THE STUDY OF PROPERTIES OF ZnFe$_2$O$_4$ IN ORGANIC COATINGS DEPENDING ON THE STRUCTURE AND MORPHOLOGY OF PRIMARY PARTICLES OF Fe$_2$O$_3$

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Abstract
Ferrites were prepared through a high-temperature process during a solid phase. Zinc ferrites were prepared from hematite ($\alpha$-Fe$_2$O$_3$), goethite ($\alpha$-FeO.OH), magnetite (Fe$_3$O$_4$), and specularite (Fe$_2$O$_3$) entering into reaction with zinc oxide at temperatures ranging from 600 °C up to 1,100 °C. The morphology of the particles of synthesized zinc ferrites was studied with regard to its effects on the physical and corrosion resistance of organic coatings. The synthesized ferrites were used to prepare epoxy coatings and water-borne styrene-acrylate coatings that were subjected to post-application tests for physical-mechanical properties and anticorrosion properties.

Keywords: Pigment, coating, anticorrosion, spinel, zinc ferrite, paints

INTRODUCTION
The development of nontoxic anticorrosion pigments that could replace chromate pigments cannot be considered complete yet [1-5] possible method of replacing toxic pigments in paints is the use of ferrites with the content of alkaline soils [6-9] The physical-chemical properties of inorganic pigments, their physical structure, reactivity, texture, morphology, the size of primary particles, the acid-base properties of their surface, the content of soluble substances, and many other qualities depend mainly on a synthesis method and on the properties of initial substances.

EXPERIMENTAL
Preparation of ferrites as pigments
High-temperature solid-phase synthesis was selected to synthesize anticorrosion pigments. The structure of the ferrite-type spinel lattice was chosen for its suitable properties, mainly for its stable physical and chemical properties, insolubility, and thermic stability. Ferrites, especially those with the content of Zn$^{2+}$ cations, display properties that fulfill the requirements for stable anticorrosion pigments in paints.

Four different forms of ferric oxide - hematite, goethite, magnetite, and specularite – were tested for ferrite synthesis and for the study of their properties. These initial substances should not have any negative impact on the properties of the product that always contains, in the conditions of practical production, a certain share of unprecipitated initial substances. In case of the anticorrosion pigments, the residual share of the unprecipitated substances may cause the initiation of corrosion processes at a pigment coating/metal base interface. As an example, we can name sulfate SO$_4^{2-}$ or chloride Cl$^-$ ions present in anticorrosion pigments obtained from

Specification of powder pigments on the basis of physical-chemical properties
The identification of the structure of the synthesized pigments was carried out by means of X-ray diffraction analysis (Diffractometer D8, Philips). The morphology of the particles was determined by SEM (JEOL 5600 LV).

Influence of the synthesized ferrites on the physical properties of the coating
Pigments influence not only the anticorrosion properties of the coatings but also the physical-chemical properties of the paint films. The shape of the particles and the optimum distribution of their size allow the pigments to enhance the barrier qualities of a binder in a paint. In principle, excellent physical properties are a primary precondition for fulfilling requirements for the anticorrosion protection of a coating system. The results of the mechanical tests were evaluated by calculating so-called total physical-mechanical efficiency (or the resistance of a specific paint film against mechanical effects). The identified properties of the mechanical tests were assigned with corresponding numerical values from a scale (100-0) for the assessment of physical-mechanical properties. The calculation of the total physical-mechanical resistance of the paints was mathematically expressed in terms of arithmetic mean.

Mechanical tests were performed on a non-pigmented coating; so-called blind test. The tests were intended to find out how certain pigments affect the physical properties of binders on paints.

Study of the anticorrosion properties of the synthesized pigments
In order to identify their anticorrosion efficiency the synthesized pigments were applied to a solution of epoxy, medium-molecular resin. Other binders
chosen for pigment testing were water-borne epoxy resin and styrene-acrylate water-borne dispersion. The coatings were selected as model ones without the content of additives that would markedly influence the final efficiency of a paint.

The volume concentration of the tested pigments (PVC) in model paints was the same for all the pigments and amounted to 10 of vol.%. Using a binder with neutral anticorrosion properties (barite), the volume concentration of the model paint was added to constant PVC/CPVC value = 0.30.

The coatings applied onto steel testing panels were subjected to these corrosion tests:

- Corrosion test with the general condensation of water (ISO 6270),
- Cyclic corrosion test in the presence of condensed H2O and SO2 (ISO 3221),
- Cyclic corrosion test in the presence of NaCl mist and humidity condensation (ISO 7253).

RESULTS AND DISCUSSION

Zinc ferrite ZnFe2O4 (α-Fe2O3) with hematite α-Fe2O3 as an initial raw material entering synthesis, displays the color perception of a red-orange hue. The particles are isometrically shaped and their distribution is relatively narrow without having a tendency towards the marked creation of secondary clusters which is the case with iron oxide red alone. Zinc ferrite ZnFe2O4 (α-FeO.OH) with goethite α-FeO.OH as an initial raw material shows the color perception of a red hue with pronounced shift into a yellow hue. The particles are rod-shaped (needle-shaped), their distribution is relatively narrow and without a tendency towards the marked creation of secondary clusters. Zinc ferrite ZnFe2O4 (FeO.Fe2O3) with magnetite FeO.Fe2O3 as an initial raw material towards displays the final color perception of a red-orange hue. The particles are isometric (nodular) and their distribution is relatively narrow. Zinc ferrite ZnFe2O4 (lam-Fe2O3) with specularite lam-Fe2O3 as an initial raw material and their distribution is relatively narrow shows the final color perception of a purple-red hue. Its particles are lamellar. Compared to the previous types, they are greater in.

High corrosion efficiency in solvent-borne epoxy films in the SO2 environment was shown by the particles of zinc ferrite ZnFe2O4 (α-FeO.OH) obtained from goethite α-FeO.OH. Zinc ferrite ZnFe2O4 (FeO.Fe2O3) based on magnetite FeO.Fe2O3 and zinc ferrite ZnFe2O4 (α-Fe2O3) made from hematite α-Fe2O3 appeared to be less anticorrosion pigments in the given corrosion environment. Nevertheless, the active chemical activity and the reinforcing effects of the particles of these zinc ferrites lead to better anticorrosion properties than those provided by standard phosphomolybdate Zn-Al. Zinc ferrite ZnFe2O4 (FeO.Fe2O3) synthesized from magnetite FeO.Fe2O3 proved very good protection in both types of water-borne. Unlike the other types of binders, zinc ferrite ZnFe2O4 (lam-Fe2O3) prepared from specularite lam-Fe2O3 displayed relative high efficiency in a styrene-acrylate dispersion-based binder. This is due to its higher pH whose effects combined with the lamellar shape of the particles create a mechanism preventing a paint film from corrosion.

The highest anticorrosion resistance against the creation of osmotic blisters in solvent-borne epoxy coatings was shown by zinc ferrite ZnFe2O4 (α-FeO.OH) prepared from α-FeO.OH. Once again, the most efficient pigment in this kind of binder was zinc ferrite with needle-shaped particles. However, in a solvent-borne epoxy resin binder all the pigments demonstrated very high efficiency that outperformed the efficiency of the commercially manufactured anticorrosion pigment phosphomolybdate Al-Zn.

Figure 1  SEM images of the particles of zinc ferrite ZnFe2O4 prepared from the initial raw material of goethite α-FeO.OH. a) SEI mode,b) the BEC mode
Figure 2. SEM images of the particles of zinc ferrite $\text{ZnFe}_2\text{O}_4$ prepared from the initial raw material of hematite $\alpha$-$\text{Fe}_2\text{O}_3$. a) the SEI mode, b) the BEC mode.

Figure 3. SEM images of the particles of zinc ferrite $\text{ZnFe}_2\text{O}_4$ prepared from the initial raw material of magnetite $\text{FeO.}_2\text{Fe}_2\text{O}_3$. a) the SEI mode, b) the BEC mode.

Figure 4. SEM images of the particles of zinc ferrite $\text{ZnFe}_2\text{O}_4$ prepared from the initial raw material of specularite (lam-$\text{Fe}_2\text{O}_3$). a) Processing of an SEM image by means of a secondary electron imaging detector in the SEI mode, magn. 3,500X, b) Processing of an SEM image by means of a bounced-back electron detector in the BEC mode, magn. 3,500X.
The most efficient anticorrosion zinc ferrites in coatings based on water-borne epoxy resin were zinc ferrite \( \text{ZnFe}_2\text{O}_4 \) (FeO.Fe\(_2\)O\(_3\)) synthesized from magnetite FeO.Fe\(_2\)O\(_3\) and zinc ferrite \( \text{ZnFe}_2\text{O}_4 \) (\( \alpha \)-Fe\(_2\)O\(_3\)) synthesized from hematite \( \alpha \)-Fe\(_2\)O\(_3\).

The results of the tests implied that the best anticorrosion properties in a styrene-acrylate dispersion binder are provided by the anticorrosion pigment zinc ferrite \( \text{ZnFe}_2\text{O}_4 \) (lam-Fe\(_2\)O\(_3\)) formulated from specularite lam-Fe\(_2\)O\(_3\) whose qualities are comparable with those of standard commercial products. The lamellar shape of its particles along with the greater content of soluble substances resulted in the best anticorrosion efficiency in this type of binder in the salt mist.

<table>
<thead>
<tr>
<th>Anticorrosion pigment</th>
<th>Blistering [dg.]</th>
<th>Base corrosion [%]</th>
<th>Corrosion in cut [mm]</th>
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</thead>
<tbody>
<tr>
<td>a</td>
<td>b</td>
<td>c</td>
<td>a</td>
</tr>
<tr>
<td>( \text{ZnFe}_2\text{O}_4 ) (( \alpha )-FeO.OH)</td>
<td>6F</td>
<td>8F</td>
<td>4F</td>
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<tr>
<td>( \text{ZnFe}_2\text{O}_4 ) (( \alpha )-Fe(_2)O(_3))</td>
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<td>8F</td>
<td>4M</td>
</tr>
<tr>
<td>( \text{ZnFe}_2\text{O}_4 ) (FeO.Fe(_2)O(_3))</td>
<td>4F</td>
<td>8F</td>
<td>8F</td>
</tr>
<tr>
<td>( \text{ZnFe}_2\text{O}_4 ) (lam-Fe(_2)O(_3))</td>
<td>2M</td>
<td>2F</td>
<td>4F</td>
</tr>
<tr>
<td>Phosphomolybdate Al-Zn</td>
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<td>4D</td>
<td>2F</td>
</tr>
<tr>
<td>Non-pigmented coating</td>
<td>6F</td>
<td>6M</td>
<td>2M</td>
</tr>
</tbody>
</table>

Figure 5. Overall anticorrosion efficiency of the coatings with regard to various binder bases and the synthesized anticorrosion pigments during corrosion stress in a condenser chamber with in the SO\(_2\) environment: A) \( \text{ZnFe}_2\text{O}_4 \) (\( \alpha \)-FeO.OH); B) \( \text{ZnFe}_2\text{O}_4 \) (\( \alpha \)-Fe\(_2\)O\(_3\)); C) \( \text{ZnFe}_2\text{O}_4 \) (FeO.Fe\(_2\)O\(_3\)); D) \( \text{ZnFe}_2\text{O}_4 \) (lam-Fe\(_2\)O\(_3\)); E) Phosphomolybdate Al-Zn (comparison pigment); F) non-pigmented coating.
CONCLUSION

Zinc ferrite ZnFe$_2$O$_4$ ($\alpha$-FeO.OH) with needle-shaped particles and synthesized from goethite proved to be most efficient in case of solvent-borne epoxy resins. In case of water-borne epoxy resins, high anticorrosion efficiency was displayed by zinc ferrite obtained from raw materials with isomeric particles with narrow distribution – i.e. by ZnFe$_2$O$_4$ (FeO.Fe$_2$O$_3$) synthesized from magnetite. Styrene-acrylate paints exhibited generally lower values of complex anticorrosion efficiency; the most efficient of these pigments being zinc ferrite ZnFe$_2$O$_4$ (lam-Fe$_2$O$_3$) formulated from specularite.

All of the formulated anticorrosion pigments with a zinc ferrite structure can be proclaimed to be quite suitable for application in epoxy water-borne and solvent-borne binders. When subjected to corrosion tests, the epoxy coatings with the content of the synthesized anticorrosion pigments achieved results comparable to those exhibited by epoxy coatings with a commercially produced pigment based on phosphomolybdate Al-Zn. The best results were identified with zinc ferrite ZnFe$_2$O$_4$ (FeO.Fe$_2$O$_3$) synthesized from magnetite (FeO.Fe$_2$O$_3$); this zinc ferrite demonstrated high anticorrosion efficiency in all types of applied binder systems. The synthesized pigments can be recommended for applications in anticorrosion paints based on both water-borne and solvent-borne formulations.

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References


