Novel, Effective, Non-toxic Zinc Free Anticorrosive Pigments for Industrial Maintenance Paints

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Recently developed, innovative family of anticorrosive pigments for paints and coatings is based on Oxy-Amino Phosphate of Magnesia (OAPM) technology,

Upon exposure to corrosive environment they form a stable layer of magnesia on the metal surface which protects it from corrosion attack.

These pigments, which are non toxic, do not contain chrome, zinc or any other hazardous material, give excellent performance in 2 components epoxy , alkyd, wash primer and water based industrial systems. They meet the requirements for long term anticorrosive protection of both steel and aluminium in industrial maintenance applications, and are especially suitable for DIY (Do It Yourself) paints where the environmentally hazard warning label of zinc compounds can be avoided.

The high effectiveness of OAPM pigments enables lower loading in the paint formula than needed with zinc chromate, zinc phosphate and modified zinc phosphates to achieve the desired protection qualities and performance.

This leads to cost effectiveness in addition to the health and environmental advantages.

The present work describes the structure of the protective film formed on the metal surface, and some of its electrochemical and analytical characteristics. The protective layer was investigated by static and dynamic potentials, impedance measurements, Auger and EDAX analyses.

In addition, guidelines for formulating organic coatings with OAPM pigments are presented along with test results.

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Introduction

The corrosion inhibiting pigments, subject of the present work, are heavy metal and zinc free pigments based on Oxy-amino-phosphates of magnesium (OAPM) (1).
Previous investigation (2) showed that both pigments, designated here as PM and PE, (differing by the type of the amine) have good corrosion protection ability on aluminum alloys 3105-H24, 6061, 6063 and 2024-T3. Seven days immersion of Al panels in 3.5% NaCl solution saturated with both tested pigments, led to the formation of continuous film, 40 to 100 nm by thickness and very similar in shape to the layer formed by chromates, as observed by HRSEM (High Resolution Scanning Electron Microscope) and shown in Figure 1).

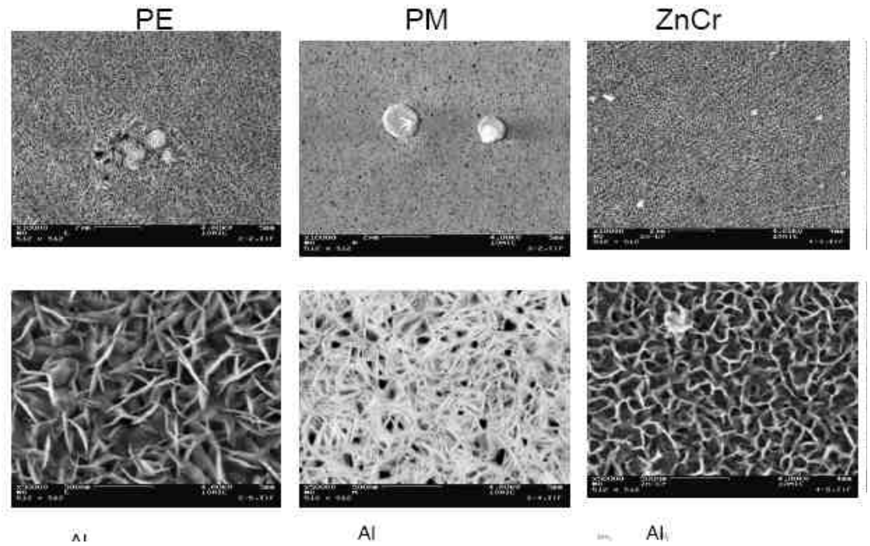

Figure 1: Immersion of Al 6063 in 3.5% NaCl for 7 days – Effect of Pigment Type on Surface Film Structure. (Ref. 2).(Upper raw - x10000, Lower raw - x 50000)

These layers were composed of oxidized Mg and P as resulted from the Auger (AES) analysis (2).
Electrochemical measurements of scribed panels coated with OAPM containing paints (3), showed that the surface potential of painted aluminum without an A/C (anti-corrosion) pigment tends to move, in the test environment, quickly into the corrosion zone.
Using OAPM A/C pigment in the paint, keeps the surface potential below the corrosion values during the test, thus, cathodically protecting the aluminum surface (Figure 2).
A painted steel surface without A/C pigment moves rapidly into the corrosion zone, while steel coated with a paint containing OAPM A/C pigment gets a surface potential above the corrosion potential thus giving anodic protecting to the steel substrate surface (Figure 3).

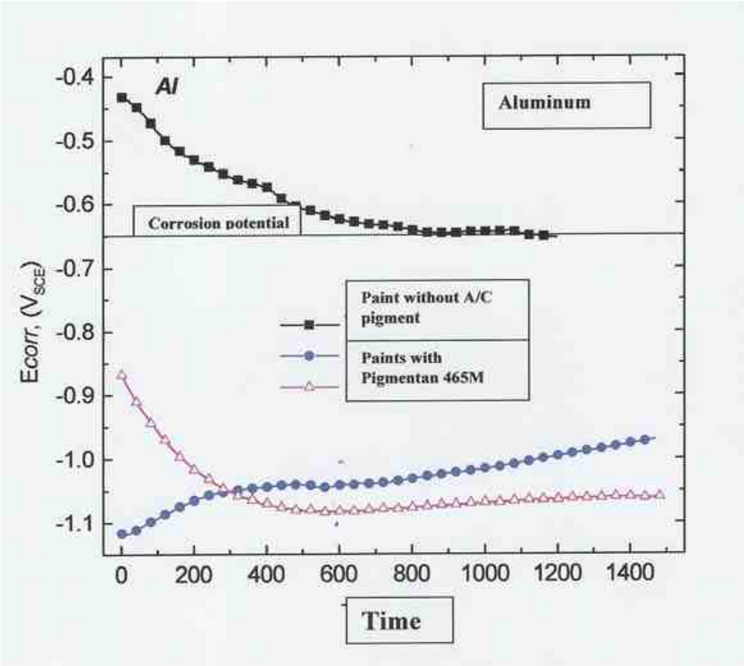

Figure 2: Potentiodynamic curves as a function of immersion time (in seconds) of aluminum plates protected by coating containing OAPM A/C pigment in comparison to a coating without A/C pigment. (Ref 3)

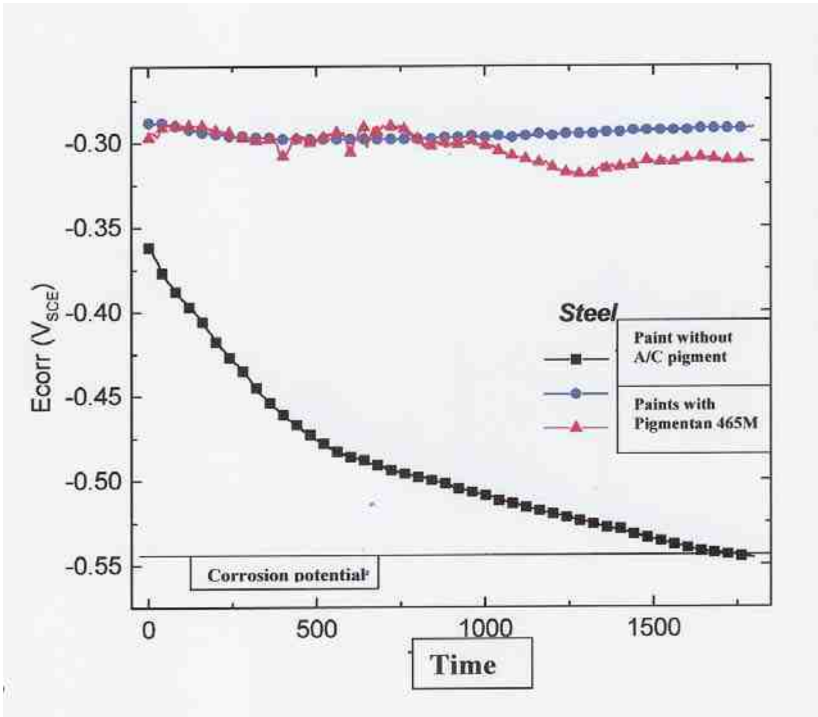

Figure 3: Potentiodynamic curves as a function of immersion time (in seconds) of steel plates protected by coating containing OAPM A/C pigment in comparison to a coating without A/C pigment. (Ref.3).

These findings were successfully applied in many fields of the anticorrosion coatings technology such as water based alkyd and emulsion paints, solvent based epoxy (4) as well in wash primer and conversion coating chrome-free replacements.
In these applications, the advantage of the OAPM products in terms of loading and cost per given performance in comparison to the common non-chromate pigments, such as basic and modified zinc phosphates is clearly evident.
Being an innovative and relatively new in the market, OAPM inclusion in a coatings formulation requires special care and sometimes reformulation.
Depending on the loading level of OAPM, the ratio of the Pigment Volume Concentration (PVC) to the Critical PVC (CPVC) of an existing paint formulation might change due to the relatively high oil absorption of the OAPM A/C pigments.
Similarly, water based coating formulators have to adjust their formulations by using carefully chosen dispersants and other ingredients in order to deal with the basic nature of OAPM A/C pigments which, otherwise, may lead to viscosity increase as happens with other basic pigments.

In order to demonstrate the efficacy of OAPM A/C pigments achieved by optimization of the formulation, the present work describes the preparation of typical alkyd based maintenance and DIY primer for steel substrates based on OAPM, and the way to develop it considering various formulation parameters.
Future publication, will describe performance of OAPM A/C pigments in chromate free conversion coatings and primers for aluminum.

Experimental

Materials

The binder used in the present work was a mixture of commercial soybean modified medium oil length alkyd and a phenol modified alkyd. The solids ratio of the alkyds was one of the design parameters.
The alkyd mixture was used with the appropriate additives such as mineral rheology modifiers, driers and anti-skinning agents, and diluted to the application consistency with measured amounts of xylene.
The OAPM anticorrosion (A/C) pigments used were PE and PM.
Additional pigmentation was red oxide (Bayerferrox 130, Bayer), Barites, Microtalc AT, Norwegian Talc) and 210 mesh grounded calcium carbonate ($CaCO_3$).
Paint formulations with various loadings of OAPM A/C pigments as well as with different combinations of barites and talc or $CaCO_3$, were designed to 3 different Λ values, were, Λ is the reduced Pigment Volume Concentration (PVC) defined by the ratio of PVC and the Critical PVC (CPVC) of the formulation.
CPVC was calculated using the Oil Absorption (OA) values of the various pigments and fillers participating in the formulation, following Engler et. al. (5).

Preparation, Application and Test Methods

Paint formulations with various combinations of the OAPM A/C pigments and fillers at different Λ values and alkyd ratio were prepared by dispersing to a Hegman value higher than 6 with a saw tooth impeller driven by a high speed stirrer using glass beads , 2-3 mm in diameter, as the dispersing media.

The paints were applied by a wire applicator to R-36 steel panels (Q-Panels) to an average Dry Film Thickness (DFT) of 40µ and rest to dry at ambient conditions for 7 days before testing.

At least 4 panels were prepared per formulation. 2 panels were X scribed and evaluated after exposure to the salt spray test (SST).

The evaluations (rating) of the coating with scribe were made in accordance to the Pigmentan scoring method for evaluation of blistering, scribe and surface rusting, where 0 is the best and 5 is the worst.

Pigmentan method is based on DIN 53 209 and DIN 53210 and is in accordance to ASTM D 610 – Standard Test Method for Evaluating Degree of Rusting on Painted Steel Surface (USA).

The resulting rating is the arithmetical average of the 4 individual ratings (0-the best, 5-the worst), of the following:

- General panel rating
- General scribe rating
- Blistering degree
- Blistering size

In addition, the blistering situation was evaluated according to ASTM D 714 - *Standard Test Method for Evaluation Degree of Blistering of Paints,* and recorded separately. In this test 10 is a perfect panel while f, M, D describe few, medium and dense blistering and the digit (9 to1) depicts the relative blister size according to the reference.

Salt Spray Chamber Test

Tests were carried out in salt spray chamber (SASS/120, Sheen Instruments LTD, England) situated in the Pigmentan Lab, with 5% NaCl solution. Apparatus parameters were checked daily according to Sheen's and ASTM B 117 instructions.

Average rating results of the tested panels were recorded.

Results and Discussion

Stage A

Formulation parameters tested in this stage were:

1. OAPM type (PE , PM)
2. OAPM loading expressed as % by weight on the total formulation.
3. Presence of either talc or $CaCO_3$ as the filler additional to Barites.

The starting point formulation of the paints prepared at this stage followed that of a commercial well established zinc phosphate alkyd primer.

Since the basic idea was to develop a "slip in" formulation, meaning, replacing the zinc containing formulation with zinc free OAPM based A/C pigment, the basic parameters of the starting formulation were kept constant, as follows:

- Phenol modified to medium oil alkyds non volatile ratio -1.0
- Total binder content - 27% by weight.
- Total pigments and fillers content – 34 % by weight.
- Red oxide pigment loading - 7.7 % by weight.
- Barites loading – 17% by weight.

As the Israeli Standard IS 1946, "Non Chromate Alkyd Primer" sets the requirement for 120 hours resistance in SST, as the qualification criterion, the tested panels' status after 120 hour in the salt spray cabinet was evaluated. The results expressed as SST rating by the Pigmentan scoring method, are described in Table 1.

Table 1: 120 hours Salt Spray resistance rating of panels coated with alkyd primer

OAPM Type	OAPM Loading , %wt on total	Fillers: Barites, Talc	Fillers: Barites, CaCO3
No A/C pigment	0	3.04	2.9
P E	1.3	-	2.5
	2.6	2.9	2.54
	4.6	-	2.5
PM	1.3	-	2.9
	2.6	2.7	2.25
	4.6	2.5	2.5

A graphic presentation of the corrosion resistance rating of stage A formulations is depicted in Figure 5 where the rating of the commercial zinc phosphate based paint (2.7) is shown as well.

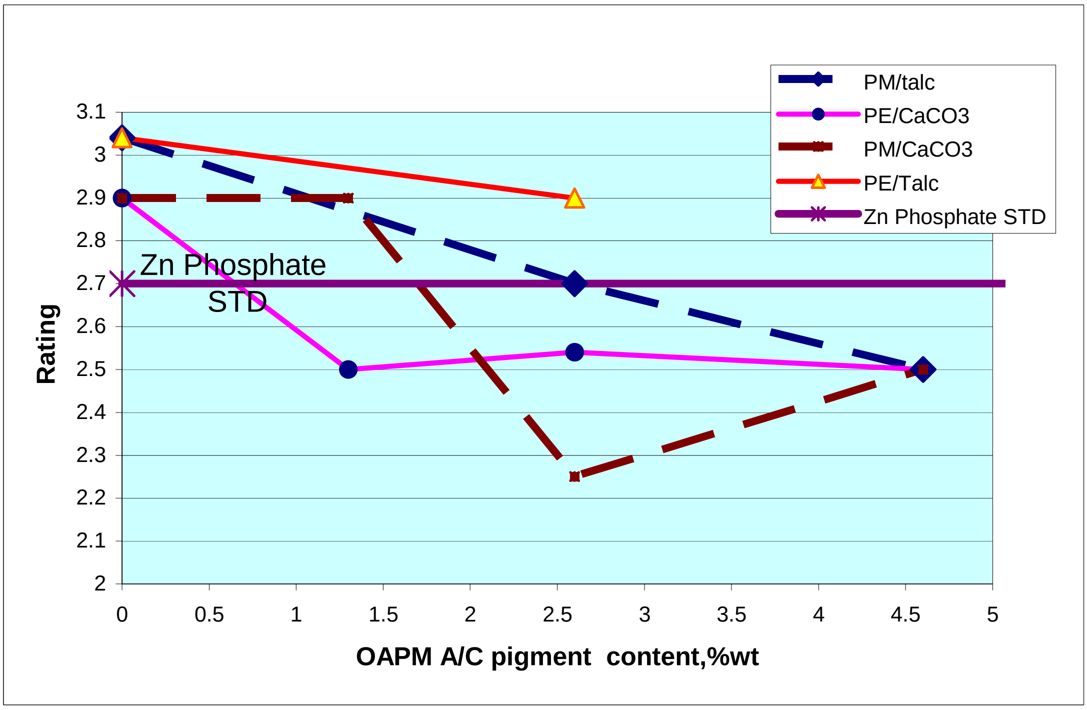

Figure 5: SST resistance rating of alkyd primers after 120 hours at SST.

<u>Discussion of Stage A</u>

<u>General</u>

The rating method described is not an exact method to determine corrosion resistance or to assess panel status after exposure to corrosion tests. However, the rating procedure depicts the average of 4 different criteria of the situation of both scribe and the surrounding paint film. In addition, the final result is the average of at least 2 panels. This assures that at least a relative rating can be made at a relative high degree of confidence.

<u>OAPM Loading</u>

It can be seen that a minimum loading of the A/C pigment is needed, a fact not specific for OAPM.

For PM, a clear optimal concentration of 2.6% is evident. PE reaches its utmost at 1.3% but performance is not further improved by increasing its loading. This is explained by the increasing osmotic effect which enhances the blistering phenomenon as loading of the relatively soluble OAPM is increased. These low loadings have their obvious impact on formulation cost.

<u>OAPM type</u>

Both PE and PM give better results than the zinc phosphate containing standard paint. However, in the formulation tested in this stage, PM performs somewhat better than PE.

Composition of the filler part

A clear advantage can be seen to the use of CaCO3 provided the correct OAPM loading is used.

This is explained by a possible synergism between Mg and phosphate from the A/C pigment and the Ca ions of the CaCO3 filler in building the passivation layer on the metal surface. This effect is known from similar applications (6, 7).

However, it should be remembered that CaCO3 cannot be used where a high chemical resistance is required.

Stage B

Formulation parameters tested in this stage were:

1. Ratio of Phenol modified to medium oil length alkyds - 35:65 and 25:75.
2. Λ values – 0.6 and 0.72.
3. Presence of talc in addition to CaCO3 and Barites in the filler part.

The main object of the present work was to show, in general, how a formulation with OAPM can be optimized by careful design. Therefore it was decided to concentrate on PM at a loading of 2.6% by weight on the total formulation which showed the results in stage A and to optimize the formulation in respect to the Λ values and the alkyd ratio.

Table 2 shows the results of the 120 hours SST rating by the Pigmentan method as well as ASTM D 714 blistering rating and the ASTM D 3359 adhesion test classifications, taken on the scribed, 24 hours at ambient condition, after the SST exposure.

Table 2: 120 hours Salt Spray resistance rating of panels coated with alkyd primers with various Formulation Parameters

Formulation No.	1	2	3	4	5	6	7	8
PVC/CPVC	0.72	0.72	0.72	0.72	0.6	0.6	0.6	0.6
Phenol to medium alkyd ratio	35/65	35/65	25/75	25/75	35/65	35/65	25/75	25/75
TALC	+	-	+	-	+	-	+	-
120 hrs SST								
RATING	2.75	2.5	2	2.25	3	3	2.5	2.5
ASTM D 714 Blistering	8F	8F	8F	6F	8F	8F	8F	8F
ADHESION on X after 24h	4B	5B	5B	4B	4B	3B	5B	5B

Discussion of Stage B

Performance in SST

Alkyd Ratio

Lower content of the phenol modified alkyd is beneficial. For both Λ values experimented in this work, ratings after 120 hours are lower (better) when ratio of 25 parts phenol alkyd to 75 parts medium oil alkyd is used.

Λ values

It is well known that CPVC is the pivot for paint formulation. At this point the solid particles contained in the paint film are at their closest packaging possible. This leads, for example, to a minimum in the resistivity of conductive paints (8), to maximum in thermal conductivity of thermally conductive paint or compound and to discontinuity in many paint film properties, such as, water permeability, adhesion, mechanical and optical properties (9).

Generally, it is recommended to design a primer coating somewhat below the CPVC of the formulation so that the maximum benefits of the high pigment and filler loading are gained without impairing the dry film properties.

In the present work, the higher Λ, 0.72, was better for both alkyd ratios. It can be explained by better spaced active particles enabling the water penetrating the film to dissolve and activate the functional species of the OAPM particles.

Filler composition

The presence or absence of talc had no definite impact on the SST performance of the formulations tested in Stage B of the present work.

Adhesion

Adhesion was tested by peeling off a standard pressure sensitive adhesive tape from the scribed area of the tested panels. The test was carried out 24 hours after terminating the 120 hours SST.

At the higher Λ, no clear advantage can be referred to any of the parameters tested. However, in the lower Λ case, a distinct advantage to the lower phenol alkyd to medium oil length alkyd ratio is evident.

Conclusions

(a) A novel, non toxic chromate and zinc free A/C pigments like OAPM products can be formulated into a paint composition to match existing standards provided the appropriate adjustments and optimization of the formula are made.

(b) OAPM A/C pigments are efficient at low loadings. It is useful to use calcium carbonate filler where a high chemical resistance is not required in order to take advantage of the synergy between Mg and phosphate ions of the A/C pigment and the Ca ions of the filler.

(c) Formulation parameters as the PVC/CPVC ratio and composition of the binder (phenol modified to medium oil alkyd ratio, as in the present case), are critical for the development of proper OAPM containing paints.

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