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The future is colourful

Durable corrosion-protection coatings made with substitutes for micaceous iron oxide

Andreas Götz, Jürgen Büttner, Marius Speth

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Durable corrosion-protection coatings made with substitutes for micaceous iron oxide

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The use of colour-neutral pigments as an alternative to conventional micaceous iron oxide in the formulation of coatings for heavy-duty corrosion protection opens up an unlimited range of colours and processing advantages, and comparable corrosion protection.

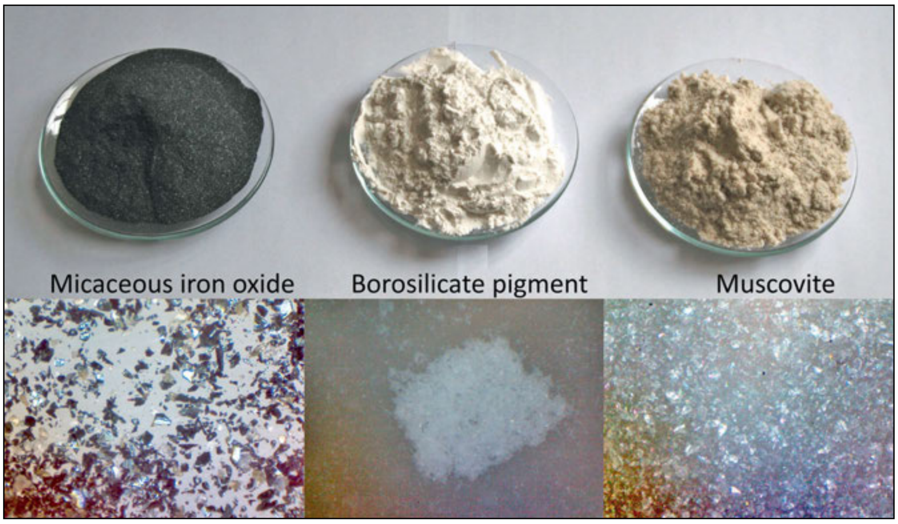

Figure 1: Corrosion-protection pigments in powder form and as reflected-light images (image width 2 mm). Muscovite and micaceous iron oxide have a definite flaky structure, whereas the borosilicate pigment is isotropic.

Micaceous iron oxide coating materials have been protecting steel structures against corrosion for many decades. They are used to style and permanently protect prestigious structures, such as the Eiffel Tower in Paris. Their weathering resistance is so good that they are prescribed in specifications all around the world. The first micaceous iron oxide coating materials were introduced in Germany by the Reichsbahn railways authority back in 1930. They have been used since then in pipeline and bridge building [1].

In the following, the paradigm is refuted that micaceous iron oxide is essential for successful passive corrosion protection. In the future, engineers will be able to avail themselves of a complete range of colours, without the need to compromise on high levels of protection.

How micaceous iron oxide works

Micaceous iron oxide is a naturally occurring, crystalline iron oxide mineral with an intrinsic colour of metallic steel-grey (*Fig. 1*). As a passive corrosion-protection pigment, its mode of action is often explained in terms of a protective barrier: this posits that the lamellar structure of the micaceous iron oxide particles in the coating acts as a protective shield that lengthens the diffusion paths and diffusion times of corrosion promoters. Film

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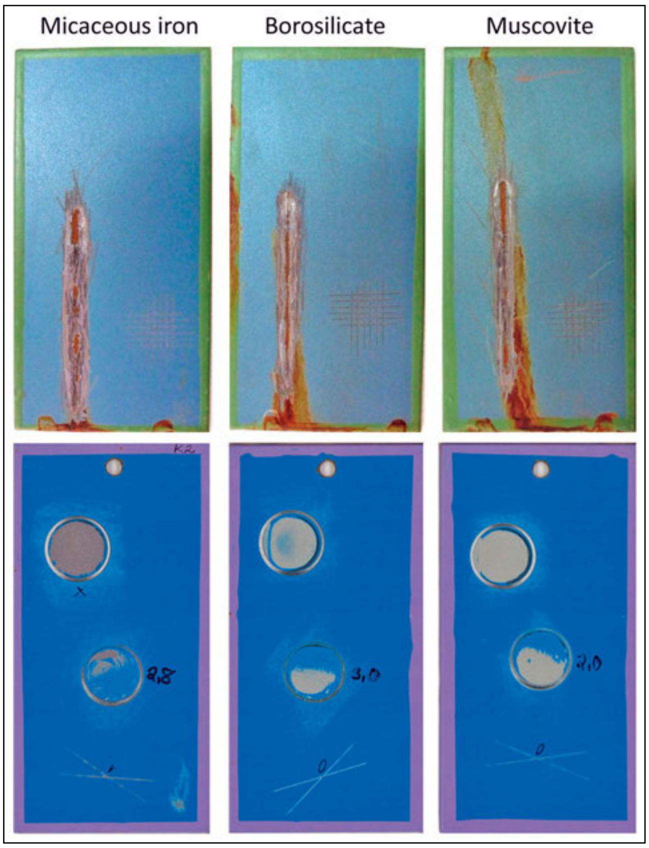

Figure 2: Top: Specimens from the salt spray test, System 2 (Tables 2 and 3). Left: Testing of penetration rusting; right: Cross-cut. Bottom: Specimens from Composite 2 (Tables 2 and 3).

degradation due to high-energy UV radiation is efficiently prevented because the micaceous iron oxide particles shield the underlying organic binder matrix effectively against decomposition.

But that is only half the story. Studies have shown that the protective effect of micaceous iron oxide is attributable not – or, if so, only partially – to the barrier mechanism presented by the lamellar structure, but rather primarily to the low adhesion forces (interfacial adhesion) between pigment and binder [2].

The intrinsic colour of micaceous iron oxide allows only muted shades to be formulated, a fact which considerably limits the scope for styling. Furthermore, the surface and colour impressions of coated objects vary with the method of application because of the lamellar structure and the pigment's intrinsic colour. Minor repairs, especially, fail to meet the highest demands on aesthetics. Added to which, the sharp edges and the relatively high hardness (Mohs hardness: 6.0-6.5) of micaceous iron oxide particles lead to abrasion of spray nozzles and pumps. Due to its high density of 4.9 g/cm³, micaceous iron oxide also has a tendency to settle out in Newtonian paint systems. This can have a deleterious effect on the protective mechanism and the appearance of the coating to be applied.

Micaceous iron oxide is a naturally occurring mineral whose composition, morphology (lamellar or granular shaped particles) and degree of contamination vary substantially with the mining location. Its salt content can, through osmosis, significantly affect the corrosion protection afforded by a coating system. The salt content can be reduced by wet grinding.

▸ Results at a glance

- Substitute pigments borosilicate pigment and muscovite provide at least as much corrosion protection as micaceous iron oxide.
- Borosilicate pigment is a recycled product with high UV-absorption power.
- Muscovite mica has a much higher lammellarity than micaceous iron oxide.
- The substitute pigments allow freedom in colour design because they are colour-neutral.
- They minimise wear on spray equipment because of their low abrasiveness and they reduce application costs.
- Regardless of the purpose of the application (e.g. repair work), optically homogeneous surfaces can be achieved.
- Due to their low density, the substitute pigments boost the spreading rate and thus lower consumption.
- They are less prone to sedimentation and thus facilitate processing.

Functional fillers as an alternative

National and international specifications and standards keep raising the demands imposed on modern corrosion-protection systems in terms of architectural design, material selection and scheduled durability. Apart from the need to offer design freedom and protect both people and the environment, it is becoming increasingly necessary in the current climate to conserve resources and adopt sustainable practices.

A possible alternative here is to employ substitute pigments that can adequately compensate for the finite availability of micaceous iron oxide as a natural resource. In this study, we investigate the anticorrosive action of muscovite and borosilicate pigment in their capacity as functional fillers. They will be referred to as "substitute pigments" below.

Muscovite – the lamellar alternative

Muscovite ($Al_2[(OH)_2|AlSi_3O_{10}]$) is a phyllosilicate with a pronounced lamellar structure. The type used here, MicaCelia 90L (*Fig. 1*), consists of selected material from which components such as quartz have been removed. Its maximum grain size is comparable to that of micaceous iron oxide (*Table 1*), but exhibits a considerably higher lamellarity. The material is

▸ Tab. 1: The most important physical properties of the micaceous iron oxide pigment and the substitute pigments muscovite and borosilicate

	Comment	Micaceous iron oxide SG	Muscovite	Borosilicate pigment
Oil number (raw linseed oil ml/10 g)	DIN EN ISO 787-5	15	79	29
Formulation wt.% of micaceous iron oxide	As per BASt Blatt 87	100%	19%	50%
pH	DIN EN ISO 787-9	9.4	9.2	8.7
Colour Whiteness (%) L*, a*, b*	Minolta CM-2600d	15,6 45,6, -1,25, -1,64	66,1 87,2, 0,02, 4,45	88,6 96,2, 0,01, 0,87
Laser granulometry D90, D50, D10 (µm)	Cilas 920L	101, 59, 26	82, 41, 12	44, 17, 3
Electrical conductivity (µS/cm)	DIN EN ISO 787-14	50	85	95
Incorporation of free salts (relative to micaceous iron oxide)	Calculated from conductivity	100%	32%	95%
Mohs hardness		Approx. 6	2 - 3	Approx. 6
Bulk density (g/l)	DIN 53466	2300	330	700
Density (g/cm³)		4.9	2.7	2.25
Lamella thickness (µm)	AFM	1.5 - 4	0.5-2	Non-lamellar
Aspect ratio		1:2 - 1:5	1:5 - 1:15	01:01
Lamellarity factor		1	> 2,2	Non-lamellar

colour-neutral and therefore does not interfere with the hue of a coating.

Borosilicate pigment – the sustainable UV absorber

Borosilicate is used in the pharmaceutical industry to make injection vials because its high UV-absorption power prevents less stable drugs from decomposing. The borosilicate pigment used here is Boruvit B140. It is a recycled product and so can be deemed to have sustainability credentials. Boruvit does not fracture with sharp edges and is thus physiologically harmless. As may be seen in *Table 1* and *Fig. 1*, it is colour-neutral and does not interfere with the hue of the coating material.

Salt content

The electrical conductivity of a mineral pigment is a direct measure of its content of soluble and corrosion-promoting salts. The micaceous iron oxide used here has a comparably low electrical conductivity of 50 µS/cm because of wet grinding. Borosilicate pigment has an electrical conductivity of 95 µS/cm while the figure for muscovite is 85 µS/cm. The salt content in the formulation is comparable to that of the wet-ground micaceous iron oxide whereas that of muscovite is significantly lower, expressed in terms of the quantity of passive corrosion-protection pigment per coated area (*Table 1*).

Lamellarity of micaceous iron oxide and muscovite

The corrosion protection afforded by micaceous iron oxide coating materials is ascribed to, among other effects, the formation of “scale armour” based on the lamellar structure. The degree of lamellarity is given by the aspect ratio, which is determined as follows. Micaceous iron oxide and muscovite were examined by means of atomic force microscopy and optical microscopy, the former serving to measure the thickness of a particle and the latter, its surface area. These measurements were then used to calculate the theoretical diameter of a circular particle of that surface area. The aspect ratio is the ratio of a particle’s thickness to its theoretical diameter. Although the theoretical diameter yields relatively low aspect ratios, it allows of objective comparison.

The micaceous iron oxide under investigation has a lamella thickness of 1.5 to 4 µm and a theoretical aspect ratio of between 1:2 and 1:5. Muscovite has a lamella thickness of 0.5 to 2 µm and a theoretical aspect ratio of 1:5 to 1:15 (Table 1). In other words, muscovite has more than twice the lamellarity of micaceous iron oxide.

Substitution on the basis of oil absorption

Substituting one pigment for another on a weight-for-weight basis makes sense only in exceptional cases. In practice, pigments are substituted on a volume-for-volume or oil-absorption-number basis. The latter is the volume of raw linseed oil absorbed by 100 g of pigment by virtue of its specific surface area. It is thus a measure of how much binder a pigment will absorb. In this study, the oil absorption number served as the basis for replacing micaceous iron oxide with substitute pigments. This should ensure that the solids particles are sufficiently wetted and that all formulations have a comparable, free binder fraction conducive to the formation of compact, durable coating films (*Table 1*).

All pigments on a par

The corrosion-protection properties of the substitute pigments were studied by testing the coating materials against the specifications of Germany’s Federal Highway Research Institute (BASt, Blatt 87 [1]). The precise details of the formulations and methods are set out in the specification [1].

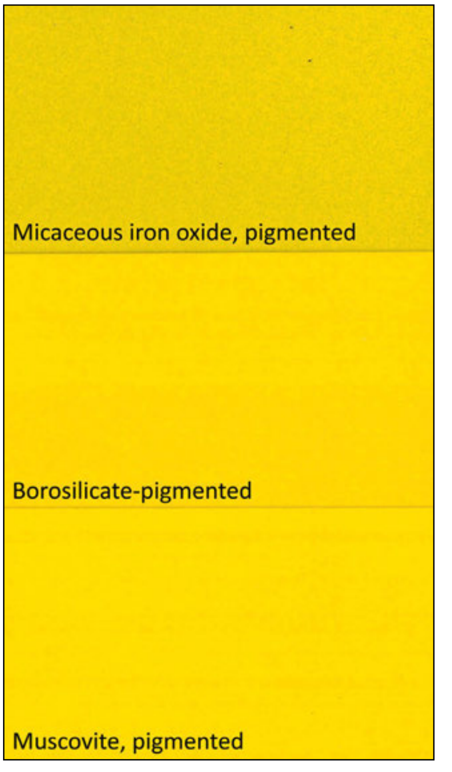

Figure 3: Panels coated with 2-component PUR topcoat in RAL 1023 hue and pigmented with micaceous iron oxide, muscovite and borosilicate pigment

The corrosion protection effect of micaceous iron oxide and the substitute pigments was compared by replacing the prescribed fraction of micaceous iron

▹ Tab. 2: Coating systems for testing in accordance with TL/TP-KOR-Steel Structures, Appendix E – Blatt 87 (BASt)

System 1	
Substrate:	Steel, blasted to Sa 2 1/2 roughness “medium (G)”
Coating system:	2-component EP zinc phosphate primer, RAL 1002 2-component EP micaceous iron oxide intermediate coat, DB 702 2-component PUR micaceous iron oxide coat, DB 501
System 2	
Substrate:	Steel, blasted to Sa 2 1/2 roughness “medium (G)”
Coating system:	2-component EP zinc dust primer, grey 2-component EP micaceous iron oxide intermediate coat, DB 702 2-component PUR micaceous iron oxide coat, DB 501
System 3	
Substrate:	Unweathered, individually galvanized steel (grade “tZn k”) surface preparation, sweep blasting
Coating system:	2-component EP micaceous iron oxide intermediate coat, DB 702 2-component PUR micaceous iron oxide topcoat, DB 501
System (Composite 2)	
Substrate:	Steel, blasted to Sa 2 1/2 roughness “medium (G)”
Coating system:	2-component EP zinc dust primer, grey 2-component EP micaceous iron oxide intermediate coating, DB 702 2-component PUR micaceous iron oxide coating, DB 501, Alternative 2-component PUR topcoat, RAL 5015

oxide in the 2-component EP micaceous iron oxide intermediate coating and the 2-component PUR micaceous iron oxide topcoat with a quantity of substitute pigments on the basis of oil absorption number (*Tables 1 and 2*).

All the systems passed tests on resistance to humidity (continuous condensation) and neutral salt spray mist, and adhesion of the 2-component-PUR topcoat to a 2-component EP intermediate coating which had undergone accelerated weathering (*Fig. 2*).

The borosilicate pigment system exhibited much less rust penetration at the scribe line than its micaceous iron oxide counterpart. The pull-off test failed to reveal any adhesion failure. All specimens exhibited good cross-cut values (*Table 3*).

All the systems met the requirements for degree of blistering 0S0 (ISO 4628-2) and degree of rusting RiO (ISO 4628-3). An overview of the other results can be found in *Table 3*.

Corrosion protection through stress relaxation

Stresses in the coating system that arise during aging can be compensated by means of partial adhesion failure at the pigment/binder interface. If the adhesive forces between the pigment and the binder are weaker than the cohesive forces in the binder, stress cracking (micro-cracks) in the binder matrix can be prevented. This stress relaxation (armouring) creates a permanent, protective effect.

This assertion is borne out by the pull-off test for determining the interfacial adhesion of micaceous iron oxide, borosilicate pigment and muscovite in the 2-component PUR and the 2-component EP systems. Not once is cohesion failure

▹ Tab. 3: Results of the tests in accordance with TL/TP-KOR-steel structures, Appendix E – Blatt 87 (BASt)

	Requirement	Micaceous iron oxide	Borosilicate pigment	Muscovite
A: Continuous condensation				
System 1		**Exposure time 720 h**		
Cross-cut	≤ Gt1	Gt 0-1	Gt 0-1	Gt 0
System 2		**Exposure time 1200 h**		
Cross-cut	≤ Gt1	Gt 1	Gt 0-1	Gt 0
System 3		**Exposure time 1200 h**		
Cross-cut	≤ Gt1	Gt 0	Gt 0-1	Gt 0
B: Resistance to neutral salt spray				
System 1		**Exposure time 1440 h**		
Rust penetration at scribe cross-cut	≤ 3 mm ≤ Gt1	2.5 mm Gt 0	2.1 mm Gt 0	2.3 mm Gt 0
System 2		**Exposure time 2160 h**		
Rust penetration at scribe cross-cut	≤ 3 mm ≤ Gt1	2.7 mm Gt 0	1.2 mm Gt 0-1	1.7 mm Gt 0
System 3		**Exposure time 2160 h**		
Cross-cut	≤ Gt1	Gt 0-1	Gt 0-1	Gt 1
C: Adhesion of the topcoat to weathered intermediate coating after artificial aging and discontinuous condensation				
System (Composite 2) – 687.51		**Exposure time 720h**		
Pull-off value Cross-cut	> 2.5 MPa 0 - 1	2.8 0	2.6 0	2.8 0
System (Composite 2) – 687.82		**Exposure time 720h**		
Pull-off value Cross-cut	> 2.5 MPa 0 - 1	2.8 0-1	3.0 0	2.6 0

Determinations were carried out to following standards: Humidity resistance DIN EN ISO 6270-1, resistance to neutral salt spray mist: DIN EN ISO 7253, resistance to moisture (discontinuous condensation):
ISO 6270-2, AHT, cross-cut: ISO 2409, pull-off value ISO 4624 In the pull-off tests, no inadmissible adhesion failure was observed.

▹ Tab. 4: Pull-off test according to ISO 4624: No cohesion failure in the binder

Substrate	Pull-off value	Failure pattern	Binder	Information on failure
Micaceous iron oxide (haematite)	5.7 MPa*	100 A/B	2-component PUR binder	Adhesion failure Pigment/binder
Coated with 2-component EP or 2-component PUR binder	16.7 MPa*	100 A/B	2-component EP binder	Adhesion failure Pigment/binder
Borosilicate pigment	15.8 MPa*	40 A/B, 60 B/Y	2-component PUR binder	40% adhesion failure Pigment/binder 60% Adhesion failure to adhesive
Coated with 2-component EP or 2-component PUR binder	16.3 MPa*	30 A/B, 70 B/Y	2-component EP binder	30% adhesion failure Pigment/binder 70% Adhesion failure to adhesive
Muscovite	< 1 MPa**	100 A	2-component PUR binder	Cohesion failure in the pigment
Coated with 2-component EP or 2-component PUR binder	< 1 MPa**	100 A	2-component EP binder	Cohesion failure in the pigment

Note: A ... Cohesion failure in the pigment
A/B ... Adhesion failure between pigment and binder
B/Y ... Adhesion failure between binder and adhesive

* Tested by the sandwich method
** Tested by the one-sided pull-off method

within the binder observed. In the vertical tensile stress test, borosilicate pigment and micaceous iron oxide experience delamination at the binder/pigment interface. In the case of the borosilicate pigment, partial failure occurs between the binder and the adhesive needed for the test. Muscovite is a phyllosilicate, whose individual layers can be delaminated with little force. In the vertical tensile stress test, stress relaxation in muscovite takes the form of failure inside the pigment grain (*Table 4*).

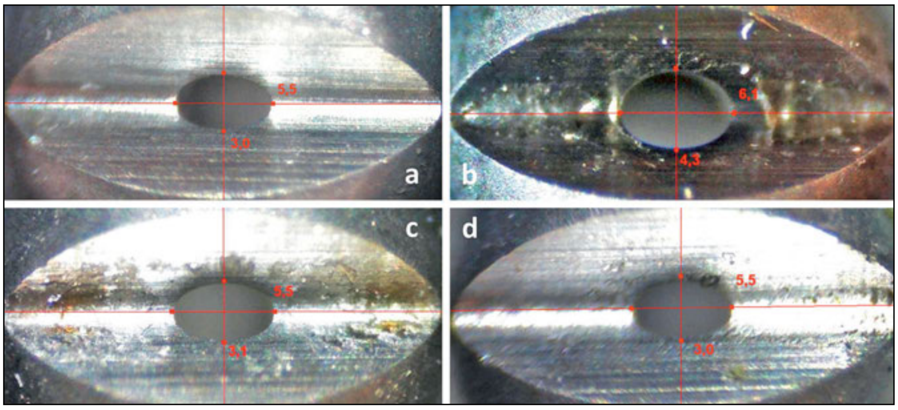

Figure 4: Wear on nozzles during spray application a) Nozzle before spraying. b) Nozzle after spraying micaceous iron oxide formulation for 8h. c) Nozzle after spraying Borosilicate pigment formulation for 8h. d) Nozzle after spraying muscovite mica formulation for 8h. Values given are size in milimeters.

New colour spectra

One advantage of the substitute pigments under investigation is the range of colours which can be achieved with them. This is in contrast to micaceous iron oxide coating materials, whose colour range is limited by its intrinsic colour. By virtue of their neutral colour, the substitute pigments can replicate a virtually unlimited colour range; one such example is shown in *Fig. 3*. This opens up architectural and design opportunities for bridges and other steel structures that require heavy-duty corrosion protection. Machine makers could also exploit this to brand equipment or to decorate machinery in the customer's corporate design.

Easier to repair

Coatings based on the substitute pigments exhibit a homogeneous surface appearance, regardless of whether they are applied by brush, spray or roller. Consequently, inconspicuous repairs can be made to components. This is not the case for micaceous iron oxide coatings.

Spraying without nozzle abrasion

The high abrasiveness of micaceous iron oxide means causes the nozzles of equipment used to spray the corresponding coatings to suffer from severe abrasion. Nozzle wear was quantified by spraying the three coating systems without interruption for a protracted period of time. After a spraying time of 4, 6 and 8 hours, the nozzles were measured under the microscope (*Fig. 4*). After the maximum test duration, the micaceous iron oxide was found to have widened the nozzle by about 60%, while virtually no wear was detected in the substitute pigments.

By minimising wear on nozzles, therefore, the use of substitute pigments boosts the efficiency of spray equipment . This lowers running costs and enhances coating quality. Wear-induced nozzle widening changes the spraying pressure and thus the layer thickness and the spray result. ◂

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