# NON-POLLUTANT CORROSION INHIBITIVE PIGMENTS: ZINC PHOSPHATE, A REVIEW

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## ABSTRACT

The study of organic coatings applied to protect metals against corrosion is of great importance. Anticorrosive paints containing lead or hexavalent chromium compounds as pigments are particularly hazardous. Zinc phosphate was proposed as an alternative non pollutant one. However, results obtained with this pigment are very contradictory.

The aim of this paper is to give a state-of-the-art-report about the pigment performance in order to clarify the causes of such contradictory and, sometimes, discouraging behaviour.

## INTRODUCTION

In the present world, corrosion phenomena are observed everywhere on cars, metallic structures, equipments, etc. In recent years, the environmental pollution has led to enhanced corrosion processes. Thus, the application of organic coatings to protect metals against detrimental effects of corrosion is of great importance. Anticorrosive paints containing lead or hexavalent chromium compounds as pigments are particularly hazardous and contribute to the mentioned pollution.

Due to the toxicity of conventional pigments and legal restrictions imposed on their use, pigments manufacturers have accorded to undertake extensive research and development programs about new, non-toxic and corrosion inhibitive compounds.

The present world trends for changing the toxic anticorrosive pigments are mainly focused on their substitution by different phosphates or ferrites. Other compounds such as borates, molybdates, silicates or ion exchanging inorganic compounds have also been proposed to a lesser extent. Barrier pigments with lamellar structure were found to be effective for restraining the steel corrosion of painted specimens.

Zinc phosphate (ZP) has reached a great diffusion as anticorrosive pigment. However, very different experimental results were obtained with this pigment; therefore, new phosphate based pigments have been developed to replace it.

Ferrites constitute a novel group of corrosion inhibitive pigments; the main difficulty being its high cost of production due to the fact they are obtained by heating at 1000°C. Its anticorrosive mechanism is not still fully understood but it was suggested that their action could be improved by adding zinc phosphate to the paint formulation.

The aim of this paper is to carry out a literature reviewing about ZP specifying its advantages, the most important characteristics, the available techniques to prepare it and a detailed description of its anticorrosive effect, in order to give the reader a state-of-the-art report on this field. Likewise, an extended list of other phosphates is included. Alternative pigments such as modified zinc phosphates, together with its anticorrosive performance compared with that of ZP, are also described. Different formulations performance, when subjected to laboratory accelerated and/or outdoor tests, are included too.

## THE IMPORTANCE OF ZINC PHOSPHATE AS ANTICORROSIVE PIGMENT. ADVANTAGES AND DISADVANTAGES

For environmentally compatible anticorrosive priming formulations, the raw materials producers often recommend using ZP together with adequate binders and metallic substrates to form adhesive and inhibitive complex substances (henceforth referred to as "complexes") assisting the phosphatizing of the metal base. It results are particularly effective in anodic areas where protective layers are formed.

ZP is:

a) A white pigment, therefore primers of all colours may be obtained.

b) Less sensitive to corrosion stimulating ions (such as chloride and sulphate) than chromates /1,2/.

c) Weldable without producing toxic fumes.

d) Able to be used with all types of binders; when added to resins it improves both the drying and the adhesion to the metal substrate /2/.

e) Particularly effective when coatings are exposed to $SO_2$ polluted environments; therefore, it is a valuable product for most industrial atmospheres /3-5/.

Hydrated ZP proved to be a very effective way to incorporate water and phosphoric acid to wash primer paints, which uptake small amounts of phosphoric acid or are almost incompatible with water. The low acidity of the system allows the binder being modified with phenolic and polyester resins, improving coating hardness and adhesion /2/.

Meyer /2/ stated that in order to protect a painted metal for longer exposure times, ZP could not be employed as the only anticorrosive pigment but must be accompanied by another one. This is due to the fact that ZP hydrolyzes itself and its content diminishes continuously in the paint film. Besides improving the anticorrosive coating performance, ZP has additional effects on brushing and flow characteristics promoting an excellent topcoat adhesion /6/.

Kukla *et al.* /7/ pointed out that inorganic phosphates did not give a suitable anticorrosive protection. On steel panels covered with a porous epoxy polyamide coating and exposed for 100 days, the electrochemical impedance spectroscopy proved that chromates were more effective than ZP /8/. However, Pietsch /9/ found that the anticorrosive properties afforded by chlorinated rubber paints pigmented with ZP at 25 wt % were equivalent to those using zinc chromate.

ZP coatings showed certain susceptibility to attack by fungi /10/. This is due to the nutritious properties of phosphate. The main difficulty concerning ZP seems to be related to its low solubility /11/, which originates a small phosphate concentration to protect the metallic base.

## TECHNICAL SPECIFICATIONS

Table I summarizes current technical data about ZP. Two types, differing in the percentage of fine particles, were recognized, one having 94.59%, the other 98.48% of particles finer than the DIN 130 sieve, respectively.

**TABLE I**
Determination of technical specifications for zinc phosphate

| Assay | Specification | Reference |
|---|---|---|
| Zinc ion ($Zn^{2+}$, %) | approx. 51 | [3] |
| Phosphate ion ($PO_4^{3-}$, %) | approx. 49 | [3] |
| Ignition loss (%) | approx. 10-14 | [3, 25] |
| Oil absorption (g/100 g) | 20 - 23 | [3, 4] |
| Water soluble chloride (% $Cl^{1-}$) | < 0.01 | [3] |
| Water soluble sulfate (% $SO_4^{2-}$) | < 0.01 | [3] |
| Water solubility, 20°C (%) | 0.05-0.08 | [25] |
| Water solubility, 23°C (g/100 ml) | 0.0155 | [3] |
| Specific density | 3.0 - 3.25 | [4, 25] |

## THE ELABORATION PROCESS OF ZINC PHOSPHATE

ZP can be prepared either by mixing disodium phosphate and zinc sulfate solutions or saturating a 68% phosphoric acid solution with zinc oxide, both methods at the boiling temperature /12/. In each case, the resulting precipitate must be adequately treated to yield a product having the composition $Zn_3(PO_4)_2 \cdot 4\ H_2O$, which loses two water molecules at temperatures up to 200°C. Water free ZP can only be obtained by heating it to a temperature of 800°C /13/. Compared with zinc chromate, ZP has an extremely coarse crystalline structure. By further grinding or sifting it is possible either to break down or remove coarser particles or aggregates improving pigment characteristics such as dispersibility, settling and/or anticorrosive behaviour. Primary particles with an average diameter comparable to that of zinc chromate could not be obtained with these methods. Controlling reaction conditions during the production process it would be possible to make metal phosphates with the desired particle size distribution /14/.

Micronized ZP has acquired ever increasing significance since it disperses better, sediments less and its content in the paint formulation may be reduced. This is probably due to the smaller particle size and the surface changes produced during the micronization process.

Pigments with particle size $< 5\ \mu m$ and a core containing titanium white, iron pigments, zinc oxide, lithopone, barium sulfate, silica, alumina, kaolin, mica, talc, alkaline earth carbonates, or magnesium carbonate, coated with a 5-30% ZP, were prepared precipitating this last one on the pigment particles in aqueous suspensions. In this form ZP consumption in anticorrosive paints is reduced to < 90% /15/.

## MODIFIED ZINC PHOSPHATES

Gerhard and Bittner /16/ sustained that the protective characteristics of zinc chromate are not achieved by ZP, therefore, modified zinc phosphates were proposed. The most important are concerned with one or more of the following properties:

a) adequate particle size distribution;
b) addition of Al, Mo, Mn, etc.;
c) addition of basic groups; and
d) an organic pretreatment.

Conventional ZP consists of large (12-20 μm) lamellar particles. As it was mentioned previously, metal phosphates with enhanced particle size distribution may be obtained /14,16,17/. A technique to obtain small spherical ZP particles was recently developed /18/.

Zinc aluminium phosphate (ZPA), obtained from the ZP and aluminium phosphate combination in wet phase, appeared interesting because it exhibited a higher phosphate content than ZP /16,17/. The acidity generated by the hydrolysis of aluminium ions cause an increasing phosphate concentration.

In binders containing aliphatic acids the addition of basic groups is important with regard to metal soap formation /14/. Furthermore, adhesion is also improved when the reaction between the basic and acid groups from the binder takes place.

The zinc molybdenum phosphate basic hydrate (ZMP) produces molybdate anion ($MoO_4^{2-}$) which is an anodic inhibitor with a passivating capacity only slightly less than that of chromate anion.

A manganese modified ZP coating for the automobile industry was reported /19/ as improving the anticorrosive performance of low ZP coatings.

## MIXING OF ZP WITH OTHER PIGMENTS. ACTIVATION.

Meyer /2/ distinguished three phases in the anticorrosive protection process. A complete anticorrosive primer must be formulated containing pigments for every phase. ZP would only be useful for the initial and prolongation ones due to a leaching process through the paint film For the late phase, consequently, another pigment such as lead phosphate ($Pb_3(PO_4)_2$), iron phosphate ($FePO_4$) or chromates must be added to achieve a protective action for at least 6 years. Likewise, addition of very small concentrations of organic chromates such as guanidine chromate or cyclohexylamine chromate when ZP is used as anticorrosive pigment was suggested /7/. These organic compounds reduce chromate level in the mixture when acting on the micropores of the paint film.

Accelerated tests have shown that activated and modified basic zinc phosphates are corrosion inhibitors as effective as ZP plus a mixture of pigments containing water soluble chromates /20/.

The anticorrosive performance of a pigment mixture such as /21/:
alkaline red oxide from bauxite 45-60%
zinc chromate 18-25%
ZP 5-10%
zinc ferrite 18-25%

was similar to the red lead one. The mixture proportion was 34-40% in

**TABLE II**
Relative solubilities in water of zinc phosphate and modified phosphate pigments

| Pigment | Water soluble matter in mg/l. (ASTM D 2448-73, 10 g pigment in 90 ml. water) | | | | |
|---|---|---|---|---|---|
| | Total | $Zn^{2+}$ | $PO_4^{3-}$ | $MoO_4^{2-}$ | $CrO_4^{2-}$ |
| Hydrated zinc phosphate | 40 | 5 | 1 | -- | -- |
| Hydrated organic modified zinc phosphate | 300 | 80 | 1 | -- | -- |
| Hydrated aluminum zinc phosphate | 400 | 80 | 250 | -- | -- |
| Hydrated zinc molybdenum phosphate | 200 | 40 | 0.3 | 17 | -- |
| Zinc potassium chromate | 1500 | -- | -- | -- | 1000 |

Note: These data were taken from reference 25.

binder; talc as the filling material and 30 μm the suggested average particle diameter.

ZP was employed with borates /5,22/, molybdates /23/ and zinc nitrophtalate /5/. Alquil acid phosphates could be added to ZP in order to improve adhesion /2/.

Multiphase pigments are also produced depositing an active chromate-phosphate together with lead on a silicate core. A multiphase anticorrosive ZP pigment containing $Ti_3(PO_4)_3$ having a good hiding power was also prepared /24.

In acid media, phosphates solubility increases due to the development of species like $PO_4H_2^{1-}$ and $PO_4H^{1-}$, whose relative amounts depend on the pH /25/.

## BINDERS

ZP can be used with all types of binders. The recommended level is 40% in the paint or 25% in the coat film. Binders include vegetable oils, alkyd resins, phenolic resins, phenolic resins modified with tung oil, vinyl chloride copolymers, chlorinated rubber, epoxy, phenolic, urethane resins and acrylic emulsions /2,4,6/. The employment of mixed binders was also reported /14/.

## FORMULATIONS PERFORMANCE

The misleading nature of the conventional salt spray test and, to a lesser extent, the humidity cabinet tests to assess the anticorrosive primers performance was noticed early in the sixties. The accelerated tests of ZP gave bad results but outdoor long exposure tests were encouraging /5,6/. It was assumed that differences in evaluating paints performance arose because sometimes accelerated but other the outdoor exposures tests were the criterion employed to monitor them.

Several researchers /26,27/ established that during accelerated test, the behaviour of a paint system is mainly governed by the binder. If the binder fails, the influence of the inhibitive pigment can be observed. For instance, there were not important differences among the anticorrosive pigments when epoxy and polyurethane were employed as binders. With chlorinated rubber ones, ZP led to good results.

Moreover, variables which are relevant to paint formulation are not always controlled during its evaluation. All these factors make difficult a reliable assessment of the ZP effectiveness as anticorrosive pigment.

During 1961, steel structures were painted and examined 3 years later. ZP pointed out the same protective properties than any conventional anticorrosive pigment with binders based on vegetable oils and alkyd resins. It offered better protection than similar paints pigmented with red oxide, red oxide/zinc chromate or zinc chromate. Furthermore, it showed advantages over red lead since it maintained a tightly bound film, whereas the lead-based primer show chalking after one year exposure /6/. In the multicoat system (two primer coats and aluminium or micaceous iron pigmented alkyd gloss topcoat paint), ZP in oil and alkyd paints took as excellent performance as those containing lead pigments. When aluminum paints were applied on the phosphate based primer there was not apparent erosion of the topcoats such as occurs when these paints are applied over red lead pigmented primer/6/.

In more recent studies, painted specimens with alkyd and epoxy water based formulations were tested using accelerated (salt spray, humidity, $SO_2$) and outdoor exposure tests (natural and industrial environments) /3,28/. Two coats, 35-40 μm dry film thickness each one, were applied on sandblasted panels with 24 hours drying between each coat. Compared with the red lead or zinc chromate pigmented alkyd or epoxy paints, those using ZP showed a lower poorer anticorrosive performance in almost all the tests. However, when exposed to an industrial atmosphere these paints behaved similarly in areas far from the scratch and better than those pigmented with iron oxide.

For moderate outdoor exposure conditions, modern specifications /29/ recommend a maximum content of ZP of about 20% by volume in the dry film when a standardization fineness was used. When spherical optimized particle size distributions are employed, the ZP content can be lowered to 10% and the painted panel is able to resist more severe exposures.

The performance of ZP pigmented coatings could be improved through an adequate surface preparation. Better results in the humidity test were obtained with grit blasted steel panels /30/. The corrosion resistance of paints with ZP is enhanced using wetting and dispersing agents. These additives have similar chemical constitution, which invariably contain a low molecular weight polycarboxylic acid polymer with multifunctional structure (carboxyl groups as well as C=C bonds, amide structure, amino groups, etc.). They do not only contain groups with pigment affinity but also reactive ones which facilitate the crosslinking reactions in the paint system. The maximum level of these additions is 1.5-2.5% of the pigment content. Higher contents would produce blistering and drying problems /31/.

Bose /32/ reported the employment of an anticorrosive epoxy-ZP primer modified with organosilanes. Five methoxysilanes were used in order to improve adhesion as well as hardness and corrosion resistance.

Results obtained by Williams Wynn /33/ reflect the differences between outdoor exposure and accelerated tests. ZP-iron oxide pigmented paints showed good anticorrosive performance for 270 days outdoor exposure while a fair behaviour was observed in a 1000 hours salt spray test. ZP alone led to fair and poor results in both conditions, respectively. However, a formulation based on yellow (10%) and red (9.2%) iron oxides and talc (8%) and ZP (25%) as anticorrosive pigment in an alkyd binder (38%) was reported as giving promising results /34/.

Compared with other anticorrosive pigments, ZP in conjunction with chlorinated rubber binder showed a very good performance in protecting steel sheets under cathodic polarization. The initial current requirement was 1.2 $mA.m^{-2}$ but increased up to 7.8 $mA.m^{-2}$ after 24 weeks exposure. With other pigments, the final current requirements were near to 30 $mA.m^{-2}$ /35/.

The anticorrosive behaviour of modified zinc phosphates was studied by several researchers /14,16/. The anticorrosive pigment was 40% by volume and the PVC/CPVC ratio (Q) was maintained in the range 0.7-0.8. The paints were applied by means of a spraying technique on pickled or sandblasted panels. The coating thickness was 50+5μm. The coated specimens were subjected to the salt spray test (DIN 550021) and the Kesternich test (DIN 500181.0.5).

ZPA and the zinc basic phosphate with an organic pretreatment (ZPO) proved to be superior to the traditional ZP with respect to the anticorrosive behaviour. In salt spray test, they exhibited better adhesion characteristics, lower blister formation and higher anticorrosive properties. Furthermore, ZPA and ZPO produced equivalent or superior results to zinc chromate in both standardized tests. ZMP showed an acceptable behaviour too. The protective action of modified zinc phosphates depends on the Q value; if Q lied between 0.8 and 1.0, the loss of adherence as well as the oxidation increased after 400 hours exposure to the salt spray chamber. If Q equals 1, considerable blistering and oxidation may occur. The optimum Q value must lie between 0.7 and 0.8 /16/; in these cases, the best protective effect was obtained with a PVC of about 33%.

The protection obtained with ZP was remarkably inferior to the other phosphates; a PVC of about 33% produced the a protective effect equal than 11% by volume of ZPA, ZMP or ZPO /16/.

The anticorrosive behaviour of these pigments was also influenced by filler. ZPA led to good results with fillers like magnesium silicate or titanium dioxide; the same occurred with ZMP and ZPO associated with magnesium or aluminium silicate, titanium dioxide, calcium carbonate, etc.). Other fillers produced either poorer or bad results /14,16,33/. The filler particle size was not important /16/.

The surface preparation also influenced the pigments response; ZPA was the most suitable. Results obtained with ZPA in accelerated tests were similar to the zinc chromate ones /30/.

The anticorrosive behaviour of ZP and modified zinc phosphate was studied in low solvent content or water thinnable systems /25,30/. High solids, alkyds, water reducible coatings based on acrylic emulsions and water borne epoxy paints were chosen and tested due to the fact that they are environmentally acceptable.

In high solids primer coatings, ZP provided the poorest anticorrosive properties compared with the other anticorrosive pigments /25/. ZMP and ZPO led to low rusting in the underlying metal surfaces covered with water reducible coatings based on acrylic emulsions. The emulsifiers enhance both the water resistance and the corrosion protection after film formation.

According to salt spray tests, ZPA is the most suitable pigment for water based epoxy coatings. As a general rule, it can be said that ZPA is the most effective anticorrosive pigment, but ZMP and ZPO led to good results too. ZP showed good results in the humidity test when grit blasted steel was employed. The performance of these coatings may be improved through changes of extenders and/or adequate surface preparation /36,37/.

In the case of water borne coatings, the salt spray test exposure produces in some cases a total destruction of the paint film. Further information could be obtained from the humidity and water immersion tests and also from that proposed by Kossman /38/.

## ZINC PHOSPHATE ANTICORROSIVE ACTION MECHANISM

The aqueous extract of ZP produces the same amount of corrosion that water. The pigment is sufficiently insoluble to act as an inhibitor. ZP slurry instead of the aqueous extract must be employed if lower weight losses are to be obtained /25/. However, the differences are not significant.

Weight losses of steel specimens are smaller in aqueous extracts from ZP ground in linseed oil than the original in water; likewise, were only slightly smaller than in the extracts obtained from linseed oil alone. The ZP-linseed oil extracts contained ten times more phosphate than those prepared with water, and had a 4.4 pH value which is similar to that attained with a zinc soap. Therefore, it was concluded that ZP in linseed oil forms soaps which may yield inhibitive degradation products. ZP soaps are not as efficient inhibitors as lead ones /39/.

Regardless of the linseed oil binder, the protective effect of phosphate pigments is due to the humidity penetrating through the pores of the coating; this causes slight hydrolysis giving rise to secondary phosphate ions. These ions affect the anodic corrosion process through the formation of a protective passive layer /14,40/. The layer build up to a thickness enough to provide apparent passivity /41/. Porosity of phosphate coatings (which is closely related to the coating protective performance) was measured by electrochemical impedance spectroscopy method /42/. Poor phosphate coating coverage leads to flash rusting /43/.

Compounds such as mixed zinc and iron phosphates were supposed to be formed on protected steel surfaces /21/; but the proposed formulas are incorrect from a stoichiometric point of view.

Because of the slight solubility of ferrous phosphate, the corrosion reaction is not totally controlled, but is reduced to an acceptable degree. Pryor and other researchers /44,45/ stated that the inhibition was due to a protective film of $\gamma$-$Fe_2O_3$, maintained in constant repair by dissolved oxygen. Such film was proposed as being formed by adsorption of oxygen, followed by heterogeneous reaction and thickening until reaching an equilibrium value of 20 nm, from which the outward diffusion of iron is prevented. It is assumed that phosphate ions do not participate directly in the oxide film formation. Their function is confined to discontinuities in the oxide film. Plugged pores of defective areas of the ferric oxide is provided by the anion precipitation. Fe(II) react with dissolved oxygen to give more insoluble Fe(III) ions. Pryor's results were obtained employing soluble phosphates, and probably they could not be extrapolated directly to very insoluble phosphates as those employed in paint formulations.

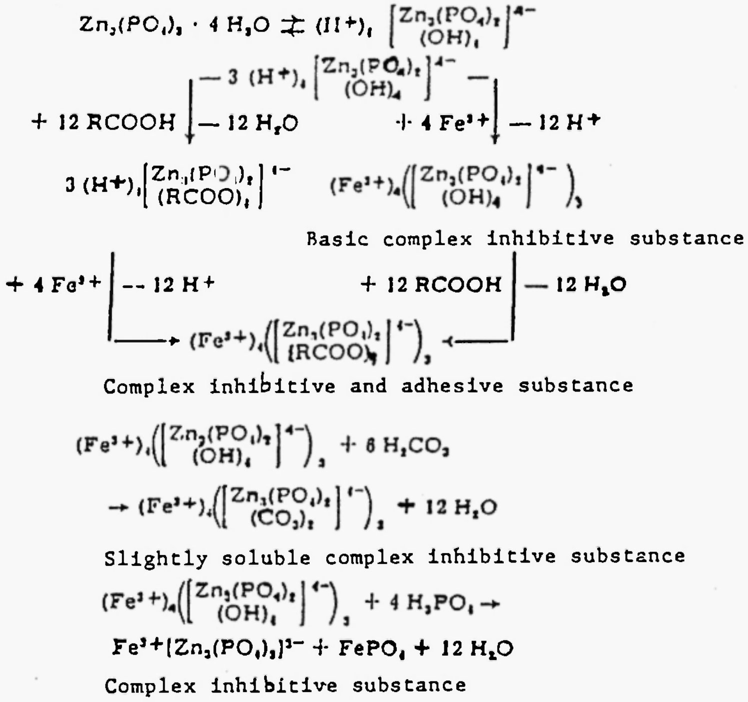
Phosphate based pigments provide corrosion inhibition in aerated solutions but they are ineffective in deaerated solutions. The corrosion potential becomes more noble in aerated solutions, and sometimes reaches the characteristic value of passivated steel.

Corrosion inhibition by phosphates takes place only when the anion concentration is higher than $10^{-3}$ M in a salt solution, which pH value ranges between 5.5-7.0 /44/.

More recent studies confirmed both the presence of increased amounts of oxyhydroxides and the incorporation of iron phosphates in the protective film /46/.

Clay and Cox /47/ have suggested that the protection mechanism involved the polarization of cathodic areas by the formation of scarcely soluble basic salts adhered to the metal surface. These salts may contain the anion. The layer is claimed to be effective by limiting the access of dissolved oxygen to the metal surface. This statement was confirmed by the work of Szklarska-Smialowska *et al.* /48/.

Meyer /49/ sustained that the major utility of ZP in paints may be found in the mixtures with other less soluble inhibitive pigments in order to avoid underfilm corrosion during the initial stage of the protective period. According to this author, ZP protective action includes the phosphatizing of the metal substrate and the formation of "complexes" products through the reactions with the binder components. Then, these "complexes" can react with corrosion products yielding a layer strongly adhered to the metallic substrate. Such "complexes", due to reactions between carboxylic acids and hydroxyl groups of the binder, and of these with the corrosion products, are possibly caused by the dissociation of hydrated zinc phosphate into various intermediate compounds. According to Meyer /2,49/, the following theoretical reaction path is proposed to interpret the inhibitive action of zinc phosphate:



$$Zn_3(PO_4)_2 \cdot 4\,H_2O \rightleftarrows (H^+)_4\left[\begin{matrix}Zn_3(PO_4)_2\\(OH)_4\end{matrix}\right]^{4-}$$

$$3\,(H^+)_4\left[\begin{matrix}Zn_3(PO_4)_2\\(OH)_4\end{matrix}\right]^{4-} \xrightarrow[-12\,H_2O]{+12\,RCOOH} 3\,(H^+)_4\left[\begin{matrix}Zn_3(PO_4)_2\\(RCOO)_4\end{matrix}\right]^{4-}$$

$$3\,(H^+)_4\left[\begin{matrix}Zn_3(PO_4)_2\\(OH)_4\end{matrix}\right]^{4-} \xrightarrow[-12\,H^+]{+4\,Fe^{3+}} (Fe^{3+})_4\left(\left[\begin{matrix}Zn_3(PO_4)_2\\(OH)_4\end{matrix}\right]^{4-}\right)_3$$

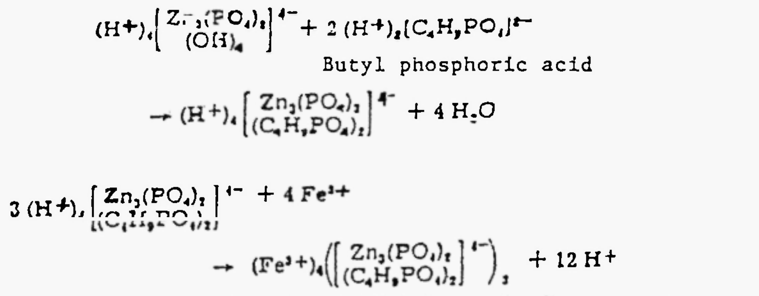
$$3\,(H^+)_4\left[\begin{matrix}Zn_3(PO_4)_2\\(RCOO)_4\end{matrix}\right]^{4-} \xrightarrow[-12\,H^+]{+4\,Fe^{3+}} (Fe^{3+})_4\left(\left[\begin{matrix}Zn_3(PO_4)_2\\(RCOO)_4\end{matrix}\right]^{4-}\right)_3 \xleftarrow[-12\,H_2O]{+12\,RCOOH} (Fe^{3+})_4\left(\left[\begin{matrix}Zn_3(PO_4)_2\\(OH)_4\end{matrix}\right]^{4-}\right)_3$$

$$(Fe^{3+})_4\left(\left[\begin{matrix}Zn_3(PO_4)_2\\(OH)_4\end{matrix}\right]^{4-}\right)_3 + 6\,H_2CO_3 \rightarrow (Fe^{3+})_4\left(\left[\begin{matrix}Zn_3(PO_4)_2\\(CO_3)_2\end{matrix}\right]^{4-}\right)_3 + 12\,H_2O$$

$$(Fe^{3+})_4\left(\left[\begin{matrix}Zn_3(PO_4)_2\\(OH)_4\end{matrix}\right]^{4-}\right)_3 + 4\,H_3PO_4 \rightarrow Fe^{3+}[Zn_3(PO_4)_3]^{3-} + FePO_4 + 12\,H_2O$$

Species responding to the general formula $[Zn_3(PO_4)_2(OH)_x \cdot n\,H_2O]$, being $n + x = 4$ and $x = 1\text{-}4$, are generated by hydrolysis. There is a slight formation of inhibitive substances on the base metal. The system becomes hydrophobic because of the fatty acids from the binder. This fact improves the stability of both the inhibitive and adhesion promoting substances by minimizing their hydrolysis.

The incorporation of alquil acid phosphates to certain binders improves



$$(H^+)_4\left[\begin{matrix}Zn_3(PO_4)_2\\(OH)_4\end{matrix}\right]^{4-} + 2\,(H^+)_2[C_4H_9PO_4]^{2-}$$

Butyl phosphoric acid

$$\rightarrow (H^+)_4\left[\begin{matrix}Zn_3(PO_4)_2\\(C_4H_9PO_4)_2\end{matrix}\right]^{4-} + 4\,H_2O$$

$$3\,(H^+)_4\left[\begin{matrix}Zn_3(PO_4)_2\\(C_4H_9PO_4)_2\end{matrix}\right]^{4-} + 4\,Fe^{3+}$$

$$\rightarrow (Fe^{3+})_4\left(\left[\begin{matrix}Zn_3(PO_4)_2\\(C_4H_9PO_4)_2\end{matrix}\right]^{4-}\right)_3 + 12\,H^+$$

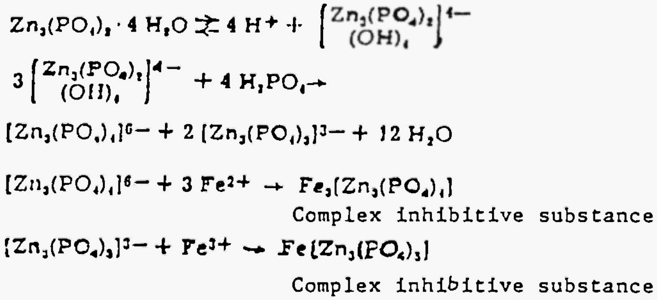
Complex inhibitive and adhesive substance

adhesion by promoting the formation of certain "adhesion complexes". The following reaction path shows the effect of adding 3% butyl phosphoric acid:

Considering that the equilibrium may occur:

$$Zn_2(PO_4)_2 + 6\,H_2O = 2H_3PO_4 + 3\,Zn(OH)_2$$

the following inhibitive compounds may be formed on the metal surface:



$$Zn_3(PO_4)_2\cdot 4\,H_2O \rightleftharpoons 4\,H^+ + \left[\begin{matrix}Zn_3(PO_4)_2\\(OH)_4\end{matrix}\right]^{4-}$$

$$3\left[\begin{matrix}Zn_3(PO_4)_2\\(OH)_4\end{matrix}\right]^{4-} + 4\,H_3PO_4 \rightarrow$$

$$[Zn_3(PO_4)_4]^{6-} + 2\,[Zn_3(PO_4)_3]^{3-} + 12\,H_2O$$

$$[Zn_3(PO_4)_4]^{6-} + 3\,Fe^{2+} \rightarrow Fe_3[Zn_3(PO_4)_4]$$

Complex inhibitive substance

$$[Zn_3(PO_4)_3]^{3-} + Fe^{3+} \rightarrow Fe[Zn_3(PO_4)_3]$$

Complex inhibitive substance

Meyer established that it is necessary to take into account these theoretical reactions to make a proper selection of the binders and the pigments which lead to the formation of adhesion and inhibition promoting substances.

## OTHER PHOSPHATES AS INHIBITIVE PIGMENTS

Because of the discouraging and contradictory results obtained with ZP, other phosphates, apart from modified zinc phosphates, were introduced to replace current toxic anticorrosive pigments.

Phosphate pigments capable of inhibiting corrosion processes may be divided into two groups /20/. The first one includes phosphates and hydroxyphosphates of metals such as Fe, Ba, Cr, Ca, Mg and Zn; but only $FePO_4 \times 2\,H_2O$, $Ca_3(PO_4)_2 \times 1/2\,H_2O$, $Ba_3(PO_4)_2$, $BaHPO_4$ and $FeNH_4PO_4 \times 2\,H_2O$ are of some importance. The usage of a $CaZn_2(PO_4)_2 \times 2\,H_2O$ was also reported /21/.

The anticorrosive performance of iron phosphate was studied with some detail /27,50/. It gave poor results in accelerated tests, when used alone, but mixtures with ZPO are promising. The employment of reaction accelerators such as sodium molybdate, sodium chlorate and sodium m-nitrobenzenesulphonate, improved the corrosion resistance of coatings containing this pigment /51/.

The second group comprises compounds based on dihydrogen aluminium triphosphate ($AlH_2P_3O_{10}$ x 2 $H_2O$), which is an acid with a $pK_a$ 1.5-1.6. The $P_3O_{10}^{5-}$ anion reacts with anodic iron to yield an insoluble layer consisting mainly of ferric triphosphate. It exhibits a higher corrosion inhibiting power and may be used with alkyd, phenolic, epoxies, epoxy-polyester, acrylic melamine resins, water-thinnable, air drying and stoving binders. Likewise, its anticorrosive properties can be improved by adding other pigments /52-55/. A freely tonable aluminium metaphosphate employed in conjunction with a zinc compound, preferably zinc oxide and/or an alkaline earth compound, was patented /54/. A titanium phosphate with good hiding powder was also prepared /56/.

Inorganic pigments such as titanium and zinc white, iron pigments, lithopone, hematite, barium sulphate, silica, alumina, bentonite, talc, chalk, mica, etc., coated with manganese phosphate ($Mn_3(PO_4)_2$ x 3 $H_2O$), were used as anticorrosive ones /57.

Chromic phosphate is not an efficient anticorrosive pigment due to its slight solubility and slow hydrolysis rate. However, it may be used together with other pigments such as strontium chromate and zinc tetroxychromate, in order to improve their inhibiting properties. Chromic phosphate is also used in the so-called one component wash primers /13,41,58,59/.

The employment of a strontium zinc phosphosilicate in solvent and water borne paints was reported /60,61/. Austin /62/ introduced a calcium strontium zinc phosphosilicate showing a performance and versatility similar to zinc chromate.

Zinc hydroxiphosphite /63,64/ is claimed to be an effective non-toxic anticorrosive primer. It has small particle size, lower oil absorption, minimizes the tendency of latex paints to flush rust, etc.

A Japanese patent recorded the employment of a hydrated basic potassium zinc phosphate-phosphite as non-toxic anti-rusting pigment /65/.

Polyphosphate pigments such as calcium hexamethaphosphate, calcium tripolyphosphate and zinc tripolyphosphate were found adequate for protecting steel against corrosion under typical conditions of the food industry /66/.

Tetramethaphosphates of bivalent metals such as zinc, manganese, cobalt, calcium and magnesium were prepared by thermal dehydration of dihydrogen phosphates or from phosphoric acid and metal oxides, hydroxides and carbonates mixtures. Single and double tetrametha-phosphates were tested as anticorrosive pigments in alkyd resins based formulations. Some of them, such as calcium and cobalt-containing pigments, showed better corrosion resistance than ZP when subjected to accelerated and natural weathering /67,68/.

Surface steel conversion with an organic film barrier were combined in a single corrosion resistance coating utilizing a phosphated polyepoxide coating with good results /69/. Phosphated polymers and related treatments were successfully employed in zinc and zinc alloy coatings /70/.

Neutral organic phosphates (triphenilphosphate) were used as corrosion inhibitors in engines using lubricant oil containing these phosphates. Their effectiveness depended on the easiness to hydrolyze forming acid phosphates on the metal surface. More readily it hydrolyzes, better its performance /71/.

## FINAL CONSIDERATIONS

In spite of the contradictory data appearing in the reviewed literature it may be seen that the employment of ZP could become successful in moderate outdoor exposures and in industrial atmospheres although poor or bad results were obtained in accelerated tests /72,73/. This fact could be explained considering the very low solubility of ZP. Thus, the penetrating rate of aggressive agents occurring in accelerated tests largely exceeds the protective action of both the phosphate anion and the formation of a thick iron oxides layers on the metal substrate.

The research carried out by the authors /74/ showed that: a) the concentration of phosphate anion is low enough as to impede the metal base oxidation /45,75/, and b) the dissolved oxygen in solution causes the steel dissolution reaction giving ferrous and ferric ions. A compact layer of iron oxyhydroxides (having certain protective characteristics) being formed on the metal surface and the zinc hydroxide precipitated in the cathodic area help to inhibit the oxygen reduction reaction. ZP produces non-adherent ferric phosphate. Further oxygen penetrating leads to the ferric oxide formation.

Experimental results and conclusions emanated from different researchers may be not always compared because:

a) Experimental variables such as particle diameter, PVC, types of pigments, additives and binders must be carefully controlled in order to use equivalent experimental conditions. These variables are not always specified in the reviewed literature.

b) ZP does not resist accelerated tests although it can perform well in moderate outdoor environments and in acid environments because it activates in such media.

c) Anticorrosive paints behaviour is highly dependent on the type of binder employed, and only after its barrier effect fails the pigment action becomes important. Modified zinc phosphates have a better anticorrosive performance and they can have good performance in accelerated tests.

In order to improve the ZP anticorrosive action it is recommended:

a) optimize both the shape and the particle size distribution;
b) increase the soluble phosphate anion concentration;
c) introduce other inhibitive species; and
d)' increase coating adhesion.

Spherical shaped particles are preferred to lamellar ones in order to improve the coating package. Modifying the specific surface area, the phosphate leaching from the pigment is enhanced.

When binders with carboxylic acids are to be employed, the addition of basic groups improved their adhesion properties.

ZP could be employed with most binders.

ZP anticorrosive mechanism is not still fully understood yet. It was believed that the phosphate anion is an anodic inhibitor producing a protective layer on ferrous substances. The building up of this layer depends on the phosphate concentration. Some researchers have found that the cathodic areas were also polarized by the sparingly soluble salts appearing on them.

Adhesion promoting substances would also enhance the anticorrosive properties of zinc phosphates.

ZPA is more acidic because of the hydrolysis of aluminium ion and gives rise to a higher soluble phosphate concentration.

ZMP incorporates molybdates as anodic inhibitors. Nevertheless, the mixtures with other toxic pigments, although useful, is not recommended due to the environmental pollution.

The authors of this review think that ZP could be employed in the terms described in the paper. At present, modified zinc phosphate is a convenient alternative pigment; however, from now on other phosphates with enhanced solubility in water must be ascertained. The anticorrosive mechanism needs to be clarified in order to find the adequate phosphate for each kind of exposure (rural, industrial, etc.) to be chosen.

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