Combination well done

Zinc rich primers with micaceous iron oxide. Libuse Hochmannová.
Micaceous iron oxide (MIO) is widespread in protective coatings due to its outstanding anticorrosive properties. A less obvious is using of MIO as a replacement of zinc dust in zinc rich primers. It follows from testing single layer coatings and paint systems at two corrosive environments that a partial replacement of spherical zinc dust by micaceous iron oxide is well founded. The micaceous iron oxide influenced positively the adhesion of paints after the exposition at corrosive cabinets. The use of micaceous iron oxide at the formulation of zinc rich primers is advantageous from ecological and also from price reasons.

Micaceous iron oxide (MIO) pigment is used in paints to provide long-term durability. MIO paints have been used continuously since the early 1900s to protect steelwork [1]. Micaceous iron oxide known also as specular haematite and flaky haematite is a natural mineral ore that consist after refining mainly of Fe₂O₃. Micaceous iron oxide differs in the form and shape from the well-known iron oxides that are used as colour pigments for red, yellow, brown and black colour pigmentation. MIO shows a flaky, lamellar structure, the colour is dark grey with a metallic sheen. The term "micaceous" is used because the lamellar particles are similar to mica [2, 3].

Building a shield of overlapping flakes
MIO is insoluble in the water, organic solvents and alkalis and is only slightly soluble in strong acids at elevated temperatures. It is non-reactive to most chemicals and is heat stable up to its melting point of over 1500°C. MIO is widespread in protective coatings due to its outstanding anticorrosive properties. When MIO is incorporated into a coating at an appropriate level, the flakes align parallel to the substrate surface producing a shield or barrier of overlapping plates. The flakes are impermeable, a physical barrier is formed to the ingress of the water, oxygen and ions that cause corrosion of steel and degrade the binder system. MIO flakes are strong UV absorbers and very weather resistant. This protects the surface of the binder system from the degrading action of UV and other weathering elements. MIO reinforces the binder matrix and increases the substrate adhesion and inter-coat adhesion.

The size of MIO flakes (normally 40 to 50µm in length and 5 to 10µm thick) dictates a dry film thickness in excess 50µm in order to achieve a shield of overlapping flakes. For this reason MIO is normally found in "high build" intermediate and finishing coats. Recent developments in MIO technology have led to the introduction of a range of "ultra thin" pigments with the flake thickness of 1 to 2µm only. There are finding increasing the use in the film applications, particularly shop primers, where they provide the cost and environmental benefits [4].

MIO pigments reduce formulation costs
A typical use of thin MIO pigments as a replacement of zinc dust in zinc rich primers. The unique chemical and physical properties of the pigment may produce a packing structure that would enable zinc levels to be reduced. This pigment offer formulators a genuine opportunity of reducing of environmental impact whilst maintaining anticorrosion performance, and - unlike many environmentally friendly technologies - at significantly reduced formulation cost [5].

Primers based on a combination of spherical zinc dust and MIO
The preparation of zinc rich primers was based on the semisolid epoxy resin, the polyaminoamide adduct like hardener, the spherical zinc dust and the micaceous iron oxide.

Paints were formulated with a pigment volume concentration (PVC) from 40 to 65%, the volume ratio of zinc dust and MIO was 1:1. The partial replacement of spherical zinc dust by MIO was examined with PVC = 65%, the ratio between spherical zinc dust and MIO was changed - 83:17, 67:33 and 50:50 respectively. The pearl mill was used for preparation of the primers.

With basic properties of paint films were evaluated. The anticorrosive effect of single layer paints and the paint systems were also determined. Such characteristics as drying time, pendulum hardness, cupping test, impact resistance, bending test and adhesion of the paint systems were tested during for 8 hours.

The adhesion of the paint systems was evaluated as cross cut test ISO 2409. The adhesion was tested before beginning of corrosion tests and after completion of these tests.

MIO enhanced mechanical properties of cured paints
The pigment volume concentration and the mutual ratio of spherical zinc dust and MIO influenced the drying time considerably. Primers based on combination of spherical zinc dust and MIO (1:1) with pigment volume concentration 40% needed the longest time for this stage - 8 hours (Figure 1). The pendulum hardness was lower when the content of MIO increased (Figure 2).

Micaceous iron oxide influenced positively the mechanical properties of the films. The coatings prepared from primers based on the combination of spherical zinc and MIO had the excellent impact resistance (Figure 3). The results of cupping test and bending test deteriorated step by step at the range of PVC from 40 to 65 (Figures 4 and 5).

It follows from the results of testing of the primers with PVC = 65% that the higher the content of MIO the better the bending test. All coatings produced excellent adhesion.

Primer with PVC 65% resistant to salt spray (fog) test
It follows from the results of testing of single layer primers exposed to salt spray that the content of MIO and PVC influenced the anticorrosive effect significantly. The anticorrosive effect at the range of PVC from 40 to 50% firstly increased and than decreased at PVC 55% and 60%. The best anticorrosive effect was found at the formulation with PVC 65% where the combination of 1/2 spherical zinc dust and 1/2 MIO was used. The formulation with PVC 50% is suitable also. The barrier mechanism of lamellar MIO played probably a grate role than the electrochemical mechanism of zinc dust and later barrier mechanism of the zinc corrosion products (Figures 6 and 7). Similar trend was observed at the paint systems (Figures 8 and 9). Differences of anticorrosive effect were lower because the results were influenced by the top coat.

Best result with half and half combination in humidity cabinet
It follows from the results of testing of single layer paints exposed to humidity cabinet with SO₂ that the barrier mechanism of the binder is asserted at PVC = 40%. This mechanism is changed to barrier mechanism of MIO. The
optimal anticorrosive effect was achieved at PVC = 50% when anticorrosive effect had a degree 82. If PVC increased the film was more porous and the anticorrosive effect decreased.

Single layer paints from the primer based on spherical zinc dust only provided low anticorrosive effect - degree 45 (Figures 6 and 7). Humidity cabinet with \( \text{SO}_2 \) showed the best anticorrosive effect of the formulation with PVC 50% where the combination of 1/2 the spherical zinc dust and 1/2 MIO was used. The pigment volume concentration, the barrier mechanism of micaceous iron oxide, the electrochemical process and the solubility of the zinc corrosion products influenced the anticorrosive effect of single layer paints (for example: the water solubility of \( \text{ZnSO}_4 \cdot 7\text{H}_2\text{O} \) is ca. 1680 g/l and the water solubility of \( \text{ZnCO}_3 \) is 10 mg/l).

It follows from the results of testing of paint systems that the top two component polyurethane enamel influenced the anticorrosive effect significantly (Figures 8 and 9).

**Good adhesion with MIO**

All paint systems had the excellent adhesion before the testing at corrosion chambers (degree 0). The adhesion of the paint system with the spherical zinc dust only was worse after 1512 hours of the exposition at both corrosion environments (degree 2). The paint systems containing MIO had excellent adhesion after completion of the corrosion tests.

**References**


**Experimental**

New degreased and ground steel panels were used for the tests. The size of panels was 100 * 150 * 1mm. Single layer coatings of zinc rich epoxy primers with dry thickness of 60 ± 5µm were prepared. Protective paint systems consisted of one coat of zinc rich epoxy primer and two component acrylic polyurethane as the finish coat (dry film thickness of 160 ± 15µm). In all cases, the panels were prepared in triplicate and stored for four weeks for hardening at 23 ±2°C and 50 ±5% relative humidity.

The single layer coatings and the paint systems were exposed to:

1. Salt spray (fog) testing according to ISO 9227
2. Humid atmospheres containing \( \text{SO}_2 \) - cyclic accelerated corrosion tests: 8 hours in humidity cabinet with \( \text{SO}_2 \) and 16 hours in the ambient atmosphere - ISO 3231.

Anticorrosive protection of the paint systems was evaluated according to ASTM D 1654-92, D 610-85 and D 714-87. Heubach rating was used for testing of anticorrosive effects - 100 is the best and 0 is the worst.

**Result at a glance**

Drying time of zinc rich primers containing MIO was longer, hardness was lower, but impact resistance, cupping test and bending test results were better. The formulation based on the combination of spherical zinc dust with the MIO at the ratio 1:1 and the PVC = 50% had the best anticorrosive effect. MIO influenced positively the adhesion of paints after the exposition in corrosive environments.

It was possible to reduce the content of zinc dust in dry film till to 49.8% by weight. 45% by weight of zinc dust could be spared compared with zinc rich primer based on spherical zinc dust only.

These results document that the use of micaceous iron oxide at the formulation of zinc rich primers is advantageous from ecological and also from price reasons. A partial replacement of spherical zinc dust by micaceous iron oxide is well founded.

**The author:**

-> Dipl. Ing. Libuse Hochmannová studied the chemistry at the University in Pardubice in The Czech Republic. Since 1981 she has been working in the research institute SYNO, a.s. in Pardubice. She has experiences above all with formulations of different types of paints. Last years she developed paint systems for heavy-duty maintenance.
Figure 1: Influence of PVC and ratio of Zn dust and MIO - results of drying time
Figure 2: Influence of PVC and ratio of Zn dust and MIO - results of pendulum hardness (after 28 days)
Figure 3: Influence of PVC and ratio of Zn dust and MIO - results of impact resistance (after 28 days)
Figure 4: Influence of PVC and ratio of Zn dust and MIO - results of cupping test (after 28 days)
Figure 5: Influence of PVC and ratio of Zn dust and MIO - results of bending test (after 28 days)
Figure 6: Anticorrosive effect of single layer zinc rich primers - Zn : MIO = 50 : 50
Figure 7: Anticorrosive effect of single layer zinc rich primers - PVC = 65 %
Figure 8: Anticorrosive effect of paint systems - Zn : MIO = 50 : 50

Anticorrosive effect (degree)

PVC (%)

- salt spray
- humidity cabinet with SO₂

Figure 8: Anticorrosive effect of paint systems - Zn : MIO = 50 : 50
Figure 9: Anticorrosive effect of paint systems with PVC = 65%
Table 1: Properties of pigments

<table>
<thead>
<tr>
<th>Property</th>
<th>spherical Zn dust</th>
<th>MIO</th>
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<tbody>
<tr>
<td>Colour</td>
<td>grey</td>
<td>grey with metallic sheen</td>
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<tr>
<td>Density (g/cm³)</td>
<td>7.1</td>
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<tr>
<td>Total zinc (% b.w.)</td>
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<tr>
<td>Content of Fe₂O₃ (% b.w.)</td>
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<td>Average particle size (μm)</td>
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<td>Residue on sieve (%)</td>
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<tr>
<td></td>
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