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**MIXED-OXIDE SPINELS USABLE  
IN ANTICORROSIVE COATING COMPOSITIONS**

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*The compounds having a general formula of  $AB_2O_4$ , containing Mg(II), Ca(II), or Zn(II) as A and Fe(III) or Al(III) as B were prepared and subjected to comparative investigations with respect to their anticorrosive activities as pigments for organic coatings. The anticorrosion efficiency data obtained in the course of standard corrosion tests indicate that these nontoxic pigments of a new generation are prospective materials for applications of interest.*

### **Introduction**

#### *Protection against Corrosion using Organic Coatings*

A majority of metallic and nonmetallic materials, the production of which is steadily rising, are exposed during their application to ever increasing mechanical and chemical loading, which causes their premature deterioration and loss of lifetime. A considerable fraction of such premature deterioration effects can be ascribed to corrosion [1], which is defined as a damage caused due to chemical or physico-

chemical medium actions [2]. The corrosion-induced damage entails conceivably also severe economical impacts. Generally we can say that the amount of losses ascribable to the corrosion effects raises with the industrialization degree of individual countries [3–5]. A considerable influence can be ascribed, of course, also to the conditions prevailing in individual climatic zones.

The most universal way of protection against corrosion consists in applying organic coats to the respective material surface. The organic coatings protect the metal surface in principle via four mechanisms consisting in barrier, adhesion, inhibition, and electrochemical effects [6]. In the coating combinations these individual mechanisms of protective actions are involved quite generally. As at present no such binders are known which could secure the long-term protection of metals against the corrosion, the barrier and adhesion mechanisms [7–9] are to be combined with the inhibiting effects of anticorrosive pigments [10].

The development of new protection systems based on the organic coatings and application thereof are affected by a number of factors, the most important ones being at present those relating to harmlessness with respect to environment and to low demands on energy. In the early days of ecological consciousness the attention focussed primarily on volatile matter of organic nature [11] present in coating compositions. At present the coating compositions as a whole are addressed, special attention being directed to toxic anticorrosive pigments, mainly those based on Pb(II) and insoluble chromate compounds [12,13].

### *Review of the New Types of Anticorrosive Pigments*

The present-time task is devoted to investigating such anticorrosive pigments which can be considered harmless from the environment protection point of view and, at the same time, highly efficient in their corrosion-inhibition action.

In principle the anticorrosive pigments can be divided, according to their action, into the following classes [14–16]:

- a) pigments acting in terms of the barrier mechanism—the pigments characterized by a flake-like structure elongating the diffusion path of the medium to the substrate surface
- b) pigments showing inhibitive activity with respect to the corrosion—the pigments reacting with the binder, metal substrate, or diffusing medium in terms of giving inhibitive acting compounds
- c) pigments showing electrochemical activity—the pigments providing a cathodic protection to the metal substrate.

The toxic pigments could be replaced in practice with zinc phosphate  $Zn_3(PO_4)_2 \cdot 2H_2O$  [17], zinc molybdate, calcium molybdate [18], and aluminum

triphosphate [19,20]. At present there exist a series of anticorrosion pigments based on phosphate anions. Also a phosphate - molybdate [21], anion is possible. The applicable cations comprise  $Zn^{2+}$ ,  $Al^{3+}$ , or  $Ca^{2+}$  and others [22]. A further possibility consists in using aluminum polytriphosphate as an anticorrosion pigment for water-dilutable and solvent-type coatings. Aluminium polytriphosphate can be modified with  $Zn^{2+}$  ions, which results in an increase in anticorrosive efficiency of the pigment concerned. The anticorrosive efficiency of primers can be secured by introducing the pigment acting on an ion-exchange principle. This concerns the pigments consisting of silicate anions and  $Ca^{2+}$  cations. Further compounds distinguished by their anticorrosive effects are represented by barium metaborate, calcium, zinc, or strontium phosphosilicate, calcium borosilicate, and zinc molybdate. Also the zinc and zinc lead(II) salts of organonitrogen compounds, organozinc compounds and calcium cyclotetraphosphate show an anticorrosive activity [23]. A separate and rather problematic group of anticorrosive pigments consists of the so-called "core" pigments, the core of which is created by an inert carrier bearing an active component. Examples of such pigments comprise iron(III) oxide, the surface of which is treated with zinc phosphate. A possible solution is presented also by calcium carbonate, zinc oxide, or calcium molybdate.

As a replacement of standard anticorrosive pigments with the pigments of an equal activity but without harmful effects the spinel-type ferrites or the spinels based on mixed metal oxides show to be prospective candidates [24–26].

Description of the properties of synthesized compounds as pigments and determination of the anticorrosive capacities thereof have required application of the methods for determining the general physicochemical and application properties of pigments on the one hand and development of the procedures usable for investigating the effective corrosion inhibition properties on the other.

## Experimental

### *Syntheses of New Spinel-Type Pigments*

The synthesis of new spinel-type pigments has made use of the possibility of isomorphous substitution in a spinel lattice of bivalent magnesium ion by the bivalent ions of other elements. The trivalent aluminium ions can also be replaced by the trivalent ions of other elements.

These pigments, representing a group of high-temperature inorganic pigments, were prepared by a procedure consisting in synthesizing a structure stable at high temperatures, the procedure being conditioned by a number of thermodynamic and kinetic factors (such as the Hedvall magnetocatalytic effect and the Tamann temperature). The process of preparing the pigments consists in 4 operations:

1. *Homogenization of starting compound mixtures.* In this stage of preparation

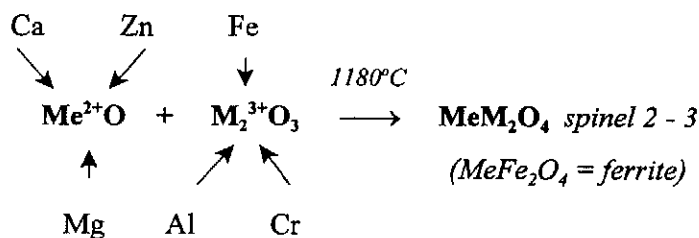
the starting materials are not only intimately mixed, but the starting substances are subjected also to mechanochemical activations, the reactivities being increased by increases in the contact area.

2. *Calcination procedure.* The calcination is accomplished via a nonisothermal firing process run in an electric furnace operated in a temperature range of 1100 to 1180 °C. In the first stage the starting materials comprising the respective metal carbonates and hydroxides undergo a decomposition process; in the second stage the oxides thus formed react with one another giving the final product. The temperatures at which the pigments were to be calcinated were based on the results obtained in course of differential thermal analyses (performed with the help of a Derivatograph Q1500 operated in a temperature range of 0 – 1050 °C at a temperature increase rate of 10 K min<sup>-1</sup>). The crystallographic product systems were identified by means of X-ray diffraction pattern analysis.
3. *Leaching the calcination products by washing with water.*
4. *Adapting the product* to obtain the size of particles as necessary by wet grinding process in a vibration ball mill for 72 hours.

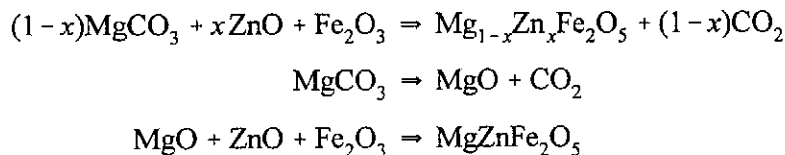
Tab. I Survey of the prepared spinel pigments

Series of the pigments	Bivalent ions	Trivalent ions	Tetravalent ions
Mg-Zn-Fe	Mg, Zn	Fe	
Ca-Mg-Fe	Ca, Zn	Fe	
Ca-Zn-Fe	Ca, Zn	Fe	
Mg-Zn-Al-Fe	Mg, Zn	Fe, Al	
Sr-Zn-Fe	Sr, Zn	Fe	
Mg-Zn-Cr-Fe	Mg, Zn	Fe, Cr	
Ti-Mg-Zn	Mg, Zn		Ti

The general scheme of the spinel (2-3) formation:



Examples of the reactions leading to the formation of the spinel-type compounds follow the scheme



Tab. II Characteristic properties of the binder used

Binder resin	Properties of the coatings obtained				
	chemical resistance	UV-radiation resistance	watertightness	heat resistance	ecological harmlessnes
alkyd	-	+	0	-	0
acrylate	-	+	0	-	+

### Results of the Corrosion Resistance Tests Performed with the Coatings Containing Spinel-Type Pigments

For testing the properties of the spinel-like pigments prepared, the model coating compositions were formulated using the polymers given in Table II as binders. The parameters characterizing an inorganic pigment-organic binder system, given as a pigment volume concentration and a critical pigment volume concentration, were determined by measuring the binder consumption by a gravimetric method under standard conditions defined in the corresponding CSN-ISO standard.

The inhibitive spinel efficiencies were tested by using accelerated laboratory-scale procedures for determining the corrosion resistance, certain characteristic properties of individual spinels were measured, and further series measurements were done starting with indirect methods for evaluating the corrosion effects. The anticorrosion properties considered were determined by means of the so-called direct and indirect laboratory tests. The proposed and performed tests are given below in paragraphs 1A – 1D and paragraphs 2A – 2C.

*1. Indirect corrosion tests* required, besides the determination of inhibition effects, a description of the action mechanisms of anticorrosive pigments:

*A. Measurement of the physicochemical properties of protective organic coatings:*

- determination of the coating-film resistances to physicochemical effects, such as the resistance to cupping, impacting, and bending
- determination of the permeability of coating films for gases and vapors on the basis of diffusion resistance

Table III Results of evaluating the properties of some synthesized pigments

Pigment	$\rho$ , g cm <sup>-3</sup>	pH value in the extract	Water soluble matter, % $\times 10^3$	CPVC, %
Mg-Zn-Fe type				
ZnFe <sub>2</sub> O <sub>4</sub>	4.998	9.2	10.1	56
Mg <sub>0.2</sub> Zn <sub>0.8</sub> Fe <sub>2</sub> O <sub>4</sub>	4.769	9.4	125.6	55
Ca-Mg-Fe type				
MgFe <sub>2</sub> O <sub>4</sub>	4.176	10.0	119.3	48
Ca <sub>0.2</sub> Mg <sub>0.8</sub> Fe <sub>2</sub> O <sub>4</sub>	4.155	10.6	139.2	41
Ca-Zn-Fe type				
CaFe <sub>2</sub> O <sub>4</sub>	4.492	9.3	181.9	43
Ca <sub>0.2</sub> Zn <sub>0.8</sub> Fe <sub>2</sub> O <sub>4</sub>	4.710	10.3	201.6	55
Al-Mg-Zn-Fe type				
0.2Al <sub>2</sub> O <sub>3</sub> 0.8ZnOFe <sub>2</sub> O <sub>3</sub>	4.713	7.4	215.8	51
MgAl <sub>2</sub> O <sub>4</sub>	3.010	10.5	103.0	43
Sr-Zn-Fe type				
Sr <sub>0.2</sub> Zn <sub>0.8</sub> Fe <sub>2</sub> O <sub>4</sub>	5.020	10.2	46.0	44
Sr <sub>0.4</sub> Zn <sub>0.6</sub> Fe <sub>2</sub> O <sub>4</sub>	4.940	10.9	172.4	42
Mg-Zn-Cr-Fe type				
MgCr <sub>2</sub> O <sub>4</sub>	3.847	8.3	3.3	61
MgOFe <sub>2</sub> O <sub>3</sub> Cr <sub>2</sub> O <sub>3</sub>	4.686	11.1	8.3	56
Ti-Zn-Mg type				
TiO <sub>2</sub> MgOZnO	4.485	8.6	115.45	67
2TiO <sub>2</sub> MgO	4.663	9.3	166.7	54

- determination of the film hardness and adhesion to the substrate
  - electrochemical follow-up procedures
- B. Measurement of the diffusion of corrosive media into coating films:*
- gravimetric determination of the coefficient of diffusion
  - microscopic determination of the coefficient of diffusion.
- C. Methods of evaluating changes of the physicochemical properties of coating films due to corrosion processes:*
- determination of the changes in colour and gloss of the coating films by

objective procedures.

*D Determination of the corrosion inhibition efficiencies of the active components of organic coatings:*

- determination of the weight losses of defined samples in media of aqueous extracts obtained from anticorrosive pigments and corrosion inhibitors
- determination of the pH and specific electric conductivity values obtained in aqueous extracts of coating films.

*2. Rapid laboratory testing procedures* for determining the anticorrosion efficiency of the pigments applied to the coating system operating by especially expressive manner. These tests comprise the procedures run in simulated corrosion atmosphere under effect of various corrosive factors accelerating the corrosion process. The procedures used in performing the tests and evaluating the results thereof are described in various CSN-ISO standards and ASTM methods; the procedures are mostly highly demanding with respect to time and labour:

- A. Accelerated corrosion tests run in an SO<sub>2</sub> atmosphere with condensing water vapour condensation, performed in a condensation chamber (the so called humidity test)*
- B. Accelerated corrosion tests run with an NaCl fog, performed in a salt-spray chamber (the so called salt spray test)*
- C. Accelerated corrosion tests run in chemical agent solutions, performed by the Mach and Schiffman procedure*

These tests give a picture of the effects of individual pigments contained in the coatings as depending on the given corrosion environment. As evidenced the results obtained from various tests can differ significantly from one another. Thus the results obtained in the condensation chamber can be diametrically opposite to those obtained in the salt chamber. Nevertheless, it is also true that when a certain pigment is capable of modifying the coating film in such a way that it succeeds in being exposed to SO<sub>2</sub> as well as NaCl, the film is really valuable from the application point of view. The results obtained were to be objectively evaluated and, at the first place quantified to get the form of clear and demonstrable data. For the purpose of this study we have used the method of evaluating the corrosion loss ( $\text{g m}^{-2}$ ) and corrosion rate ( $\text{g m}^{-2} \text{day}^{-1}$ ). Using the method of evaluating the corrosion effects by appropriate standard (ASTM B 117-90/DIN 50021, ASTM D 2247-92/DIN 50017, ASTM D 714-87/DIN 53209, ASTM D 1654-92, ASTM D 610-85) procedures, several parameters were determined: osmotic blisters having appeared at the coating surface with respect to size and frequency, corrosion at a scribing line in the coating and surface corrosion of the substrate. The results obtained are evaluated in such a way that individual effects are assigned the point designations, which were subsequently substituted into the formulas [27] for The Salt Spray Test and the Humidity Test.

Tab. IV Results of the humidity test after 1000 h (ASTM D-1654-92)

Pigment	Corrosion in a scratch, mm	Frequency and size of blisters, degree	Corrosion of substrate, %
Alkyd resin-based composition			
ZnFe <sub>2</sub> O <sub>4</sub>	0 – 0.5	10	0.3
Mg <sub>0.2</sub> Zn <sub>0.8</sub> Fe <sub>2</sub> O <sub>4</sub>	0 – 0.5	10	0.3
MgFe <sub>2</sub> O <sub>4</sub>	0 – 0.5	8	0.3
Ca <sub>0.2</sub> Mg <sub>0.8</sub> Fe <sub>2</sub> O <sub>4</sub>	0 – 0.5	8	10
CaFe <sub>2</sub> O <sub>4</sub>	0 – 0.5	8	10
Ca <sub>0.2</sub> Zn <sub>0.8</sub> Fe <sub>2</sub> O <sub>4</sub>	7 – 10	5	16
0.2Al <sub>2</sub> O <sub>3</sub> 0.8ZnOF <sub>e</sub> <sub>2</sub> O <sub>3</sub>	0.5 – 1	10	1
MgAl <sub>2</sub> O <sub>4</sub>	0	10	3
Sr <sub>0.2</sub> Zn <sub>0.8</sub> Fe <sub>2</sub> O <sub>4</sub>	0 – 0.5	8	3
Sr <sub>0.4</sub> Zn <sub>0.6</sub> Fe <sub>2</sub> O <sub>4</sub>	0.5 – 1	6	10
MgCr <sub>2</sub> O <sub>4</sub>	2 – 3	3	16
MgOF <sub>e</sub> <sub>2</sub> O <sub>3</sub> Cr <sub>2</sub> O <sub>3</sub>	0	10	0.3
TiO <sub>2</sub> MgOZnO	0 – 0.5	8	10
2TiO <sub>2</sub> MgO	0 – 0.5	8	10
Aqueous styrene-acrylate dispersion-based composition			
ZnFe <sub>2</sub> O <sub>4</sub>	0	10	0.1
Mg <sub>0.2</sub> Zn <sub>0.8</sub> Fe <sub>2</sub> O <sub>4</sub>	0	10	0.03
MgFe <sub>2</sub> O <sub>4</sub>	0 – 0.5	10	0.3
Ca <sub>0.2</sub> Mg <sub>0.8</sub> Fe <sub>2</sub> O <sub>4</sub>	0	10	0.3
CaFe <sub>2</sub> O <sub>4</sub>	7 – 10	10	16
Ca <sub>0.2</sub> Zn <sub>0.8</sub> Fe <sub>2</sub> O <sub>4</sub>	0 – 0.5	9	1
0.2Al <sub>2</sub> O <sub>3</sub> 0.8ZnOF <sub>e</sub> <sub>2</sub> O <sub>3</sub>	0 – 0.5	10	0.3
MgAl <sub>2</sub> O <sub>4</sub>	0	10	0.1
Sr <sub>0.2</sub> Zn <sub>0.8</sub> Fe <sub>2</sub> O <sub>4</sub>	0	9	0
Sr <sub>0.4</sub> Zn <sub>0.6</sub> Fe <sub>2</sub> O <sub>4</sub>	0 – 0.5	10	0.3
MgCr <sub>2</sub> O <sub>4</sub>	0	0	0.03
MgOF <sub>e</sub> <sub>2</sub> O <sub>3</sub> Cr <sub>2</sub> O <sub>3</sub>	0	0	10
TiO <sub>2</sub> MgOZnO	0 – 0.5	8	0.3
2TiO <sub>2</sub> MgO	0 – 0.5	8	0.3



Tab. V Results of the salt-spray test after 800 h (ASTM D-7654-92)

Pigment	Corrosion in a scratch, mm	Frequency and size of blisters, degree	Corrosion of substrate, %
Alkyd resin-based composition			
ZnFe <sub>2</sub> O <sub>4</sub>	0.5 – 1	8	10
Mg <sub>0.2</sub> Zn <sub>0.8</sub> Fe <sub>2</sub> O <sub>4</sub>	0	10	0.01
MgFe <sub>2</sub> O <sub>4</sub>	0 – 0.5	10	10
Ca <sub>0.2</sub> Mg <sub>0.8</sub> Fe <sub>2</sub> O <sub>4</sub>	0.5 – 1	8	10
CaFe <sub>2</sub> O <sub>4</sub>	7 – 10	5	1
Ca <sub>0.2</sub> Zn <sub>0.8</sub> Fe <sub>2</sub> O <sub>4</sub>	0	8	0.1
0.2 Al <sub>2</sub> O <sub>3</sub> 0.8 ZnOFe <sub>2</sub> O <sub>3</sub>	1 – 2	6	16
MgAl <sub>2</sub> O <sub>4</sub>	0	6	0.1
Sr <sub>0.2</sub> Zn <sub>0.8</sub> Fe <sub>2</sub> O <sub>4</sub>	0	10	0.03
Sr <sub>0.4</sub> Zn <sub>0.6</sub> Fe <sub>2</sub> O <sub>4</sub>	3 – 5	6	16
MgCr <sub>2</sub> O <sub>4</sub>	0	10	0.1
MgOFe <sub>2</sub> O <sub>3</sub> Cr <sub>2</sub> O <sub>3</sub>	0	10	0
TiO <sub>2</sub> MgOZnO	0 – 0.5	8	3
2 TiO <sub>2</sub> MgO	0 – 0.5	9	1
Aqueous styrene-acrylate dispersion-based composition			
ZnFe <sub>2</sub> O <sub>4</sub>	5 – 7	3	16
Mg <sub>0.2</sub> Zn <sub>0.8</sub> Fe <sub>2</sub> O <sub>4</sub>	1 – 2	10	3
MgFe <sub>2</sub> O <sub>4</sub>	3 – 5	6	16
Ca <sub>0.2</sub> Mg <sub>0.8</sub> Fe <sub>2</sub> O <sub>4</sub>	1 – 2	8	10
CaFe <sub>2</sub> O <sub>4</sub>	2 – 3	6	16
Ca <sub>0.2</sub> Zn <sub>0.8</sub> Fe <sub>2</sub> O <sub>4</sub>	1 – 2	9	10
0.2 Al <sub>2</sub> O <sub>3</sub> 0.8 ZnOFe <sub>2</sub> O <sub>3</sub>	1 – 2	9	10
MgAl <sub>2</sub> O <sub>4</sub>	3 – 5	8	33
Sr <sub>0.2</sub> Zn <sub>0.8</sub> Fe <sub>2</sub> O <sub>4</sub>	5 – 7	3	33
Sr <sub>0.4</sub> Zn <sub>0.6</sub> Fe <sub>2</sub> O <sub>4</sub>	5 – 7	3	33
MgCr <sub>2</sub> O <sub>4</sub>	7 – 10	3	33
MgOFe <sub>2</sub> O <sub>3</sub> Cr <sub>2</sub> O <sub>3</sub>	5 – 7	6	33
TiO <sub>2</sub> MgOZnO	7 – 10	6	33
2 TiO <sub>2</sub> MgO	10 – 13	8	33

Tab. VI Weight losses of steel samples (K) exposed to a 10 % aq. coating film suspension for 28 days

Pigment	$K, \text{g m}^{-2}$	
	Alkyd film	Styrene-acrylate film
$\text{ZnFe}_2\text{O}_4$	1.87	3.42
$\text{Mg}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$	4.40	5.36
$\text{MgFe}_2\text{O}_4$	3.97	10.96
$\text{Ca}_{0.2}\text{Mg}_{0.8}\text{Fe}_2\text{O}_4$	7.50	15.97
$\text{CaFe}_2\text{O}_4$	1.82	6.89
$\text{Ca}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$	1.01	7.72
$0.2\text{Al}_2\text{O}_3 \cdot 0.8\text{ZnO} \cdot \text{Fe}_2\text{O}_3$	3.50	7.35
$\text{MgAl}_2\text{O}_4$	4.93	8.98
$\text{Sr}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$	4.20	4.83
$\text{Sr}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$	3.95	4.52
$\text{MgCr}_2\text{O}_4$	11.02	12.46
$\text{MgO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{Cr}_2\text{O}_3$	8.94	11.23
$\text{TiO}_2 \cdot \text{MgO} \cdot \text{ZnO}$	7.89	11.11
$2\text{TiO}_2 \cdot \text{MgO}$	7.16	10.76

For the purposes of determining the comparative efficiencies of anticorrosive pigments of the spinel type prepared, also the following commercial pigments were tested:

1. Basic calcium zinc phosphate
2. Aluminum zinc phosphate
3. Zinc and boron oxide hemihydrate pigments

Red ferric oxide was used as an inert pigment. By changing the anti-corrosive pigment to inert pigment ratio, various active-component contents in the coatings were adjusted (0, 10, 20 and 30 % corrosion-inhibiting pigment). Tables III – VI. give some results of the tests performed.

## Conclusion

The new anticorrosive pigments prepared, which do not exhibit any toxic effects, can be classified into a new fundamental group of spinel-type pigments. Based on

the tests made with these pigments it is possible to get evidence on the mechanisms of the anticorrosion action concerned.

The results obtained indicate a strong neutralizing capacity of the newly developed and prepared series of spinel-type pigments. The spinel-type pigments are characterized by an aqueous extract in alkaline region, and their solubility in water is low. The pH values measured in the extracts, however, cannot affect the properties of saponifiable binders, but are, at the same time, appropriate to enforcing the inhibiting effects of the zinc, calcium, and magnesium soaps formed by the reactions between the spinel pigments and the products appearing in the coating films on drying. The neutralization of binder prevents formation of corrosion spots in the protective system. Most binders are of rather acidic nature, and thus a shift to alkaline pH region resulting from the effects of the spinel-type pigments hinders the corrosion process at organic coating/metallic substrate interface. Individual types of the spinel-type pigments can differ from each other in their efficiencies due to the cations comprised therein. The highest anticorrosion efficiency is shown by the pigments containing Zn or Mg cations.

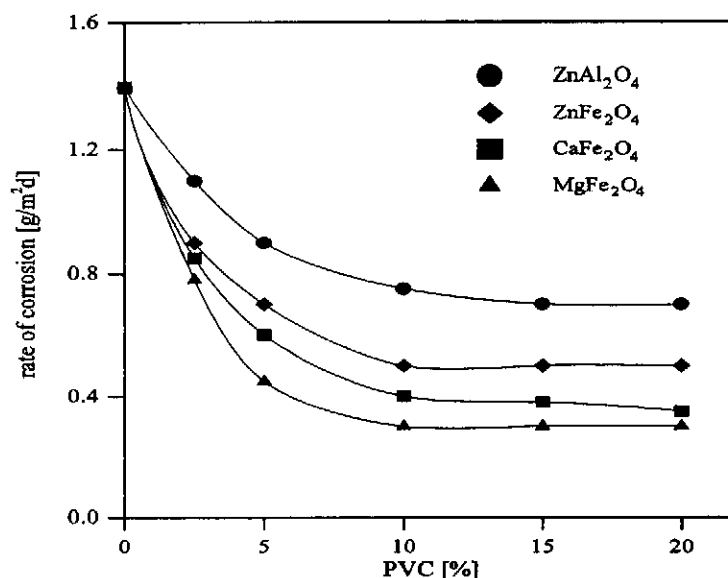


Fig. 1 Rates of corrosion of the substrate metal versus the PVC (related to the inhibiting pigment)

It was found that the diffusion of acidic corrosion medium through the film pigmented with Zn, Ca, and Mg ferrites proceeded more slowly than in the absence of the pigments. This phenomenon explains why these anticorrosive pigments work also in the binders of alkaline nature and where the neutralization mechanism cannot operate. The corrosion test evaluations performed for aqueous extracts of the

prepared pigments allow to assume the formation of the complex compounds appearing at the metal substrate-film interface.

The experimental results were used for plotting the rate of corrosion ( $v_k$ ) vs. the effective anticorrosive-pigment content (Fig.11). The given examples of graphical dependences obtained show clearly that in all the cases an addition of the anticorrosive pigment entails a reduction of the rate of corrosion. The deepest drop of corrosion occurs after adding 0 to 10 vol. % pigment (calculated on the dry coating-film substance). A further addition results in a further but inexpressive reduction of the rate of corrosion. These conclusions have been verified by the measurement of the corrosion losses encountered on the steel sheets under protective films so as by the rate of corrosion. Also the test results obtained in a salt spray chamber and those in a condensation chamber indicate high efficiencies of these pigments even at low concentrations.

The corrosion tests performed with the prepared pigments allow the conclusion that from the protection point of view the zinc and magnesium containing spinels appear to be more effective than the calcium-containing ones. The comparative pigments do not reach, in many aspects, the quality parameters of the spinel-type pigments prepared on laboratory scale. The spinel-type pigments prepared and tested are prospective pigments with respect to their high anticorrosion activities and primarily with respect to the absence of any toxicity effects.

### Aknowledgements

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