Behaviour of Surface-Treated Mica and Other Pigments with Lamellar Particles in Anticorrosive Coatings

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Summary: The paper deals with using lamellar pigments for anticorrosive barrier coatings. By depositing a ferric oxide layer on a muscovite particle a pigment is obtained, which being applied to coatings improves the mechanical properties thereof, resistance to UV radiation and acts as an anticorrosion barrier. The optimum concentration of lamellar surface-treated muscovite in the coatings amounts to 20 vol. %.

Introduction

Nonisometric lamellar pigments are used in anticorrosive coatings for a series of years. The most widely used lamellar pigment for this purpose is ferric mica.[1] From the chemical point of view it is a ferric oxide in crystalline lamellar structure (specularite). For the designation of natural-origin lamellar pigment the name „micaceous iron oxide" *(MIO)* has become popular in time. Specularite (also the so called iron mica) modified to the pigment form is characterized by a typical metal-gray color of sparking appearance. Practical experience and published papers concerning the application of *MIO* pigments to coatings destined to metal protection show the outstanding results.[2] The anticorrosive coatings pigmented with a MIO pigment show excellent barrier properties - they hinder the permeation of corrosive substances and water through the film, increase the adhesion of coating to the substrate, and the particles protect also binder to ultravioleght (UV) radiation. The *MIO* pigments are of natural origin and the deposits of specularite will be exhausted in the future and are also not rather broadened. In the first stage a path of preparing synthetic specularite (synthetic MIO pigment) was selected.[3] The synthetic *MIO* pigment preparation was performed at high temperatures

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and pressures in an autoclave. The pigment obtained is characterized by rather regular lamellar particles, color and chemical composition identical with the *MIO* pigment of natural origin.[4] When a synthetic *MIO* pigment is used, the anticorrosive barrier properties reach high values in the coatings. The economic evaluation is not favorable for the synthetic preparation of *MIO* pigment. With respect to this reason the synthetic pigment cannot compete with a cheeper starting material of natural origin. On the basis of preceding papers published in this research region a path of using mica was selected,[5] which has also the lamellar structure. Mica is chemically an aluminosilicate, occurring in large amounts in natural deposits and is more easily available than specularite. From a broad pallet of aluminosilicate minerals the potassium aluminosilicate $K_2O.3Al_2O_3.6SiO_2.2H_2O$, designated as muscovite is an especially appropriate compound for coatings. Muscovite has compared to *MIO* pigments an advantage consisting in a lower specific density (2.9 $g.cm^{-3}$) and thus a lower tendency to sedimentation in a liquid medium. Papers published already in the past indicate a lower anticorrosion barrier efficiency in the coatings in comparison to *MIO* pigments.[6] A contribution to solving this disproportion between two types of lamellar pigments consists in forming a ferric oxide layer on a muscovite particle. The chip of muscovite is a carrier and offers to a particle a lamellar shape. On the particle surface a thin ferric oxide layer (hematite) is precipitated, which nears a surface treated muscovite particle also from the properties point of view to a specularite particle - a *MIO* pigment.

Experimental part

Preparation of the surface-treated muscovite (Fe-muscovite)

The preparation of surface-treated muscovite (the so called surface-treated Fe-muscovite) was performed by a controlled hydrolysis with urea, at which a mixture of iron oxides-hydroxides is precipitated at the lamellar particle surface.[7] By annealing a strong chemical bond (Fe_2O_3-muscovite) is formed at the muscovite particle surfaces. The reaction mixture is heated to boiling and the change in pH value is continuously followed. The synthesis is completed after reaching pH = 8, which corresponds to a reaction time of 8 hours. The completion of reaction is indicated by ammonia developing in the reactor. The mixture is further kept in the reactor in moving at switched off heating. Then decantation, filtration, and drying at a temperature of 110 °C follow. The dry pigment was annealed at a temperature of 600 °C. Figure 1 shows the scanning electrone micrographs (SEM) of the sections of surface-treated Fe-muscovite. Tables 1-2 give physicochemical properties of pigments tested.

Preparation of coatings

To enable determining the most appropriate concentration of surface-treated muscovite in coatings the samples on a binder base of epoxyester resin were prepared. A concentration series of 5 to 30 vol. % pigments in the binder was prepared. The pigment component was replenished by titanium dioxide to an overall pigment volume concentration (PVC) of 60%. The formulation of model coating contains in addition to it bentonite to improve the rheological properties, and organic and inorganic corrosion inhibitors.

Cross section through the surface of particle (1.000x, Philips XL 30CP)

Morphology of the particle in detail (15.000x, Jeol 5600 LV)

Figure 1. Cross section and morphology of surface-treated Fe-muscovite.

Table 1. Characterization of lamellar pigments used.

Lamellar pigment	Composition	Density g/cm^3	pH[a)]	Specific surface[b)] m^2/g	Oil absorption[c)] g/100g
Muscovite (white color)	Potassium aluminosilicate	2.92	9.51	5.83	28.0
Fe-muscovite (red color)	Potassium aluminosilicate Fe_2O_3 (5%)	3.31	7.23	34.28	30.0

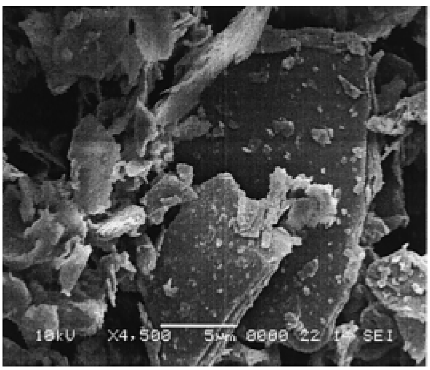
[a)] Determination of the pH value of water extracts for pigments (DIN ISO 787/9)
[b)] Specific surface calculated by BET isotherm (*ASAP 2000*)
[c)] Determination of oil absorption for pigments (DIN ISO 787/2)

Table 2. Characterization of lamellar pigments used.

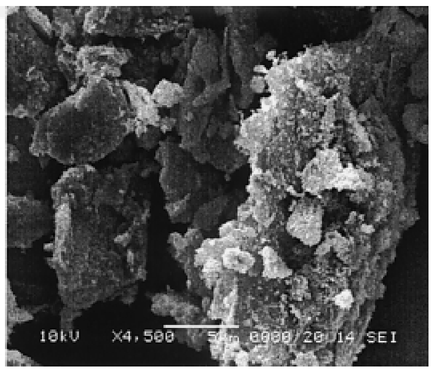
Lamellar pigment	CPVC[a] (linseed oil)	Solubility in water[b]		Particle size distribution[c]		
		at 23 °C	at 100 °C	90%	50%	10%
		%	%	μm	μm	μm
Muscovite	53.04	0.291	0.314	22.51	11.85	2.46
Fe-Muscovite	47.95	0.185	0.266	26.36	11.56	1.57

[a] critical pigment volume concentration calculated by linseed oil consumption
[b] Determination of water soluble matter for pigments (CSN EN ISO 787/3)
[c] by laser beam difraction (*Coulter LS 100*)

Figure 2 shows morphology of lamellar pigments used (Jeol, JSM 5 600 LV).



Muscovite (4.500x)



Fe – muscovite (4.500x)

Figure 2. Morphology of lamellar pigments used.

Results

Effects of lamellar pigment concentrations on the coating properties

With the prepared coatings the development of coating hardnesses in dependence on the pigment concentration was followed. The measurements were performed by means of a pendulum instrument of the Perzos type (Pendulum damping test, ISO 1522). Figure 3 shows the dependence of coating hardnesses on the lamellar muscovite pigment concentrations (PVC). The dependences given in Figure 3 indicate that the coating hardnesses raise with the increasing concentration of lamellar muscovite in a range of 0 - 30 vol. %. The difference between the surface-treated muscovite and nontreated muscovite is minimal. Both the dependences show the same trend, and the difference can be caused by more porous structure of surface-treated muscovite. The porous structure appearing at the surface of a Fe_2O_3-mica particle consumes probably a higher amount of binder. The results indicate that the differences will appear at a concentration round PVC=20%. Practically the differences in coatings tested between both lamellar pigment types can be seen in the SEM photos (Fig. 4.).

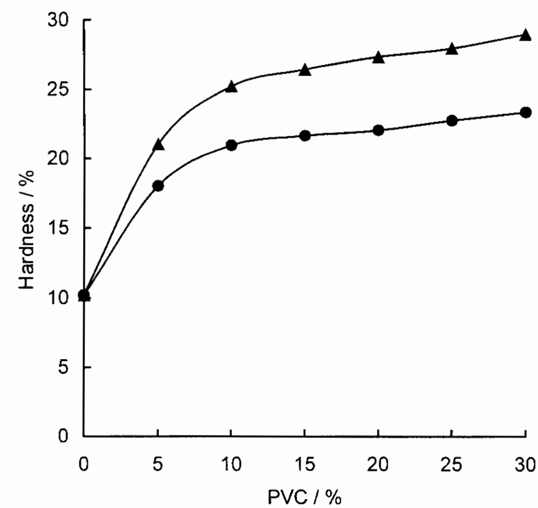
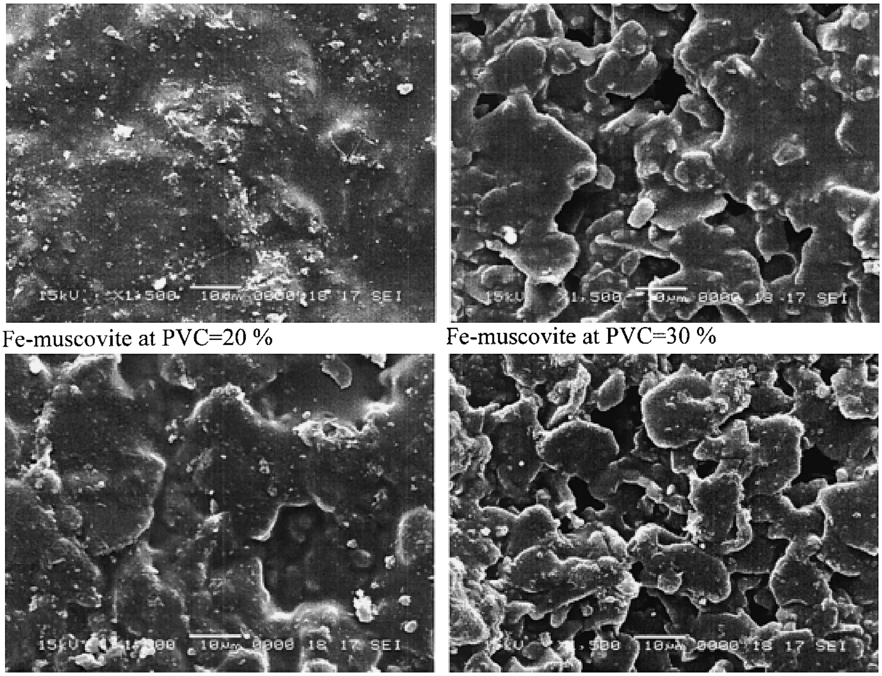


Figure 3. Dependence of the hardnesses of coatings pigmented with lamellar pigments on the pigment volume concentrations; ◆ = muscovite, ▲ = Fe-muscovite.

The lamellar mica particles positively affect the coating property, which is the coating adhesion to the substrate metal. Also affecting the cohesion of the coating alone is positive. Testing the coatings with all concentrations of both lamellar pigments was always connected with 100% cohesion fracture in the coating film.[8] Figure 5 quantifies the cohesion coating strengths in dependence on lamellar pigment amounts. As shown clearly by the dependence represented in Figure 5, the surface muscovite treatment by ferric oxide exhibits a positive effect on the cohesion in the coating. The surface treatment of lamellar particles contributes at a concentration of 20 vol. % in the coating with 0.5 MPa. At a pigment volume concentration of 30% the contribution to the cohesion strength equals 0.6 MPa. For the increase of film strength the Fe_2O_3 structure at the muscovite surface is responsible.



Fe-muscovite at PVC=20 % | Fe-muscovite at PVC=30 %

Muscovite at PVC=20 % | Muscovite at PVC=30 %

Figure 4. Structure of epoxyester coatings pigmented with lamellar pigments tested at a content of 20 and 30 vol. % (1.500x).

The corrosion testing results obtained with epoxyester coatings pigmented with surface-treated and untreated muscovite show the outstanding improvement of coating resistances to osmotic blistering. The appearance of blisters in the coating film is a reason of reduced adhesion of the film to substrate and local corrosion under the blister arch. The evaluation of blister sizes and frequencies was performed following the corrosion exposure by means of the ASTM D 714-87 Standard, and the obtained results were transformed to a numeric expression in a scale (0-100). The quantification method for evaluating the corrosion testing results was described already in the paper .[9,10]

Figure 6 brings the results of coating corrosion resistances after a 500 hour exposure to a salt spray chamber (Resistance to neutral salt spray, ISO 7253). The evaluation is directed to the appearance of osmotic blisters for the coatings with a fluctuating concentration of lamellar muscovite particles.

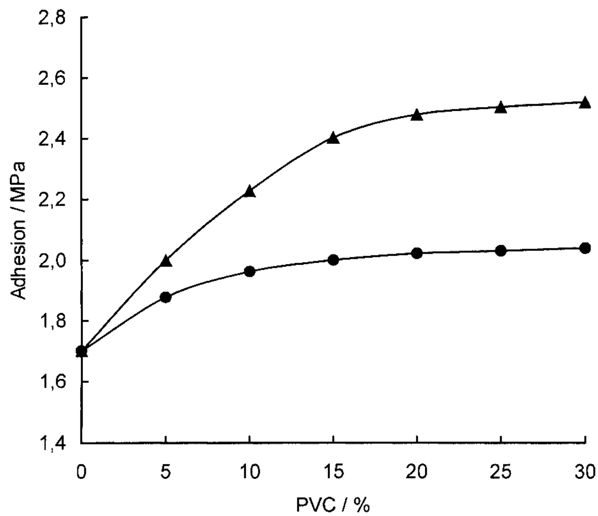


Figure 5. The cohesion component of the coating adhesion in dependence on the lamellar pigment concentrations; ◆ = muscovite, ▲ = Fe-muscovite.

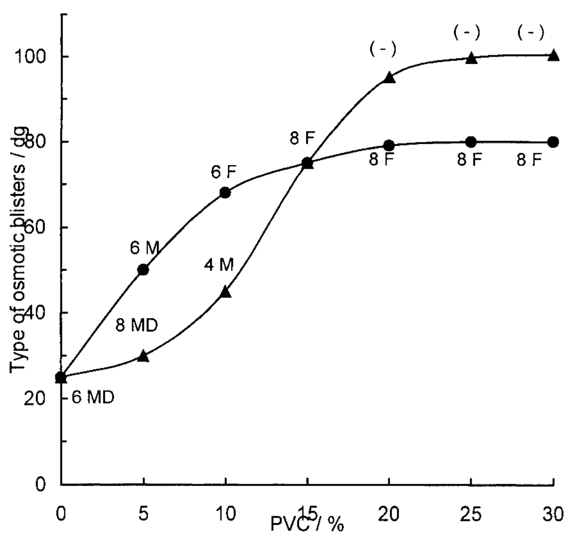


Figure 6. Manifestations of osmotic blisters in dependence on the lamellar pigment concentrations after a 500 hour exposure to a salt spray chamber (dg. 100 - without any blisters, dg. 0 - blisters of the type 2D); ◆ = muscovite, ▲ = Fe-muscovite.

As indicated in Figure 6, reproducing the dependence of osmotic blister appearances on the muscovite and Fe-muscovite concentrations, at a PVC value of 20% no changes are observed with both pigments anymore. The surface-treated Fe-muscovite in the coating at a PVC value of 20% hinders totally the appearance of blisters. At the same concentration of non-treated muscovite in the coating only a state can be reached, when the blisters of size number eight and frequency few (8F) type appear. With both the lamellar pigment types in the coating in a PVC range of 20 - 30% the blister type does not suffer a change. For muscovite without any surface treatment the blister type 8F is considered, with the surface-treated Fe-muscovite no blisters appeared at all. The overall anticorrosion efficiency of the coatings containing particles of both muscovite types is, as it was already described, considerably affected by the ability of these coatings to affect the appearance of osmotic blisters. Less affected appears to be the overall result of subcorroding under a coating, which manifests itself with the coatings containing a low amount of lamellar particles of both muscovites at a PVC of 5 - 10%. Also at higher particle concentrations there appears a state when no homogeneous coating is formed, but the pores enabling permeation of water or chloride solutions, and this results in subcorroding of steel under the coating. The effect of coating resistances to corrosion in an artificially prepared cut is really problematic for barrier pigments to be evaluated, as already from the principle of mechanism of anticorrosion action of lamellar particles this property is not afected in any way. The corrosion in cut values fluctuate round 2 mm without any respect to the concentration or type of muscovite in the coating film.

Figure 7 brings the dependences of overall anticorrosion coating efficiency on the muscovite and Fe-muscovite concentrations. In the evaluation the following factors were considered: osmotic blisters, subcorroding under the coating in surface, and subcorroding in the place of cut scribe. The results quite unambiguously indicate the positive effect of surface-treated muscovite on the anticorrosion barrier properties in the coating. The tests with a natural non-treated muscovite have shown that the effect of particles in the coating is not of such a significance as on using the surface-treated Fe-muscovite.

Both pigments show as the most suitable concentration for the coatings with respect to anticorrosion properties a PVC of 20%.[9] For the comparison of observed results at a PVC of 0% (pure epoxyester binder) and a PVC of 20% (an optimum concentration) the growth of protection anticorrosion efficiency was shown:

- non-treated muscovite an 18% improvement
- treated Fe-muscovite a 39% improvement

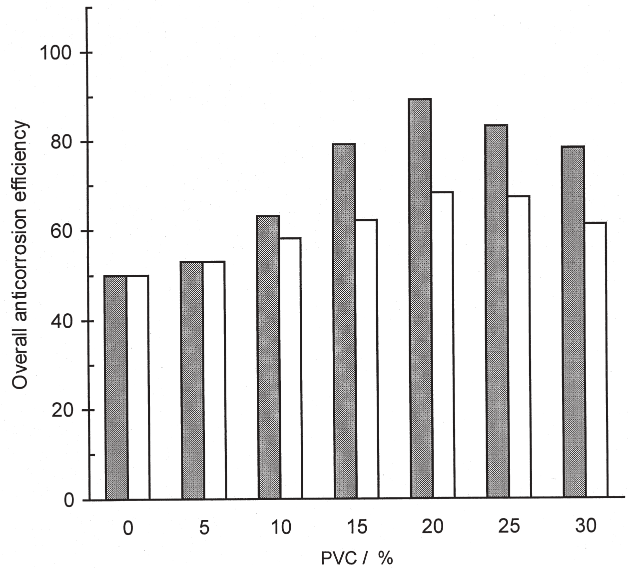


Figure 7. Dependence of the overall anticorrosion coating efficiencies on the muscovite and Fe-muscovite particle concentrations; ▒ = Fe-muscovite, □ = muscovite.

Conclusion

It was found that the surface muscovite treatment by controlled hydrolysis and precipitating a hematite layer on the lamellar natural-muscovite particles appropriately affects the properties of pigment particles. The surface treatment of muscovite by ferric oxide gives the pigments for the anticorrosive coatings acting as corrosion barriers. The surface-treated muscovite really advantageously causes a reduction of the formation of osmotic blisters in the coatings. From the anticorrosion efficiency point of view the surface-treated muscovite is more effective than the same muscovite type without any surface treatment. Also the mechanical coating properties show an advantageous effect of the surface-treated muscovite. A significant factor is connected with the improved cohesion coating strength. Also the film appearance and coating resistance prior to effects of the ultravioleght radiation which acts in the sense of degradation is better on using the treated Fe-muscovite. The optimum concentration of such lamellar anticorrosive pigment in the coating is a PVC value of 20%. At this concentration the best properties are reached in the coatings.

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References

[1] E. Carter, *Pigment and Resin Technol.* **1990**, 15, 18.
[2] S. Wiktorek, E.G. Bradley, *JOCCA* **1986**, 69, 172.
[3] T.V. Kalinskaja, *Lakokras. Mater.* **1987**, No. 2, 4.
[4] A. Kalendová, P. Tamchynová,in: *5th International Conference „Inorganic Pigments and Binders"*, Ústí nad Labem, Czech Republic, **2001**, Book of papers pp. 154-158.
[5] N. Sprecker, *JOCCA* **1983**, 66, 52.
[6] A. Kalendová, *Pigment and Resin Technol,* **2000**, 29, 277.
[7] V. Štengl, S. Bakardjieva, J. Šubrt, in: *XXXII. International Conference KNH,* Pardubice, Czech Republic, **2001**, Book of papers pp. 83-86.
[8] A. Kalendová, *Pigment and Resin Techno.* - in press.
[9] P. Kalenda, *Dyes and Pigment* **1993**, 23, 215.
[10] P. Kalenda, *Acta Mechanica Slovaca* **1999**, 3, 103.