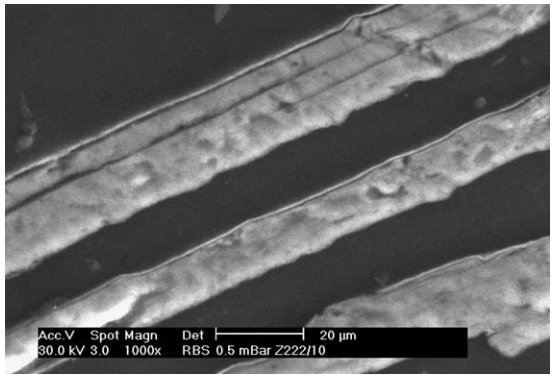

Fig. 3. Cross section through the surface-treated Fe-muscovite (SEM).

osmotic blistering, peeling and cracking of the coating films. The anticorrosion function of the coating consists in a prerequisite that if no mechanical failure of the protective film takes place the corrosion of the substrate does not spread. Fig. 7 quantifies the adhesion coating strengths depending on lamellar pigment amounts.

The corrosion testing results obtained with the epoxyester coatings pigmented with modified mica and untreated muscovite, show an outstanding improvement in coating resistances to osmotic blistering. The appearance of blisters in the coating film is the result of reduced adhesion of the film to the substrate and local corrosion under the blister arch. The evaluation of blister sizes and frequencies was performed following corrosion using the ASTM D 714-87. ASTM D 714-87 classifies the osmotic blisters in groups according to size designated by figures of 2, 4, 6, and 8

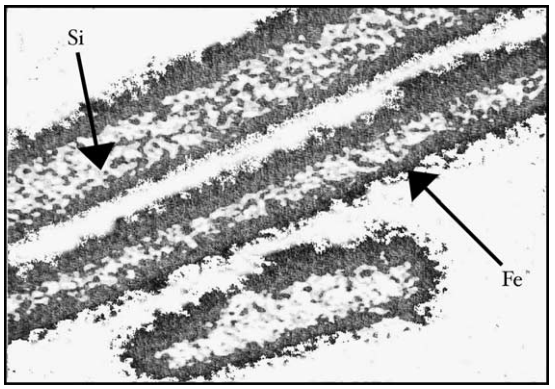

Fig. 4. Surface analysis performed at the Fe-muscovite section.

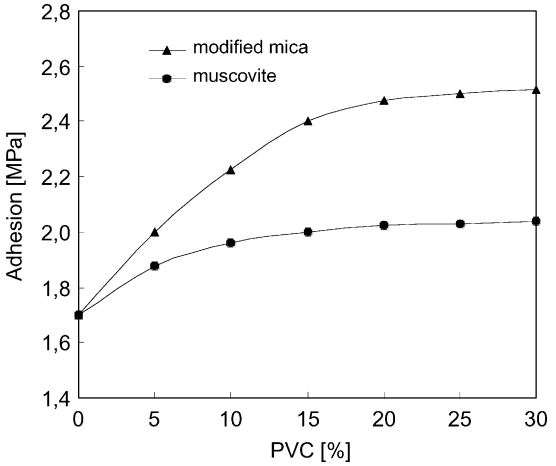

Fig. 7. Dependence of the coating adhesion in dependence on the lamellar pigment concentrations PVC.

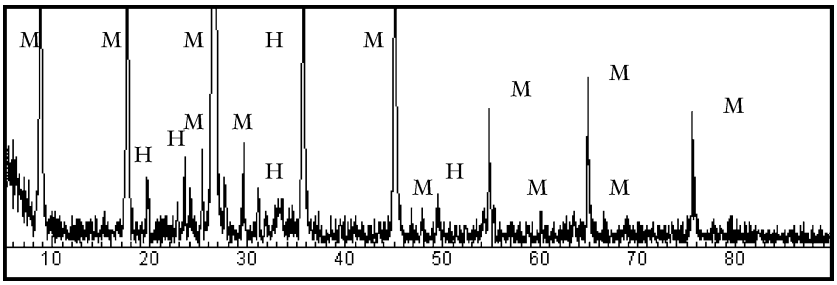

Fig. 5. XRD pattern of mica covered with α-Fe_2O_3 (hematite) layer: M, mica; H, hematite.

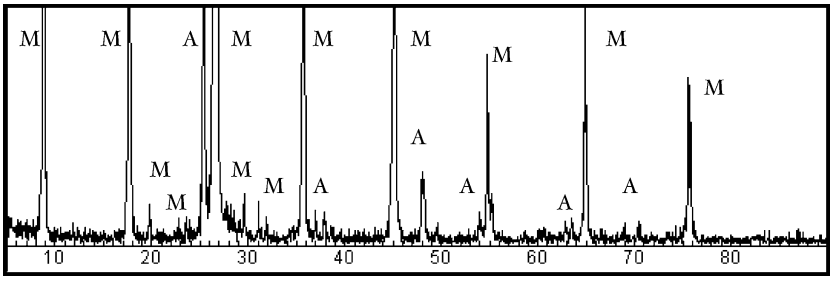

Fig. 6. XRD pattern of mica covered with TiO_2 (anatase) layer: M, mica; A, anatase.

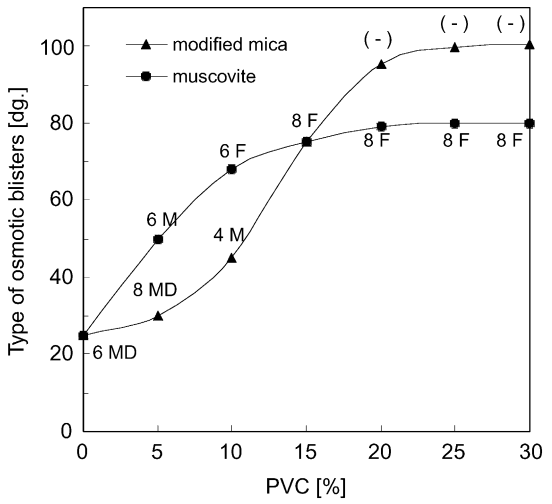

Fig. 8. Manifestations of osmotic blisters in dependence on the lamellar pigment concentrations after a 500 h exposure to a salt chamber medium (dg. 100 = without any blisters, dg. 0 = blisters of the type 2D).

(2 denotes the largest size, 8 the smallest) and information on the frequency of occurrence is also given. The highest occurrence density of blisters is designated as D (dense), the lower ones as MD (medium dense), M (medium) and F (few). In such a way a series from the surface area attacked at least by the osmotic blisters up to the heaviest occurrence can be formed as follows: 8F-6F-4F-2F-8M-6M-4M-2M-8MD-6MD-4MD-2MD-8D-6D-4D-2D. The obtained results were transformed to a numeric expression on a scale (0–100).

Fig. 8 shows the results of coating corrosion resistances after 500 h exposure to a salt chamber medium. The test is based on affecting the test panels with an aqueous 5% NaCl solution in the form of an aerosol at a temperature of 35 °C. The evaluations were performed again following 500 h exposure. The evaluation is directed to the appearance of osmotic blisters for the coatings with a fluctuating concentration of lamellar muscovite particles. According to these results, the mica coated with Fe_2O_3 layer exhibited a significantly higher protective effect than the uncoated starting material, comparable to MIOX grades.

4. Conclusions

Homogeneous hydrolysis of aqueous solutions of metal sulphates with urea, followed by annealing of the reaction products, can be used for the synthesis of coloured pigments based on mica coated with strongly bound metal oxide layers. The properties of the final pigment depend mainly on mica granularity and particle thickness, thickness of the metal oxide deposit and its chemical composition and crystal structure.

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