

Nontoxic Anticorrosion Pigments of the Spinel Type Compared with Condensed Phosphates

Andrea Kalendová, Jaromír Šňupárek & Petr Kalenda*

Department of Chemical Technology, University of Pardubice,
532 10 Pardubice, Czech Republic

(Received 7 July 1995; accepted 11 August 1995)

ABSTRACT

The spinel-type compounds of a general formula corresponding to AB_2O_4 containing as A the ions Mg^{2+} or Zn^{2+} and as B the ions Fe^{3+} or Al^{3+} or combination of both the A and B given were prepared and investigated with respect to their anticorrosive activities as pigments used in organic coatings. For comparative purposes pigments known for their efficiency as metal-corrosion-inhibiting ingredients in similar formulations were used. Condensed phosphates were also evaluated as anticorrosion pigments. The results obtained shown high anticorrosion activities of the spinel-type pigments.

1 INTRODUCTION

Organic coatings protect a metal surface in principle via four mechanisms, viz. by barrier, adhesion, inhibition, and electrochemical effects. In coatings, combinations of these individual mechanisms are generally involved.¹ No binders are known which can secure the long-term protection of metals against corrosion and the barrier and adhesion mechanisms need to be combined with the inhibition effects of anticorrosion pigments.

A prerequisite for the onset of corrosion² is the presence of an electrolyte at the surface of the metal substrate, this presence being the result of diffusion taking place in the coating.³ Therefore, it is necessary to provide protective coatings with a high diffusion resistance, which can be achieved by selection of an appropriate binder and by prevention, or at least inhibiting, the corrosion process running at the organic coating-metallic substrate

* Corresponding author.

interface.⁴ It is also necessary that the binder, which is most usually a high-molecular weight compound, does not undergo hydrolysis or another chemical or physical attack due to water penetrating the coating. Other pigments and fillers present in addition to the inhibitory pigments should not be soluble in the water entering the film.⁵

2 DISCUSSION

2.1 Selection of anticorrosion pigments

From the group of pigments which show inhibiting effects on corrosion, lead and chromium compounds have been used as the anticorrosion components of primers.⁶ Replacement of these is an increasing problem since these pigments are toxic⁷ and environmentally harmful but they are also highly efficient from the point of view of their action as the corrosion-inhibiting components of primers.^{8,9} This group of classic pigments is represented by red lead, lead suboxide and pigments based on chromium in the oxidation stage VI.

These pigments could be replaced in practice by zinc phosphate¹⁰ $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, zinc molybdate,¹¹ calcium molybdate,¹¹ and aluminium triphosphate.^{12,13} There now exist a series of anticorrosion pigments based on phosphate anions, and a phosphate anion–molybdate anion combination is also possible; the applicable cations comprise Zn^{2+} , Al^{3+} , or Ca^{2+} and others.^{15–18}

A further possibility consists in using aluminium polytriphosphate^{13,19} 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 the anticorrosion efficiency of the pigment concerned.

The anticorrosion efficiency of primers can be secured by introducing pigments acting on an ion-exchange principle, the pigments consisting of silicate anions and Ca^{2+} cations.^{20–22}

Further compounds distinguished by their anticorrosion effects²³ are typified by barium metaborate, calcium, zinc, or strontium phosphosilicate, calcium borosilicate, and calcium zinc molybdate.¹⁶ The zinc and zinc lead(II) salts of organonitrogen compounds, organozinc compounds, calcium borosilicate, manganese dihydrogen phosphate, and calcium cyclotetraphosphate²⁴ also show anticorrosive activity.

A separate and rather problematic group of anticorrosion 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 or titanium(IV) oxide, the surface of which is

treated with zinc phosphate.^{25,26} A possible solution is presented also by calcium carbonate treated with zinc phosphate, zinc oxide, or calcium molybdate.

In our development work devoted to new nontoxic anticorrosion pigments, we have prepared two groups of new pigments showing a certain degree of inhibitory activity.

3 EXPERIMENTAL

3.1 Preparation of spinel-type pigments

Spinel-type pigments have been prepared using the possibility of isomorphous replacement of the bivalent magnesium ion in a spinel ion by the bivalent ions of other elements; trivalent aluminium ions can also be replaced by the trivalent ions of other elements.

These pigments, representing a group of high-temperature inorganic materials, were prepared by a process of 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 spinel structure is formed at high temperatures via solid-phase reactions. The process of preparing the pigments comprises four operations, viz.

(1) *Homogenization of starting compound mixtures.* In this stage, the starting materials are not only intimately mixed, but are also subjected to mechano-chemical activations, the reactivities being increased by increase in the contact area.

(2) *Calcination procedure.* The calcination is accomplished via a non-isothermal firing process in an electric resistance furnace operated in the temperature range of 1100 to 1150°C, as derived from the DTA results. 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.

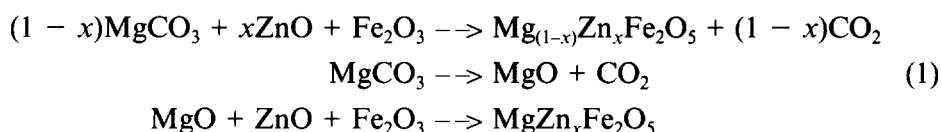
(3) *Leaching the calcination products by washing with water.*

(4) *Adapting the product* to obtain the required particle size by a wet grinding process using a vibration ball mill for about 60 hours.

3.2 Preparation of the Mg–Zn–Fe-type spinels

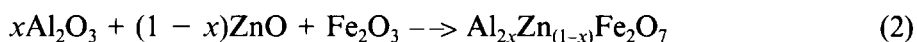
The starting materials for the preparation comprised the appropriate metal carbonates and oxides: MgCO_3 , ZnO , and red Fe_2O_3 . The calcination temperature was kept at 1150°C.

The reactions leading to the formation of these spinel-type compounds follow the scheme:



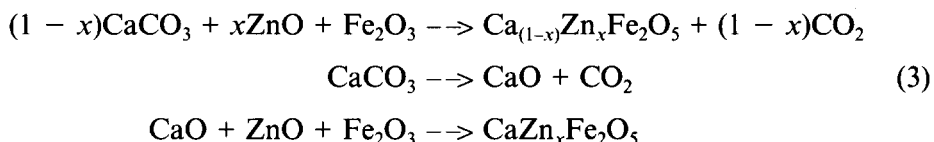
3.3 Preparation of the Zn-Fe-Al-type spinels

The starting materials were Al_2O_3 , ZnO , and red Fe_2O_3 ; the calcination temperature was 1140°C .



3.4 Preparation of the Ca-Fe-Zn-type spinels

The starting materials were CaCO_3 , Fe_2O_3 , and ZnO ; the calcination temperature was 1150°C .



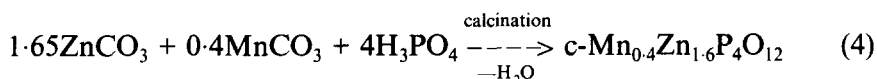
3.5 Preparation of the condensed phosphates

Two series of anticorrosion pigments were prepared, viz. (a) Al(III), Cr(III), and Fe(III) metaphosphates and (b) Mn(II) and Zn(II) cyclo-tetraphosphates. The formation of cyclo-tetraphosphates preferentially occurs with bivalent metal ions having a medium ionic radius, i.e. Zn(II), Mn(II), Mg(II), and Fe(II). The use of bivalent ions of either very small or large ionic radii results, in contrast, in the formation of higher linear phosphates—metaphosphates—similar to the products from trivalent metal ions.

The condensed phosphates were synthesized via a single-stage medium temperature thermal procedure. The starting mixtures were prepared by mixing appropriate amounts of the respective cation oxides, hydroxides, and carbonates in the form of an aqueous suspension, and 85% phosphoric acid diluted with distilled water. The mixtures were concentrated by evaporating sufficient water to give the material a pasty consistency. Subsequent calcinations were carried out in an electric resistance furnace at temperatures derived from the DTA results. The calcined products were wet ground and leached with water.

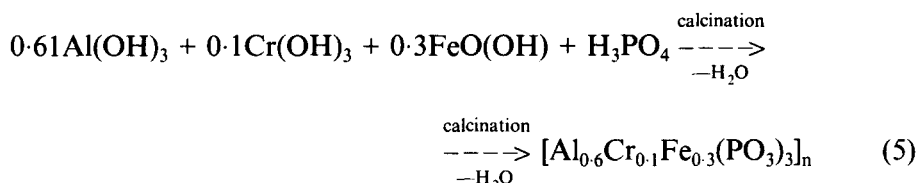
3.6 Preparation of Mn(II) and Zn(II) cyclo-tetraphosphates

The starting materials were MnCO_3 , ZnCO_3 , yellow $\text{FeO}(\text{OH})$, and 85% H_3PO_4 ; the pigment was prepared by the thermal dehydration procedure at 550°C , the starting materials being used in the mole ratios shown in the left-hand side of eqn (4):

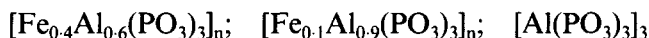


3.7 Preparation of Al(III), Cr(III), and Fe(III) metaphosphates

The starting materials were $\text{Al}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$, $\text{FeO}(\text{OH})$, 85% H_3PO_4 ; these pigments were also prepared by the thermal dehydration of the starting mixture at 800°C following the mole ratios shown in eqn (5).



Following similar procedures, pigments with the following compositions were prepared:



3.8 Other anticorrosive pigments used in the investigation

For the purpose of determining the comparative efficiencies of anticorrosive pigments of the spinel and condensed phosphate types prepared as above, the following pigments of commercial origin were also tested:

- (1) Basic calcium zinc phosphosilicate

$$\rho = 2.80 \text{ g/cm}^3, \text{ oil absorption } 31.5 \text{ g/100 g}$$

- (2) Aluminium zinc phosphate

$$\rho = 2.80 \text{ g/cm}^3, \text{ oil absorption } 40.0 \text{ g/100 g}$$

- (3) Zinc and boron oxide hemihydrate pigments

$$\rho = 2.80 \text{ g/cm}^3, \text{ oil absorption } 34.0 \text{ g/100 g}$$

3.9 Calculating the rate of corrosion

The experimental values, treated mathematically, gave the uniform surface corrosion as:

$$K = \frac{(m - m_1) \cdot 10^4}{S}$$

where K = the loss of mass per surface unit area due to corrosion (g/m^2), m = the mass of clean metal sheet (g), m_1 = the mass of the sheet after exposure (g), and S = the surface area of the sheet (cm^2).

Based on the known density for plain carbon steel, the thickness loss may be obtained from the formula:

$$V = \frac{K}{10^3 \cdot \rho} = \frac{10 \cdot (m - m_1)}{S \cdot \rho}$$

where V = the thickness loss (mm), and ρ = density of steel (g/cm^3).

The mass losses (X) can be expressed also in percentage units based on the losses in mass related to the values obtained in distilled water (representing a blank) considered as 100 percent, when

$$X = \frac{K}{K(\text{H}_2\text{O})} \cdot 100$$

From the loss value and the time (t) of corrosion effects, the rate of corrosion can be derived as the mass-loss rate $V_k \text{ g m}^{-2} \text{ day}^{-1}$

$$V_k = \frac{K}{t}$$

Similarly, the rate of corrosion expressed as the thickness loss (V_v (mm/year)) can be given as

$$V_v = \frac{V}{t} \cdot 365$$

t = time of exposure of the sample (in days), V = the thickness loss (mm).

4 RESULTS

For determining the anticorrosion efficiency of the new pigments, coating compositions containing an alkyd ethylene glycol-fumarate resin as a binder were prepared. All the samples prepared contained, in addition to the anti-corrosive pigment, a filler and inert pigments (calcium carbonate and ferric oxide) and also additives (Co(II), Ba(II), and Zr(IV) 2-ethylhexanoates)

TABLE 1
Anticorrosive Pigments Prepared and Their Properties

Pigment	$W \times 10^3$ (%)	pH	Resistivity $\times 10^3$ ($\Omega \cdot \text{cm}$)	Density (g/cm^3)	CPVC (%)
<i>Anticorrosive spinel-type pigments</i>					
CaFe_2O_4	127	10.2	1.72	4.34	56.2
$\text{Ca}_{0.67}\text{Zn}_{0.33}\text{Fe}_2\text{O}_5$	292	10.6	1.47	4.40	55.3
$\text{Ca}_{0.33}\text{Zn}_{0.67}\text{Fe}_2\text{O}_5$	207	11.0	2.94	4.70	54.2
ZnFe_2O_4	71	7.9	4.35	5.20	60.6
MgFe_2O_4	38	8.2	4.35	4.45	56.1
$\text{Mg}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_5$	30	7.9	5.05	4.96	55.8
$\text{Mg}_{0.33}\text{Zn}_{0.67}\text{Fe}_2\text{O}_5$	42	8.1	4.16	4.98	56.2
$\text{Mg}_{0.67}\text{Zn}_{0.33}\text{Fe}_2\text{O}_5$	41	8.2	3.85	4.76	56.8
ZnAl_2O_4	118	7.9	8.69	3.45	63.1
$\text{Al}_{0.66}\text{Zn}_{0.67}\text{Fe}_2\text{O}_7$	304	7.6	9.26	4.58	55.4
$\text{Al}_{1.34}\text{Zn}_{0.33}\text{Fe}_2\text{O}_7$	216	7.2	8.92	4.08	59.9
$\text{CaFe}_2\text{O}_4 + \text{ZnAl}_2\text{O}_4$ (mixed pigment)	224	9.4	2.86	3.95	54.2
<i>Condensed phosphates</i>					
$[\text{Al}_{0.6}\text{Cr}_{0.1}\text{Fe}_{0.3}(\text{PO}_3)_3]_n$	430	8.5	3.85	2.62	47.8
$\text{c-Mn}_{0.4}\text{Zn}_{1.6}\text{P}_4\text{O}_{12}$	368	2.4	3.34	3.94	48.2
$[\text{Fe}_{0.4}\text{Al}_{0.6}(\text{PO}_3)_3]_n$	325	2.3	3.12	2.55	47.8
$[\text{Fe}_{0.1}\text{Al}_{0.9}(\text{PO}_3)_3]_n$	1021	2.3	2.04	2.63	47.1
$[\text{Al}(\text{PO}_3)_3]_n$	285	2.6	8.00	2.61	48.3
<i>Comparative pigments</i>					
Basic calcium zinc phosphosilicate	215	7.6	4.74	2.97	47.3
Aluminium zinc phosphate	188	4.6	4.83	2.80	46.6
Hemihydrate of zinc and boron oxides	2763	6.6	8.55	2.80	47.6

W —content of water soluble matter, $CPVC$ —critical pigment volume concentration.

used as catalysts accelerating the autooxidation reactions, together with Disperbyk 161 (Byk-Chemie GmbH, Germany) as a dispersing agent. These coating compositions were coated on test steel sheets which had been subjected to a sand-blasting treatment prior to the coating operation.

The test samples were subjected to tests in a condensation chamber operating in a sulfur dioxide-containing atmosphere ($30 \text{ g SO}_2/\text{m}^2$) at 40°C and 100% relative humidity, after 30 days air-drying at 23°C . The efficiency of anticorrosive pigments is affected not only by the chemical composition but also by the microstructure parameters of the primary pigment particles. Only a pigment showing a certain distribution of primary particles is

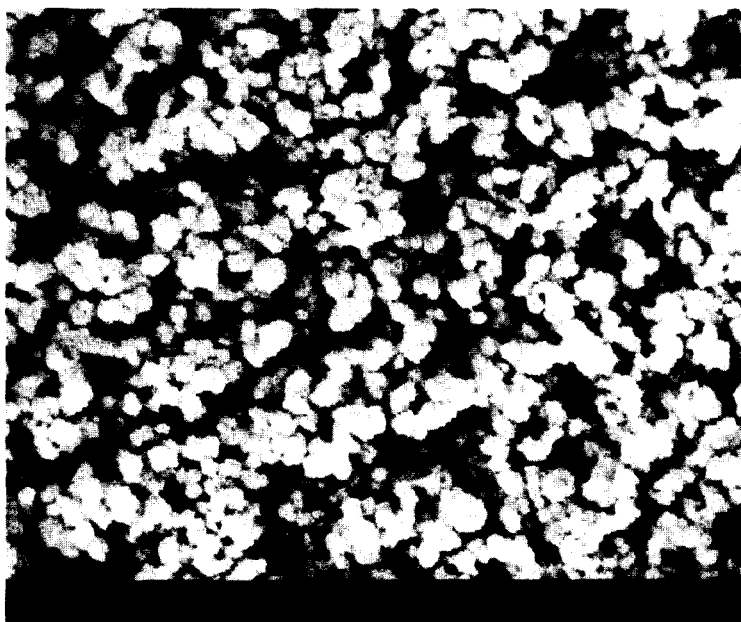


Fig. 1. Photomicrograph showing a ZnFe_2O_4 pigment taken by scanning electron microscopy, operating at 20 kV.

characterized by sufficient activity. Figure 1 represents an example of complete pigment preparation after grinding in a vibrating ball mill for 72 h.

5 CONCLUSIONS

The new anticorrosion pigments prepared, which do not exhibit any toxic effects, can be classified into two fundamental groups: spinel-type compounds and condensed phosphates. Based on the tests made with these pigments it is possible to obtain evidence on the mechanism of the anticorrosion action concerned. The spinel-type pigments are characterized by an alkaline aqueous extract and their solubility in water is low. This is in an agreement with a low conductivity value of their aqueous extracts. The mechanism of their action consists in the formation of soaps with a binder and in the alkaline action in the binder base. The neutralization of the binder prevents the formation of corrosion spots in the protective system. Most binders are of a rather acidic nature, and thus a shift to the alkaline pH region resulting from the effects of the spinel-type pigments hinders the corrosion process at the organic coating/metallic substrate interface. Individual spinel-type pigments can differ from each other in their efficiencies, due to the cations therein. The highest anticorrosion efficiency was shown by the pigments

TABLE 2

Chromaticity Coordinates of the Pigments Prepared (X, Y, Z—Trichromatic Components of the Colour L^* , a^* , b^* —Colour Expressed by Means of the CIE system— L^* , a^* , b^*)

Pigments	X	Y	Z	L^*	a^*	b^*
<i>Anticorrosive spinel-type pigments</i>						
CaFe_2O_4	11.86	16.12	7.30	45.15	9.01	7.45
$\text{Ca}_{0.67}\text{Zn}_{0.33}\text{Fe}_2\text{O}_5$	11.99	8.99	6.53	37.29	8.85	8.09
$\text{Ca}_{0.33}\text{Zn}_{0.67}\text{Fe}_2\text{O}_5$	13.02	10.21	6.07	36.73	16.16	13.51
ZnFe_2O_4	11.05	8.77	6.14	44.47	29.00	32.53
MgFe_2O_4	12.86	10.26	6.30	38.32	20.06	18.26
$\text{Mg}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_5$	10.09	8.49	5.53	35.00	21.41	15.73
$\text{Mg}_{0.33}\text{Zn}_{0.67}\text{Fe}_2\text{O}_5$	13.02	9.81	7.07	35.52	17.88	13.91
$\text{Mg}_{0.67}\text{Zn}_{0.33}\text{Fe}_2\text{O}_5$	11.05	8.77	6.17	35.56	19.46	14.12
ZnAl_2O_4	86.17	87.89	98.92	95.15	0.17	2.83
$\text{Al}_{0.66}\text{Zn}_{0.67}\text{Fe}_2\text{O}_7$	17.04	12.40	7.53	41.87	15.31	23.54
$\text{Al}_{1.34}\text{Zn}_{0.33}\text{Fe}_2\text{O}_7$	14.58	14.09	7.79	45.23	15.66	18.83
$\text{CaFe}_2\text{O}_4 + \text{ZnAl}_2\text{O}_4$ (mixed pigment)	96.17	77.89	88.92	49.78	29.71	36.41
<i>Condensed phosphates</i>						
$[\text{Al}_{0.6}\text{Cr}_{0.1}\text{Fe}_{0.3}(\text{PO}_3)_3]_n$	85.44	87.98	102.94	88.67	-0.67	0.471
$c\text{-Mn}_{0.4}\text{Zn}_{1.6}\text{P}_4\text{O}_{12}$	89.43	91.22	101.91	95.22	-0.21	0.342
$[\text{Fe}_{0.4}\text{Al}_{0.6}(\text{PO}_3)_3]_n$	93.56	93.87	102.23	93.24	0.21	0.420
$[\text{Fe}_{0.1}\text{Al}_{0.9}(\text{PO}_3)_3]_n$	95.65	97.23	104.87	89.45	0.15	0.396
$[\text{Al}(\text{PO}_3)_3]_n$	93.21	92.34	110.45	89.43	-0.09	0.234
<i>Comparative pigments</i>						
Basic calcium zinc phosphosilicate	94.56	96.66	112.94	98.73	-0.136	0.403
Aluminium zinc phosphate	93.13	94.82	108.91	98.00	-0.14	0.400
Hemihydrate of zinc and boron oxides	94.56	97.02	113.53	98.88	-0.38	0.380

containing Zn or Mg cations or by the cation Zn-Mg and Zn-Ca-Al combinations. When the spinel-type pigments were evaluated with respect to their effects in aqueous extracts in the absence of a binder (with which they form effective metal soaps in a standard binder system), their actions depend only on the alkalinity of the aqueous extract. A higher content of water-soluble active components in a spinel gives a better result of the values of V_k and V_v obtained. In real binder systems used in the coatings, the pigments give significantly better results due to their reaction with the binder (e.g. an alkyd resin).

The condensed phosphates prepared are also nontoxic and are therefore of interest from an environmental point of view. The principle of their anti-

TABLE 3
Anticorrosion Properties of Aqueous Extracts

<i>Pigments</i>	<i>K</i> ($g\ m^{-2}$)	<i>V</i> · 10 ³ (mm)	<i>V_k</i> ($g\ m^{-2}\ day^{-1}$)	<i>V_v</i> (mm/yr)	<i>X</i> (%)
<i>Anticorrosive spinel-type pigments</i>					
CaFe ₂ O ₄	8.35	1.09	0.48	0.014	96
Ca _{0.67} Zn _{0.33} Fe ₂ O ₅	7.57	1.08	0.30	0.016	97
Ca _{0.33} Zn _{0.67} Fe ₂ O ₅	5.10	0.67	0.18	0.009	59
ZnFe ₂ O ₄	8.22	1.07	0.30	0.013	93
MgFe ₂ O ₄	8.32	1.03	0.15	0.014	94
Mg _{0.2} Zn _{0.8} Fe ₂ O ₅	7.62	0.99	0.27	0.020	88
Mg _{0.33} Zn _{0.67} Fe ₂ O ₅	8.02	1.04	0.29	0.014	92
Mg _{0.67} Zn _{0.33} Fe ₂ O ₅	7.93	1.03	0.28	0.013	91
ZnAl ₂ O ₄	7.09	0.92	0.26	0.012	78
Al _{0.66} Zn _{0.67} Fe ₂ O ₇	6.82	0.36	0.10	0.005	61
Al _{1.34} Zn _{0.33} Fe ₂ O ₇	2.80	0.89	0.24	0.012	78
CaFe ₂ O ₄ + ZnAl ₂ O ₄ (mixed pigment)	7.82	0.96	0.28	0.024	89
<i>Condensed phosphates</i>					
[Al _{0.6} Cr _{0.1} Fe _{0.3} (PO ₃) ₃] _n	2.74	0.36	0.05	0.005	31
c-Mn _{0.4} Zn _{1.6} P ₄ O ₁₂	8.65	1.12	0.17	0.015	98
[Fe _{0.4} Al _{0.6} (PO ₃) ₃] _n	8.80	1.14	0.16	0.015	99
[Fe _{0.1} Al _{0.9} (PO ₃) ₃] _n	8.58	1.11	0.15	0.014	97
[Al(PO ₃) ₃] _n	4.75	0.62	0.09	0.008	54
<i>Comparative pigments</i>					
Basic calcium zinc phosphosilicate	9.42	0.99	0.31	0.013	88
Aluminium zinc phosphate	7.18	0.98	0.27	0.030	87
Hemihydrate of zinc and boron oxides	9.20	1.12	0.30	0.010	98

K—loss in weight due to the corrosion per unit surface area, *V*—thickness loss, *V_k*—corrosion rate due to losses in weight due to corrosion effects, *V_v*—corrosion rate in thickness; *X*—corrosion as a percentage of that in distilled water, weight.

corrosion action is quite different from that of the spinel pigments. The condensed phosphates act effectively in a neutral pH region, and their protection mechanism involves the formation of complex compounds resulting from reactions with a binder containing hydroxyl or carboxyl groups and from reactions with a metal substrate.

From the colour point of view the spinel-type pigments are almost all brownish and reddish-brown in tint. The condensed phosphates and all the types of comparative pigments are of off-white colour and exhibit a reduced coverage power, although this is not necessarily a disadvantage in all cases.

Comparative studies of the efficiency of the anticorrosive pigments show

TABLE 4
Anticorrosion Properties of the Pigments Prepared in a Binder

<i>Pigments</i>	<i>Corrosion of substrate^a</i>	<i>Loss in a section (mm)</i>	<i>State of coating^b</i>
<i>Anticorrosive spinel-type pigments</i>			
CaFe ₂ O ₄	2	0-1	Kr10
Ca _{0.67} Zn _{0.33} Fe ₂ O ₅	3	1-2	Kr10
Ca _{0.33} Zn _{0.67} Fe ₂ O ₅	3	1-2	Kr10
ZnFe ₂ O ₄	2	0	Kr10
MgFe ₂ O ₄	0	0	0
Mg _{0.2} Zn _{0.8} Fe ₂ O ₅	0	0	0
Mg _{0.33} Zn _{0.67} Fe ₂ O ₅	0	0	Kr10
Mg _{0.67} Zn _{0.33} Fe ₂ O ₅	1	0	Kr10
ZnAl ₂ O ₄	3	0-1	Kr20
Al _{0.66} Zn _{0.67} Fe ₂ O ₇	0	0	Kr10
Al _{1.34} Zn _{0.33} Fe ₂ O ₇	0	0	Kr10
CaFe ₂ O ₄ + ZnAl ₂ O ₄ (mixed pigment)	0	0	0
<i>Condensed phosphates</i>			
[Al _{0.6} Cr _{0.1} Fe _{0.3} (PO ₃) ₃] _n	2	1-2	Kr40
c-Mn _{0.4} Zn _{1.6} P ₄ O ₁₂	3	1-2	Kr40
[Fe _{0.4} Al _{0.6} (PO ₃) ₃] _n	3	1-2	Kr40
[Fe _{0.1} Al _{0.9} (PO ₃) ₃] _n	2	0-1	Kr30
[Al(PO ₃) ₃] _n	3	2	Kr40
<i>Comparative pigments</i>			
Basic calcium zinc phosphosilicate	2	0	Kr20
Aluminium zinc phosphate	1	0-1	Kr30
Hemihydrate of zinc and boron oxides	3	0-1	Kr40

^a Key to the 'degree of corrosion' column: 0—sheet completely without any corrosion traces; 5—sheet completely corroded.

^b KrY—corrosion spots at Y % of the surface.

that the spinel pigments in an alkyd resin binder system exhibit a higher efficiency than the pigments based on condensed phosphates. The reference pigments based on calcium zinc phosphosilicate, aluminium zinc phosphate and the hemihydrates of zinc and boron oxides do not attain, in many aspects, the quality parameters of the spinel-type pigments prepared on the laboratory scale used in this investigation.

Several reports²⁷⁻³⁰ have been made with regard to spinel-type pigments, and there is continuing interest in investigations of them as anticorrosion pigments and the possibility of their future commercial utilisation.

REFERENCES

1. Kalendová, A. & Kalenda, P., *Koroze a ochrana mater.*, **38** (1994) 81.
2. Funke, W., *Prog. Org. Coat.*, **9** (1981) 29.
3. Kalenda, P. & Kalendová, A., *Dyes and Pigments*, in press.
4. Kalenda, P., *International Conference on the Production and Application of Special Inorganic Pigments*, Pardubice, 1993, p. 169.
5. Svoboda, M., *Protikorozi ochrana kovů organickými povlaky*. SNTL, Praha, 1985.
6. Jotischky, H., *Polymers Paint Colour J.*, **178** (1988) 236.
7. Harc, C. H. & Fernald, M. G., *Paint and Resin*, **55** (1985) 22.
8. Supel, M. & Kwiatkowski, A., *Ochrana przed korozja*, **31** (1988) 58.
9. Handley, R. G., *JOCCA*, **67** (1984) 200.
10. Barraclough, J. & Harrison, J. B., *JOCCA*, **48** (1965) 341.
11. Šrank, Z., Jiráková, D., Charvát, I. & Hájek, B., *Chem. Prům.*, **40** (1990) 190.
12. Kinagasa, M., Nagita, M. & Murakami, M., *Polymers Paint Colour J.*, **174** (1984) 590.
13. Takahashi, M., *Polymers Paint Colour J.*, **174** (1984) 281.
14. Kamiya, K., Okuda, H. & Okajima, M., *Polymers Paint Colour J.*, **178** (1988) 976.
15. Gibson, M. G. & Camina, M., *Polymers Paint Colour J.*, **178** (1988) 232.
16. Jackson, M. A., *Polymers Paint Colour J.*, **180** (1990) 612.
17. Svoboda, M., Kubátová, H. & Braun, S., *Koroze a ochrana mater.*, **36** (1992) 31.
18. Svoboda, M. & Braun, S., *Koroze a ochrana mater.*, **28** (1984) 101.
19. Taketani, Y., Kondo, H. & Kropman, M., *Polymers Paint Colour J.*, **183** (1993) 270.
20. Bartoň, K., Knotková, D. & Beránek, E., *Werkstoffe und Korrosion*, **9** (1958) 519.
21. Goldie, B. P., *Paint and Resin No. 2*, (1985) 16.
22. Anon, *Pigment and Resin Technol.*, **15** (1986) 10.
23. Vleeshauwers, A. R., *Polymers Paint Colour J.*, **178** (1985) 788.
24. Svoboda, M., *Koroze a ochrana mater.*, **29** (1985) 33.
25. Milič, R., *International Conference on the Production and Application of Special Inorganic Pigments*, Pardubice, 1993, p. 141.
26. Kalenda, P., *International Conference on the Production and Application of Special Inorganic Pigments*, Pardubice, 1993, p. 154.
27. Bota, F. et al. *FATIPEC Congress XXII*, Budapest, 1994, III-113.
28. Kresse, P., *Farbe und Lack*, **84** (1978) 156.
29. Kalendová, A. & Kalenda, P., *Polymers Paint Colour J.*, **184** (1994) 570.
30. Kalenda, P., *Dyes and Pigments*, **23** (1993) 215.