University of Pardubice
Faculty of Chemical Technology
Institute of Chemistry and Technology of Macromolecular
Materials

Development and Preparation of Oxide Mixture-based Pigments for Anticorrosion Paints and Testing Their Properties in Organic Coatings

Annotation of Ph.D. Thesis

Petr Benda

Pardubice, April 2017

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FACULTY OF CHEMICAL TECHNOLOGY

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Ing. Petr Benda

Study program: Chemistry and Technology of Materials

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Supervisor: prof . Ing. Andréa Kalendová, Dr.

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Summary

The properties of paints containing synthesized oxide mixture-based pigments at various volume concentrations and with the Q factor Q = PVC/CPVC = 0.65 were examined. A series of ferrite pigments were also synthesized for a comparison. Paints of both types with PVC = 10%, 15%, and 20% were used. The Q factor was kept constant by adding titanium white. The pigment properties examined included applicability in paints, morphology, particle size distribution, and composition. Steel panels coated with the paints were subjected to corrosion and mechanical tests. The anticorrosion efficiency of the oxide mixture-based pigments was expected to be higher than that of the isometric ferrites. The best results were achieved with paints pigmented with the oxide mixture-based pigments at PVC = 10% and 15%.

1. Introduction

Anticorrosion paints are routinely used to protect metals from corrosion in many industrial sectors [1,2,3,4,5,6,7]. Preconditions for a long-term protecting effect include proper formulation of the paint and thorough pre-treatment of the substrate metal surface [8]. The anticorrosion pigment in the paint and the pigment-binder combination play a key role in the paint's protective capacity.

One of the current directions in the development of nontoxic pigments, free from chromium and lead, is towards pigment mixtures that would exhibit a higher anticorrosion efficiency. [9] Typically, such mixtures contain metal oxides acting through different anticorrosion mechanisms [10,11,12,13,14, 15] and use is made of their combined effect. Such pigments are described, e.g., in the paper by Havlík, Kalendová, Veselý [16]. Test results suggest that such pigments are promising for practical use. [13, 14, 16, 17, 18, 19, 20] The present paper includes the result obtained for a ferrite-ZnO-Zn-based system.

The anticorrosion effect of ferrites involves two mechanisms. The first, most important mechanism, is associated with the basic nature of aqueous extracts of ferrites, also with regard to their very limited solubility [21] which, though, is sufficient for the pigment to exert an inhibiting effect [22] that, as L. Chromy and Kaminska [23] suggest, extends the effective time of the paint's corrosion-inhibiting action. The time extension of the inhibiting effect is so appreciable compared to other pigments that addition of ferrites to pigment mixtures is beneficial. Also, the extract is basic enough to shift the pH to the basic region, which effect is enhanced by the presence of water-soluble substances in the pigment. Selection of the cations in the ferrite structure is also relevant. Bulky cations such as Ca and Mg are more readily released from the elementary lattice to exert an effect in the paint film. These elements are used just owing to their ability to form base-forming oxides.

A mechanism of action described in many papers is based on the fact that ferrite hydrolyses in aqueous systems [24, 25, 26], and the hydrolysate is precipitated leading to formation of a thin passivation layer on the substrate surface. [12, 27, 28] Precipitation is a consequence of adequate basicity of the

pigment extract medium and occurrence of local pH maxima in the basic region during the cathodic reaction due to the formation of OH⁻ ions. [24]

The second mechanism contributing to the anticorrosion effect is associated with saponification of the alkaline earth elements in the ferrites by suitably chosen binders (alkyds, epoxy-esters), whereby the acid components in the binder are neutralised. [23, 25] The formation of soaps enhances the paint film's hardness and impermeability. [12, 13, 26, 29]

The lamellar shape of iron(III) oxide crystals in the specularite form is also beneficial [30, 31]. Application of the ferrite pigment onto a lamellar core (carrier) is a favourable option too. [12, 13, 32, 33, 34, 35, 36, 37, 38, 39] Added to a paint, such pigments exert a barrier effect: the particles assume a plane-parallel orientation to the substrate metal and form a fish-scale-like system, thereby hindering penetration of the corrosive substance through the paint film.

The action of ZnO is another important component of the anticorrosion effect. [40] It is assumed to be able to polarise cathodic regions owing to its ability to precipitate virtually insoluble salts. [9, 41] Zn, present in the form of the pigment core, and ZnO with its reactivity and strongly basic effect deactivate efficiently any acidic corrosion agents passing through the protective paint film. The basic nature enables the system to react with the carboxy groups of the (appropriately selected) binder. Zinc oxide is also known for its very good miscibility with other pigments, high covering power and ability to enhance the binder's oxypolymerisation rate.

In broader application field ferrite pigments offer unique electromagnetic [24, 25, 42, 43], chemical [21] and physical properties rarely seen with other materials [24, 25]. They are heat resistant and are excellent choices as pottery pigments for various glazes and porcelain [43]. They are also convenient for high-temperature resistant coatings.

For the paint industry one of the most important factors is the wide choice of color shades available, extending from yellow-orange to dark brown and black. Ferrite color shades are controlled according to the order of the electrons in the energy levels and electron shifts within these energy levels in the lattice. The absorption band position is also one factor. That can be controlled by proper cation selection in the spinel lattice.

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When imagined on the nano-scale, ferrites add new properties with additional applications. As a result of their greater atomic surface they are appropriate for catalysis. They also absorb light in the infrared spectrum, produce magnetic waves [42, 43] and are excellent for electromagnetic shielding and magnetic materials. In paint industry applications, it is possible to create nano-wires [44] or needle-shaped particles that significantly increase the adhesion and mechanical properties of the coatings thanks to the parallel ordering of the needles, which reinforce the linear chains of the binder [45] that are also in parallel order.

Due to the properties of these pigments, a number of studies describing the synthesis of ferrite compounds are available [31, 44, 46] There is a choices as to method of synthesis, each of which has been examined in detail. One can use high temperature techniques i.e. calcination [23, 47, 48, 49] or low temperature reactions i.e. coprecipitation, the sol-gel method [45, 50] or a polymeric precursor method [51]. It is also possible to control the morphology of the product, especially during low temperature reactions, as a relationship has been found between the synthesis parameters and the mass median diameter of the final particles. [42, 45]. It is also possible to synthesize different morphological variations in ferrite pigments i.e. isometric and lamellar ferrites, needle shaped ferrites with interesting dimension ratios (ratio of length vs. diameter of the needle or nanotube) or core-shell ferrites where the ferrite particles are bonded to a lamellar core of zinc, aluminium, muscovite, carbon, iron, glass flakes or glass fibers offering other paint applications [51].

2. Experimental

2.1. Preparation of spinel type $Me_xZn_{1-x}Fe_2O_4$ and mixture-based $Me_xZn_{1-x}Fe_2O_4/Zn$ pigments
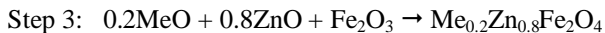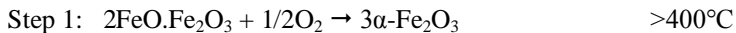
The synthesis of the ferrite–ZnO–lamellar zinc mixture-based pigment, possessing the core-shell structure in the ideal case, is based on a modification of the lamellar Zn particles. The starting materials included lamellar-particle zinc dust (Benda-Lutz® Zinc Powder Flakes Z 2012, Germany) and Bayferrox 316 magnetite (Lanxess-Bayer Leverkusen, Germany) as the best source of

iron(III) oxide for ferrite synthesis. Zinc oxide and alkaline earth carbonates of reagent grade purity were also used.
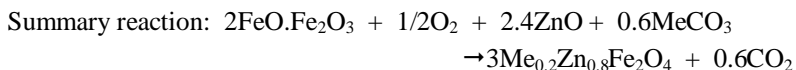
Zn particle modification consists in partial oxidation of the particle surface. Then the ZnO present on the surface of the lamellar particles reacts with α-Fe_2O_3 and the alkaline earth oxides CaO or MgO, obtained by thermal transformation of magnetite and by thermal decomposition of the carbonate, respectively – see reactions below. Magnetite, which is more reactive than hematite, is considered the best ferric ion source for ferrite calcination and reacts together with Ca^{2+} and Mg^{2+} cations, which are most suitable for the formation of the cubic ferrite structure owing to their atomic radii. Zn^{2+} cations are also suitable to form the cubic ferrite structure.

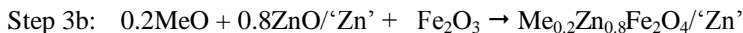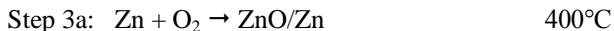The reactions giving rise to the pigments can be expressed, in a simplified manner, as follows.

$Me_{0.2}Zn_{0.8}Fe_2O_4$ and $Me_{0.2}Zn_{0.8}Fe_2O_4$/Zn formation:

Step 1: $2FeO.Fe_2O_3 + 1/2O_2 \rightarrow 3\alpha$-$Fe_2O_3$ $\quad\quad\quad$ >400°C

Step 2: $MeCO_3 \rightarrow MeO + CO_2$ $\quad\quad\quad\quad\quad$ >900°C

Step 3: $0.2MeO + 0.8ZnO + Fe_2O_3 \rightarrow Me_{0.2}Zn_{0.8}Fe_2O_4$

Ferrospinel formation, weak exothermic reaction (1050 – 1180°C)

Summary reaction: $2FeO.Fe_2O_3 + 1/2O_2 + 2.4ZnO + 0.6MeCO_3$
$$\rightarrow 3Me_{0.2}Zn_{0.8}Fe_2O_4 + 0.6CO_2$$

Step 3: Zinc oxidation and summary reaction for oxide mixture-based pigments

Step 3a: $Zn + O_2 \rightarrow ZnO/Zn$ $\quad\quad\quad\quad\quad$ 400°C

Step 3b: $0.2MeO + 0.8ZnO/‘Zn’ + Fe_2O_3 \rightarrow Me_{0.2}Zn_{0.8}Fe_2O_4/‘Zn’$

Ferrospinel formation, weak exothermic reaction (400°C)

Summary reaction:

$2FeO.Fe_2O_3 + 1/2O_2 + 2.4ZnO/‘Zn’ + 0.6MeCO_3 \rightarrow$
$$3Me_{0.2}Zn0_{.8}Fe_2O_4/‘Zn’ + 0.6CO_2$$
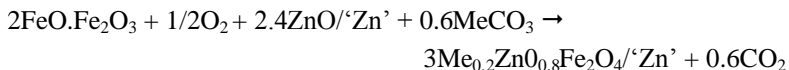
Calcination temperature must attain 400°C and must be held at that level for 30 minutes to obtain the cubic ferrite lattice, which is occupied by Fe^{3+} cations combined with the above suitable cations, and to achieve the required partial oxidation of the core. It is clear that a certain calcination temperature must be attained to get through the barrier posed by the activation energy of the reactions involved. On the other hand, the calcination temperature must not be too high to prevent morphology changes and/or complete oxidation of the lamellar zinc particles.

The pigment obtained by the calcination process is ground and milled, first manually in a mortar then in a planetary ball mill. Unfortunately, this procedure disturbs the pigment's core-shell structure and the result is rather a ferrite–zinc oxide–zinc mixture-based pigment.

The ground pigment is rinsed to remove water-soluble substances, which are largely impurities (salts) reducing the pigment's anticorrosion efficiency. An ideal water-soluble content and corrosion efficiency of the pigment is achieved by rinsing it with 3 liters of demineralized water.

2.2. Determining the properties of pigments in a pulverized state

Structural purity control (X-ray diffraction analysis)

The measurement of X-ray diffraction spectra was performed using a MPD 1880 diffractometer (Philips). An elemental composition of the pigments was determined by X-ray fluorescence analysis (Philips PW 1660).

Determinations of the morphologies of pigment particles

The surface and shapes of the pigment particles were studied using an electron microscope, JEOL-JSM 5600 LV.

Determinations of mass median diameters and particle size distributions

A MASTERSIZER 2000 particle size analyzer was used for determination of the particle size distribution.

Determination of the specific densities of the pigments

This determination according to standard EN ISO 787-10 was carried out with a gas density bottle, Micromeritics AutoPyknometr 1320.

Determination of the pH of aqueous extracts of the pigments

The procedure of determining the pH value of each aqueous extract was derived from standard ISO 787-9. The 10 per cent-pigment suspensions in double-distilled water were prepared; the suspensions were measured regularly for 29 days, then filtered and their pH was measured again.

Determination of the conductivities of aqueous extracts of the pigments

The conductivity of the aqueous extracts was performed using a conductometer. The measurements were carried out in double-distilled water, which contained 10 per cent of the pigment. This determination was derived from standard ISO 787-14. The measurements were conducted over a period of 29 days.

Determination of oil absorption (OA)

This determination was made by means of a pestle-mortar method. The specific density and oil consumption determination is important for the calculation of the critical pigment volume concentration (CPVC) and for the formulation of paints. This determination was derived from standard EN ISO 787-5.

2.3. Determination of the corrosion-inhibition efficiency of the synthesized pigments in organic coatings

Determination of resistance to humidity (continuous condensation)
EN ISO 6270

During this test, the samples were exposed to condensing distilled water at 38°C. The samples were evaluated after 2100 h of exposure.

Determination of resistance to neutral salt spray EN ISO 9227

During this test, samples of the paint films were exposed to a 5 per cent solution of NaCl at 35°C. Spraying was carried out at 12 h intervals: 10 h of saline solution, 1 h of distilled water condensation at 40°C, and 1 h of drying at 23°C. The samples were evaluated after 2100 h of exposure.

Determination of resistance to humid atmospheres containing sulfur dioxide EN ISO 6988

Exposure to this corrosive environment took place in 24 h intervals: 8 h of distilled water condensation at 36°C with SO_2 content and 16 h of drying at 23°C. The samples were evaluated after 2100 h of exposure.

Anticorrosion efficiency of the paints containing the tested pigments

The paints were applied to test steel panels and subjected to conventional corrosion tests. The results were evaluated by standardized methods, i.e. as per ASTM D 714-87 (American Society for Testing and Materials), ASTM D 610, and ASTM D 1654-92 for the accelerated corrosion tests. The corrosion processes were assigned numerical scores on the (100–0) scale.

The arithmetic means were calculated for the degree of corrosion of the metal, degree of paint film blistering, and degree of corrosion in an artificial cut through the paint film. The data were combined to obtain a single protective efficiency value, referred to as the overall anticorrosion efficiency.

2.4. Formulation of model paints with the anticorrosion tested pigments

In order to determine their anticorrosion potential, the synthesized pigments were added to a 60% solution of a high-molecular-weight epoxy-ester resin (epoxide resin esterified with dehydrated castor and soya oil) in xylene. Paints containing the commercially available Bayferrox 316 pigment and the non-pigmented binder itself served as reference systems for the evaluation.

The test paints contained each pigment at pigment volume concentrations (PVC) 10%, 15% and 20%. Titanium dioxide (a nontoxic white

pigment exhibiting a high covering power) was also added to keep the Q factor (Q = PVC/CPVC where CPVC is the critical pigment volume concentration) at Q = 0.65. The paints were denoted by using three-digit numbers where the first two digits are the anticorrosion pigment's PVC and the last digit identifies the pigment – see Tables 5-10.

3. Aim of the thesis

- The present dissertation has aimed at the demonstration of efficiency of eco-friendly primers in dependence on the pigment concentration.

- The goal is not only to determine the paint efficiency through series of mechanical and accelerated corrosion tests, but also to increase knowledge of the pigment mechanism of action.

- The determination of the distribution curve shapes for the synthesized morphologically interesting pigments is also a target.

- The aim is to summarize knowledge of the ferrite, core-shell ferrite and mixture based pigments synthesis and properties including their willingness to create mixtures and to show possibilities that oxide mixture-based pigment application bring to paint industry.

4. Evaluation of results and discussion

4.1. Properties of the anticorrosion pigments

4.1.1. Evaluation of the pigments' physico-chemical properties

As to their color, the lamellar zinc-based mixture pigments exhibited various shades of grey while the simple isometric $Me_xZn_{1-x}Fe_2O_4$ ferrites were red-orange. The following Tables I-II and Figs. 1–6 show the pigments' physico-chemical properties (density, oil consumption, CPVC), particle size distribution, elemental composition results, and SEM images of the particles.

Table I Pigment properties: density, oil absorption, CPVC and morphology of particles

Pigment	Density	Oil absorption	CPVC	Morphology of particles
1 $Mg_{0.2}Zn_{0.8}Fe_2O_4/Zn$	5.773	22.86	41.34	Lamellar
2 $Ca_{0.2}Zn_{0.8}Fe_2O_4/Zn$	5.721	19.11	45.96	Lamellar
3 $ZnFe_2O_4/Zn$	5.334	16.06	52.05	Lamellar
4 $ZnFe_2O_4$	5.057	21.22	46.06	Isometric
5 $Ca_{0.2}Zn_{0.8}Fe_2O_4$	5.000	14.63	55.97	Isometric
6 $Mg_{0.2}Zn_{0.8}Fe_2O_4$	5.075	12.57	59.31	Isometric
7 Bayferrox 316	4.578	21.36	48.75	Isometric
TiO_2 R280	4.111	25.39	47.12	Isometric

Figure 1 $Ca_{0.2}Zn_{0.8}Fe_2O_4$ pigment particles in a pulverized state (A) magnification 3,500 x, (B) magnification 10,000 x. (taken by the authors)
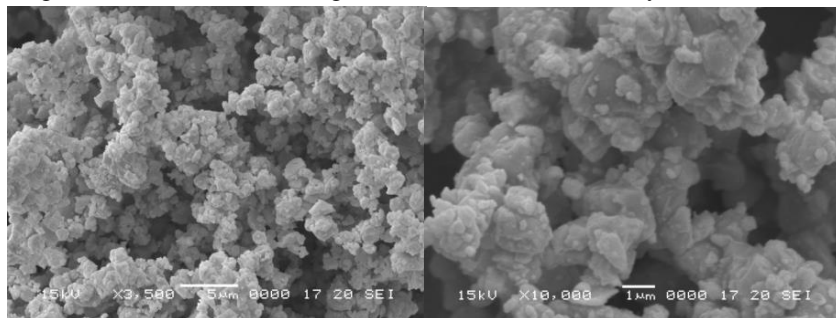
Table II Identification of elemental composition for the synthesized pigments

| Pigment/ Present compounds	$ZnFe_2O_4$ [%]	$ZnFe_2O_4/Zn$ [%]	$Ca_{0.2}Zn_{0.8}Fe_2O_4$ [%]
MgO	0.19	-	0.17
Al_2O_3	1.90	-	0.46
SiO_2	1.83	0.33	1.72
P_2O_5	0.05	0.01	0.05
SO_3	0.11	0.03	0.15
CaO	0.06	0.03	5.00
TiO_2	0.35	0.06	0.34
Fe_2O_3	61.9	12.1	62.5
ZnO	32.5	87.2	28.7
Pigment mixtures	$Ca_{0.2}Zn_{0.8}Fe_2O_4/Zn$ [%]	$Mg_{0.2}Zn_{0.8}Fe_2O_4$ [%]	$Mg_{0.2}Zn_{0.8}Fe_2O_4/Zn$ [%]
MgO	-	2.89	0.85
Al_2O_3	-	0.46	-
SiO_2	0.41	1.81	0.33
P_2O_5	0.01	0.06	0.02
SO_3	0.03	-	0.02
CaO	1.20	0.10	0.03
TiO_2	0.06	0.06	0.06
Fe_2O_3	12.5	65.7	11.8
ZnO	85.5	28.2	86.4

4.1.2. Determination of the particle size distributions
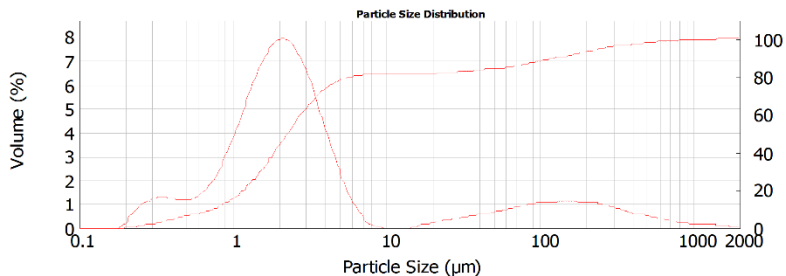
Figure 2 $Ca_{0.2}Zn_{0.8}Fe_2O_4$ pigment particle distribution (determined at the Institute of Inorganic Chemistry, Ústí nad Labem)
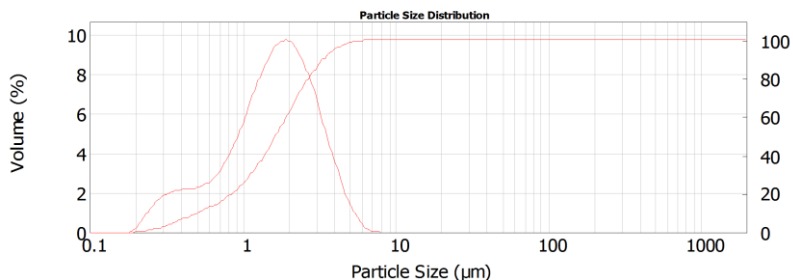

Figure 3 $Ca_{0.2}Zn_{0.8}Fe_2O_4$ particle size distribution after application of ultrasonic waves (determined at the Institute of Inorganic Chemistry, Ústí nad Labem)

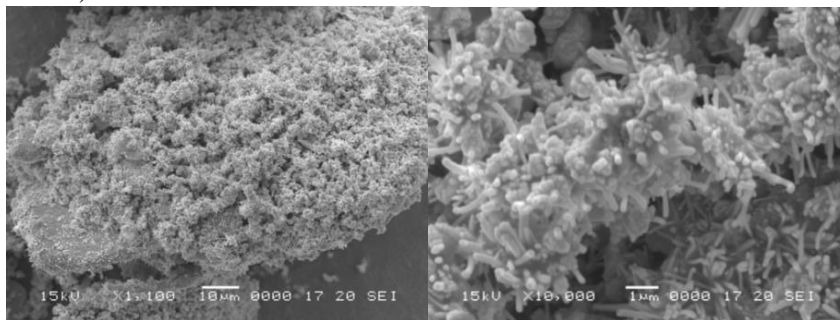Figure 4 $Ca_{0.2}Zn_{0.8}Fe_2O_4/Zn$ pigment particles in a pulverized state (A) magnification 1,100 x, (B) magnification 10,000 x. (taken by the authors)

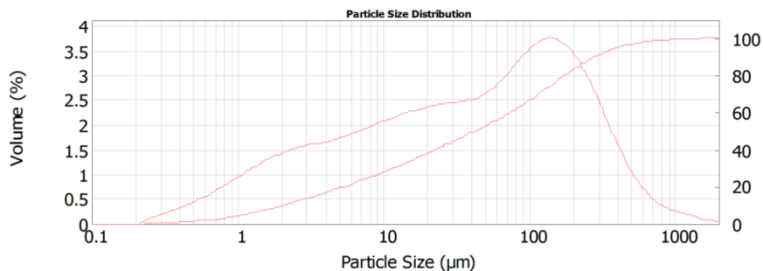Figure 5 $Ca_{0.2}Zn_{0.8}Fe_2O_4/Zn$ pigment particle size distribution (determined at the Institute of Inorganic Chemistry, Ústí nad Labem)
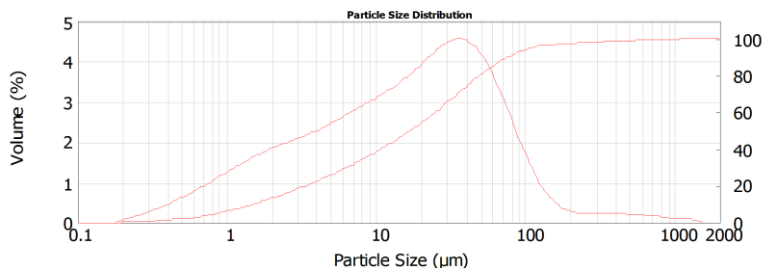

Figure 6 $Ca_{0.2}Zn_{0.8}Fe_2O_4/Zn$ pigment particle size distribution after application of ultrasonic waves (determined at the Institute of Inorganic Chemistry, Ústí nad Labem)

The distribution curve shapes for the lamellar zinc-based metal oxides were different for the different calcinated pigments but all of the curves had an ascending trend roughly up to 100-200 µm particle size. A curve may be constantly ascending or may have a local peak on the ascending segment. The constantly ascending nature of the curves is due to the steadily increasing particle size of the pigment components, which applies to the entire range from the smallest ones such as ferrites and zinc oxide to the large oxidized zinc cores coated by ferrite. The higher mean particle size suggests that the cores form agglomerates. Presumably, an agglomerate consists of 2 initial lamellar zinc particles: in fact, the mean $Ca_{0.2}Zn_{0.8}Fe_2O_4/Zn$ particle size is 107.76 µm (38.09 µm after application of ultrasonic waves) while the mean

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lamellar zinc particle size as declared by the manufacturer is 27 µm. Considerably larger agglomerates are also formed to a lesser extent: really, the distribution curve indicates the presence of particles up to 1400 µm size.

The distribution curve of isometric $Ca_{0.2}Zn_{0.8}Fe_2O_4/Zn$ (Figure 2 and 3) is different: the mean isometric particle size is 43.91 µm (1.83 µm after application of ultrasonic waves) and the curve exhibits a nearly uniform particle size distribution. The presence of aggregates between 15-1500 µm particle sizes can be identified.

Sensitivity to ultrasonic waves was also tested for the two pigment types. It appears to be convenient to expose the pigments to ultrasound prior to the dispersing step: the forces between the secondary particle aggregates are thereby disturbed and the mean particle size is favorably reduced [52, 53]. The destroying effect of ultrasonic waves on the integrity of the secondary $Ca_{0.2}Zn_{0.8}Fe_2O_4$ and $Ca_{0.2}Zn_{0.8}Fe_2O_4/Zn$ pigment particles is shown in Figure 3 and 6.

4.1.3. Evaluation of the conductivities of aqueous extracts of the pigments

The specific electric conductivity levels increased with time, due to the release of ions from the pigments. Ferrites which release ions give rise to a higher conductivity than the mixture-based oxides. A significant increase in conductivity during the 29-day period was also observed in aqueous extracts of the $Mg_{0.2}Zn_{0.8}Fe_2O_4/Zn$ mixed oxides pigment.

4.1.4. Evaluation of the pH of aqueous extracts of the pigments

The final measured pH values of the aqueous extracts of the prepared pigments ranged between 7.7 and 10.3. The measured values suggest the possible behavior of the pigments in a paint. Those pigments whose aqueous extract pH values fall within the alkaline range can be included in a group of pigments with basic effects. The highest pH value in an aqueous extract was displayed by the pigment $Ca_{0.2}Zn_{0.8}Fe_2O_4$.

4.2. Evaluation of pigments according to physical tests on the paints

The results from the overall evaluation of the physico-mechanical resistance of the epoxyester paints are shown in Figure 7 and quantify, through a single numerical value, all tests completed. Among the pigmented epoxyester films the highest values for overall physico-mechanical properties were displayed by the paints pigmented at PVC 20%.
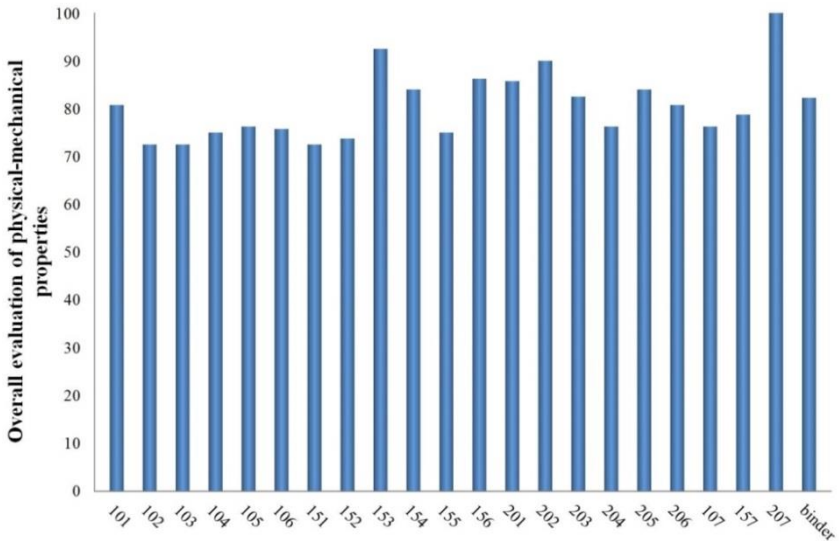
Figure 7 Overall evaluation of the physico-mechanical properties of epoxyester films (DFT= 60 μm)

4.3. Evaluation of pigments based on corrosion testing of the paints - Summary of the findings:

4.3.1. Determination of resistance to humidity (continuous condensation).

- **Suprisingly enough, the metal substrate of the coated panels exhibited corrosion while the paint films on them appeared to be undisturbed. The paint films with oxide mixtures consisting of**

lamellar particles were intact and the paint films with the isometric ferrite pigments exhibited small blisters only.

- **The minimal corrosion in the cut suggests an electrochemical effect of the pigment in this environment.**

- **Metal substrate corrosion is due to an increased paint film vapour permeability caused by the increased Q factor.**

- **The anticorrosion efficiency of the oxide mixtures with lamellar particles is stable and increases slightly with increasing PVC.**

- **The anticorrosion efficiency data for the isometric ferrites are very variable depending on the pigment type.**

4.3.2. Determination of resistance to neutral salt spray

- **Protection against corrosion in the cut is similar for the ferrites with isometric particles and for the oxide mixtures with lamellar particles. The paint films are prone to blistering in the cut irrespective of the pigment type.**

- **Isometric ferrites exhibit a higher efficiency against paint film surface blistering, possess better barrier properties (form more homogeneous films) than the oxide mixture-based pigments.**

- **Anticorrosion efficiency of paint films with the oxide mixture pigments decreases with increasing pigment volume concentration.**

- **Isometric ferrites exhibiting the highest anticorrosion efficiency include $Ca_{0.2}Zn_{0.8}Fe_2O_4$ at PVC 10% (score 90) and $Mg_{0.2}Zn_{0.8}Fe_2O_4$ at PVC 15% (score 87).**

4.3.3. Determination of resistance to humid atmospheres containing sulfur dioxide

- **Corrosion in the cut is less pronounced when using the oxide mixtures with lamellar Zn/ZnO particles than when using the isometric ferrites.**

- **The oxide mixtures with lamellar particles provide better metal surface protection and prevent corrosion propagation near the cut better than the isometric pigments.**

- **The appreciably better protective properties of paint films containing the oxide mixtures with lamellar particles are due to the better solubility of the ZnO/Zn core in the acid environment used in the corrosion test.**

- **Anticorrosion efficiency of the oxide mixtures with lamellar particles at PVC = 10%, 15%. and 20% decreases in order: $ZnFe_2O_4/Zn$ (scores 87, 87, 77) $\geq Mg_{0.2}Zn_{0.8}Fe_2O_4/Zn$ (scores 88, 87, 73) $\geq Ca_{0.2}Zn_{0.8}Fe_2O_4/Zn$ (scores 87, 83, 73).**

5. Discussion

Discussion of the corrosion test results

The paints containing lamellar oxide mixture-based pigments and isometric oxides exhibit generally poorer anticorrosion efficiency at Q = 65% than at Q = 35% [17]. It is well known that vapour permeability of the paint films increases with increasing Q factor, thus degrading the protective film's anticorrosion efficiency and bringing about change in some other properties such as surface coarseness and gloss [54]. Increased permeability to water vapour was apparent particularly in the results of the corrosion test in the condensed humidity environment, where appreciable metal surface corrosion was observed. Pit corrosion in the salt mist environment also increased with increasing Q-factor.

The anticorrosion efficiency of the oxide mixture-based pigments was expected to be higher than that of the isometric ferrites. This hypothesis was confirmed by the measurements, although the difference between the two pigment types diminished with increasing PVC to be nearly nil at PVC = 20%. And in fact, either of the two pigment types was differently efficient in the different environments.

The anticorrosion effect was highest when using paints with the lamellar oxide mixture-based pigments at PVC = 10% and 15% (roughly identical at the two concentrations). The results obtained at PVC = 20% were poorer than at PVC = 10% or PVC = 15%.

As to the isometric ferrites, the paints' anticorrosion efficiency decreased in PVC order 15% > 20% > 10%.

Resistance to humidity – continuous condensation: Taking into account the results of the corrosion tests in the condenser chamber with general water condensation it can be concluded that the lamellar oxide mixture-based pigments impart the paints generally a higher anticorrosion efficiency than the isometric ferrite-based pigments.
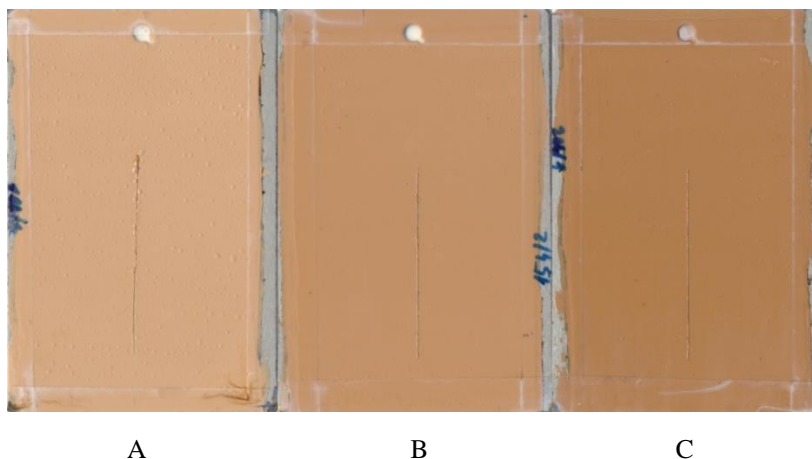

<div align="center">A   B   C</div>

Figure 8 Paints containing $ZnFe_2O_4$ ferrite pigment at PVC A)10%, B)15% and C)20% after 2100 hours exposition

| A | B | C |

Figure 9 Example of metal surface corrosion beneath a paint film with the isometric $ZnFe_2O_4$ ferrite at PVC A)10%, B)15% and C)20% after 2100 hours exposition

This is primarily due to the lower capacity of the isometric pigments to prevent corrosion in general and corrosion of the metal surface in particular. On the other hand, it was the isometric $Ca_{0.2}Zn_{0.8}Fe_2O_4$ pigment that provided the highest overall anticorrosion efficiency; it scored 98. Corrosion in the cut was very low for all of the tested paints. The permanent action of the water mist and condensed humidity resulted in appreciable corrosion of the substrate metal surface although the paint film seemed to be acceptable on visual inspection (Figure 8 and 9).

Resistance to neutral salt spray: It follows from the paint film degradation patterns in the salt spray cabinet that the differences between the paint films with the isometric ferrites and with the oxide mixtures diminish with increasing pigment concentration. Blistering was observed for many of the paint films. Blisters occurred only in a close vicinity to the cut, some other paints with the $Ca_{0.2}Zn_{0.8}Fe_2O_4$/Zn pigment exhibited blisters on the paint film surface. Blisters arise from liquid accumulation beneath the film, largely due to diffusion of the liquid through the paint film, as a response to osmotic

pressure arising from the presence of the salt or due to disturbances in the structure (Kalendová, 2003) such as paint popping. Still, corrosion in the cut was minimal in all cases, the corrosion propagation distance was never longer than 2 mm. All the paints retained their color, no significant shade change was observed. Overall, however, it is difficult to assess the degree of sample degradation in the salt spray cabinet and draw any conclusions: in fact, the corrosion patters did not indicate any dependence on the particle shape, starting substance or any other factor.

Resistance to humid atmospheres containing sulfur dioxide: Paints with the lamellar ZnO/Zn-based pigments are considerably more efficient against corrosion in the SO_2 environment than the paints with the isometric ferrites.

Figure 10 Corrosion in the cut: (left) $Mg_{0.2}Zn_{0.8}Fe_2O_4$/Zn pigment with lamellar particles at PVC 10%; (right) $Mg_{0.2}Zn_{0.8}Fe_2O_4$ pigment with isometric particles at PVC 10%

Their high anticorrosion efficiency is documented not only by the low degree of corrosion in the cut but also by the low metal surface corrosion. The former attests to the oxide mixture has high inhibiting capacity due to the electrochemical mechanism of action, the latter is due to the presence of Zn and ZnO and their anticorrosion effect.

The extent of corrosion in the cut is considerably higher if the isometric ferrite pigments are used (Figure 10). The paint films with any of the pigments turned lighter in color and their gloss decreased. This effect was more pronounced with the oxide mixtures, some of the paints turned nearly white, which may be due to oxidation of zinc in the paint giving the white zinc oxide. Zinc dissolves in acid systems to produce ZnO and other materials that enhance the paint film's impermeability and create a perfect barrier against the diffusing SO_2.

Overall comparison evaluation of system degradation in the chambers: It follows from a comparison of all the results that **most of the synthetized pigments enhance the pigment-binder system's anticorrosion efficiency**: the anticorrosion efficiency of the paint was poorer than that of the binder alone only for the systems with the isometric ferrite pigments in the sulfur dioxide atmosphere and condensed humidity atmosphere. The lamellar zinc-based pigments were found superior to the pigments with isometric particles as far as their anticorrosion efficiency is concerned. Zn and ZnO in the pigments support the anticorrosion properties.

The different pigments, however, provide very different results in the various environments. Generally, oxide mixtures with lamellar particles are excellent in the sulphur dioxide atmosphere, their results in the salt mist atmosphere are not that unambiguously good and are poorer in the condensing humidity environment. The anticorrosion efficiency differences between the various oxide mixture pigments in the different chambers are not so pronounced. Also, the anticorrosion properties of the various paints with the Zn core-based pigment mixtures are very similar at the same PVC.
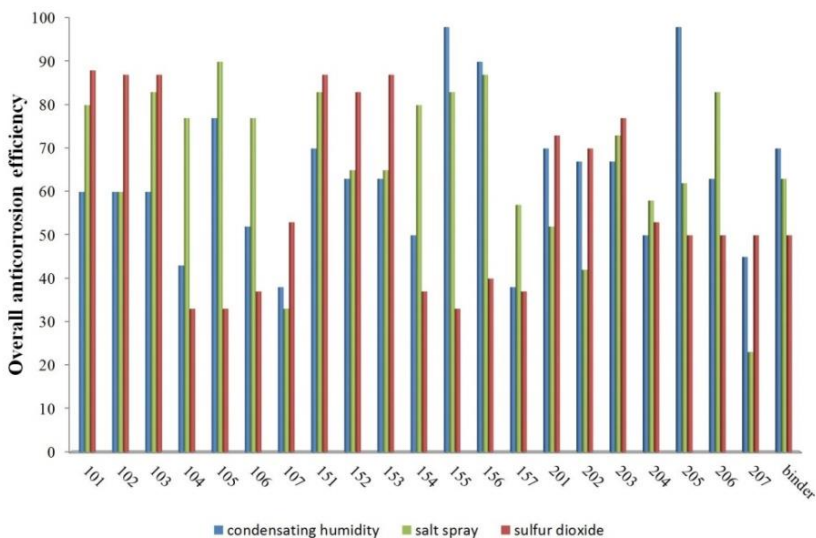
Figure 11 Overview and comparison of the overall anticorrosion efficiency for the 3 test chamber types: PVC 10% - (101) $Mg_{0.2}Zn_{0.8}Fe_2O_4/Zn$; **(102)** $Ca_{0.2}Zn_{0.8}Fe_2O_4/Zn$; **(103)** $ZnFe_2O_4/Zn$; **(104)** $ZnFe_2O_4$; **(105)** $Ca_{0.2}Zn_{0.8}Fe_2O_4$; **(106)** $Mg_{0.2}Zn_{0.8}Fe_2O_4$; **(107)** Bayferrox 316 Fe_3O_4; **PVC 15% - (151)** $Mg_{0.2}Zn_{0.8}Fe_2O_4/Zn$; **(152)** $Ca_{0.2}Zn_{0.8}Fe_2O_4/Zn$; **(153)** $ZnFe_2O_4/Zn$; **(154)** $ZnFe_2O_4$; **(155)** $Ca_{0.2}Zn_{0.8}Fe_2O_4$; **(156)** $Mg_{0.2}Zn_{0.8}Fe_2O_4$; **(157)** Bayferrox 316 Fe_3O_4; **PVC 20% - (201)** $Mg_{0.2}Zn_{0.8}Fe_2O_4/Zn$; **(202)** $Ca_{0.2}Zn_{0.8}Fe_2O_4/Zn$; **(203)** $ZnFe_2O_4/Zn$; **(204)** $ZnFe_2O_4$; **(205)** $Ca_{0.2}Zn_{0.8}Fe_2O_4$; **(206)** $Mg_{0.2}Zn_{0.8}Fe_2O_4$; **(207)** Bayferrox 316 Fe_3O_4.

The higher the overall anticorrosion efficiency of the paint, the more the pigment contribution to it.

As to the isometric ferrites, here the differences in the anticorrosion efficiency between the paints with the different pigments at the same PVC are considerably more pronounced than between the paints with the different oxide mixture-based pigments. The differences in the behavior of the paints with the various ferrite pigments between the different corrosion

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environments are also appreciable. For instance, while the $Ca_{0.2}Zn_{0.8}Fe_2O_4$ pigment exhibited outstanding results in the water condensation environment, the $Mg_{0.2}Zn_{0.8}Fe_2O_4$ pigment was efficient in the salt environment. The compound ferrites were more efficient than the simple ferrite $ZnFe_2O_4$.

In conclusion $Mg_{0.2}Zn_{0.8}Fe_2O_4/Zn$ at PVC = 15% emerges as the best universal anticorrosion pigment. Its anticorrosion properties are very good and its anticorrosion effect is versatile, providing very good results against all of the tested corrosive environments (score 70, 83, 87). Where specific applications are involved, the ferrite-based isometric pigments may be more appropriate, particularly in environments with high humidity, condensing moisture or chloride ions.

6. Conclusion

Oxide mixtures with lamellar particles can be used in epoxyester primers with the Q factor 0.65. The optimum pigment volume concentration in the paint was PVC = 15% and 10%. Panels with paint films were exposed to various aggressive corrosion environments for an extremely long time of 2100 hours and very good test results were obtained: the best pigments attained anticorrosion efficiency scores 70 – 90 on the 100 point scale. The paint systems contained no additives, and it is believed that their properties can be additionally improved by adding appropriate organic corrosion inhibitors, defoamers and materials improving the paints' adhesion as well as flow properties and the pigments' homogeneity. Modification of the pigment preparation chain, i.e. of the grinding/milling and drying process and filtration of the resulting paint, may be very promising for future research where changing the particle morphology in relation to the pigment properties is of interest.

Research implications

The properties of the oxide mixtures with lamellar particles are described. Their particle distribution curves can be obtained by particle size analysis methods with a view to obtaining additional information on the status

and properties of the pigment particles that may be useful in the development of better paints/coating materials.

Accomplisment of PhD thesis goals

The oxide mixtures with lamellar particles were synthesized. Subjected to particle size analysis, the mixture-based pigments were found to make up a broad distribution curve. Electron microscopy photographs confirmed that the pigments contained lamellar particles with a surface layer. A high anticorrosion effect at PVC 10 and 15 percentage and $Q = 65$ percentage was achieved owing to the combination of different oxide types.

Benefits of work to educational and scientific communities

The work presents the latest development in the field of non-toxic pigments based on oxide mixtures. It also presents the latest instrumental methods of testing pigments' and paints' properties.

Benefits of work to technical praxis

Oxide mixtures with lamellar particles can be used in paints protecting construction steel.

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