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

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A recently developed, innovative family of anticorrosive pigments for paints and coatings is based on Oxy-Amino Phosphate of Magnesia (OAPM) technology. On exposure to corrosive environments, 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 chromium, zinc or any other hazardous material, give excellent performance in two-component epoxy, alkyd, wash primer and water-based industrial systems. They meet the requirements for long term anticorrosive protection of both steel and aluminum in industrial maintenance applications, and are especially suitable for DIY (Do It Yourself) paints where the environmental hazard warning label of zinc compounds can be avoided. The high effectiveness of OAPM pigments enables lower loading in the paint formula than that 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. This article 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.

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), provide good corrosion protection on aluminum alloys 3105-H24, 6061, 6063 and 2024-T3. Seven days immersion of aluminum panels in 3.5% NaCl solution saturated with both tested pigments, led to the formation of a continuous film, 40 to 100 nm in thickness and very similar in shape to the layer formed by chromates, as observed by high resolution scanning electron microscopy (HRSEM) and shown in Fig. 1. These layers were composed of oxidized magnesium and phosphorus, as noted by 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 tended to move, in the test environment, quickly into the corrosion zone. Using an OAPM A/C pigment in the paint kept the surface potential below the corrosion values during the test, thus cathodically protecting the aluminum surface (Fig. 2). A painted steel surface without the anti-corrosion pigment moved rapidly into the corrosion zone, while steel coated with a paint containing OAPM A/C pigment reached a surface potential above the corrosion potential, thus giving anodic protection to the steel substrate surface (Fig. 3).

These findings were successfully applied in many fields of the anticorrosion coatings technology such as in water-based alkyd and emulsion paints, solvent based epoxies[4] as well in wash primer and conversion coating chromium-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 was clearly evident.

Being an innovative and relatively new concept in the market, OAPM inclusion in a coating 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, because of the relatively high oil absorption of the OAPM A/C pigments. Similarly, water based coating formulations have to be adjusted 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 a viscosity increase, as happens with other basic pigments.

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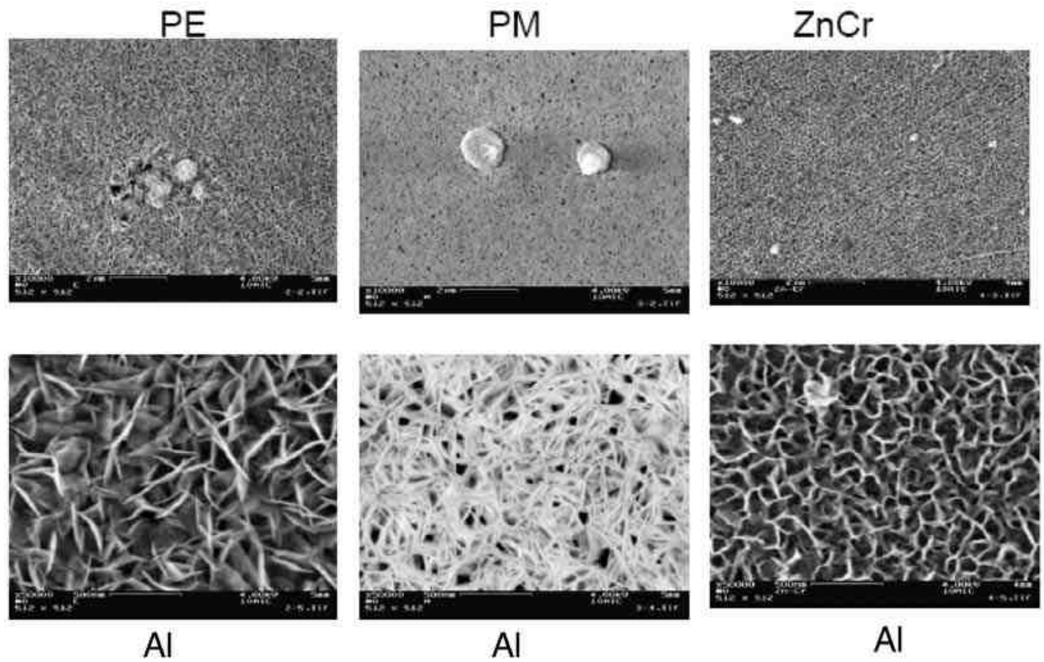

Figure 1—Immersion of Al 6063 in 3.5% NaCl for seven days; Effect of pigment type on surface film structure[2] (Upper row - 10,000×; Lower row - 50,000×).

In order to demonstrate the efficacy of OAPM A/C pigments achieved by optimization of the formulation, this paper describes the preparation of typical alkyd-based maintenance and DIY primers for steel substrates based on OAPM, and the way to develop it considering various formulation parameters. Future publications will the 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, including 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 specified for three different Λ values,

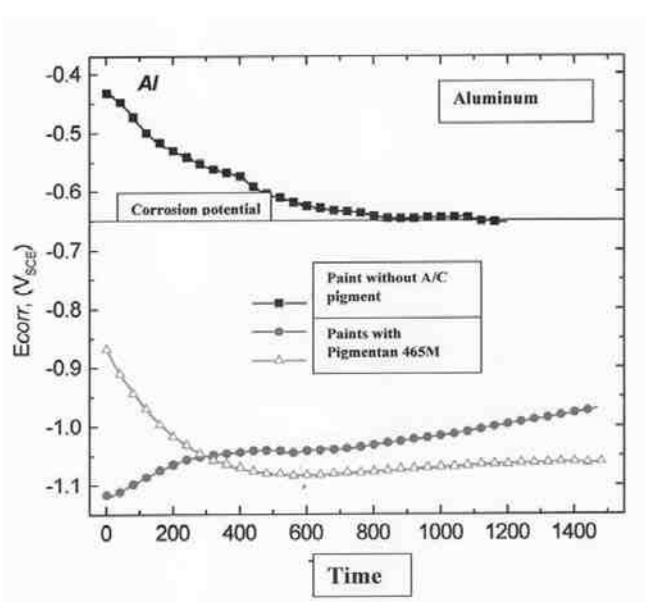

Figure 2—Potentiodynamic curves as a function of immersion time (in sec) of aluminum plates protected by coating containing OAPM A/C pigment in comparison to a coating without A/C pigment.[3]

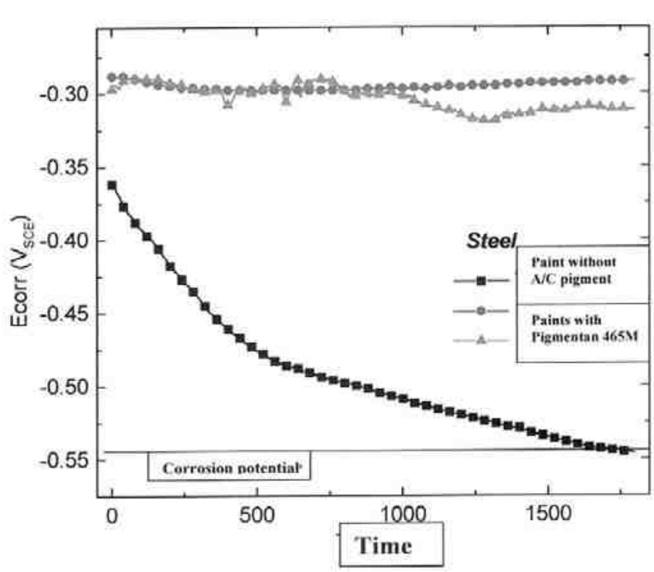

Figure 3—Potentiodynamic curves as a function of immersion time (in sec) of steel plates protected by coating containing OAPM A/C pigment in comparison to a coating without A/C pigment.[3]

where, Λ is the reduced pigment volume concentration (PVC), defined by the ratio of PVC and the critical PVC (CPVC) of the formulation. The CPVC was calculated using the oil absorption (OA) values of the various pigments and fillers used 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 ratios 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 to 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 40 μm and left to dry at ambient conditions for seven days before testing. At least four panels were prepared per formulation. Two panels were X-scribed and evaluated after exposure to the salt spray test (SST).

The evaluation (rating) of the coating with the scribe were made in accordance with the Pigmentan scoring method for evaluation of blistering, scribe and surface rusting, where zero is the best and five is the worst. The Pigmentan method was based on DIN 53209 and DIN 53210 and was in accordance with ASTM D610-07 – Standard Test Method for Evaluating Degree of Rusting on Painted Steel Surfaces (USA). The resulting rating was the arithmetical average of the four individual ratings (0 - the best, 5 - the worst), of the following:

- General panel rating
- General scribe rating
- Degree of Blistering
- Blister size

In addition, the blistering situation was evaluated according to ASTM D714-02e1 - Standard Test Method for Evaluation of Degree of Blistering of Paints, and recorded separately. In this test, ten is a perfect panel while f, M, D describe few, medium and dense blistering and the digit (9 to 1) depicts the relative blister size according to the reference.

Salt spray chamber test

Tests were carried out in a salt spray chamber (SASS/120, Sheen Instruments Ltd., England) located in the Pigmentan Lab, with 5% NaCl solution. Operating parameters were checked daily according to Sheen's and ASTM B117 instructions. The 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 in addition 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 a 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 wt%
- Total pigments and fillers content – 34 wt%
- Red oxide pigment loading - 7.7 wt%.
- Barites loading – 17 wt

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

A graphic presentation of the corrosion resistance rating of the Stage A formulations is depicted in Fig. 4 where the rating of the commercial zinc phosphate-based paint (2.7) is shown as well.

Discussion of Stage A

General discussion. 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 four different criteria of the situation of both the scribed area and the surrounding paint film. In addition, the final result is the average of at least two panels. This assures that at least a relative rating can be made at a relative high degree of confidence.

OAPM loading. 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 the 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.

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

Table 1
120 hr salt spray resistance rating of panels coated with alkyd primer

OAPM type	OAPM Loading , wt% on total	Fillers: Barites, Talc	Fillers: Barites, $CaCO_3$
No A/C pigment	0	3.04	2.9
PE	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

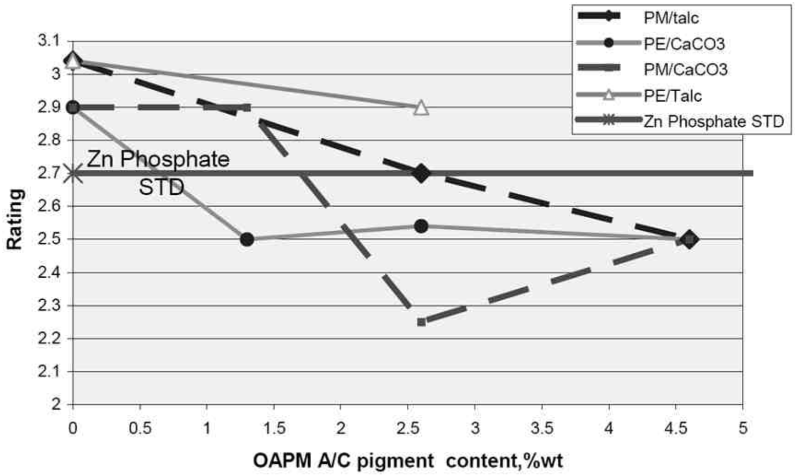

Figure 4—SST resistance rating of alkyd primers after 120 hr at SST.

Composition of the filler part. A clear advantage can be seen with the use of $CaCO_3$ provided the correct OAPM loading is used. This is explained by a possible synergism between magnesium and phosphate from the A/C pigment and the calcium ions of the $CaCO_3$ filler in building the passivation layer on the metal surface. This effect is known in similar applications.[6,7] However, it should be remembered that $CaCO_3$ 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 $CaCO_3$ 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 wt% 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 hr SST rating by the Pigmentan method as well as ASTM D714 blistering rating and the ASTM D3359 adhesion test classifications, taken on the scribed area after 24 hr under ambient conditions, after the SST exposure.

Discussion of Stage B

Performance in SST

Alkyd ratio. The reduced content of the phenol-modified alkyd was beneficial. For both Λ values studied in this work, the ratings after 120 hrs were lower (better) when ratio of 25 parts phenol alkyd to 75 parts medium oil alkyd was 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 a maximum in thermal conductivity of thermally conductive paint or compound and to discontinuities in many paint film properties, including water permeability, adhesion, mechanical and optical properties.[9]

Generally, it is recommended that one 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. This 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 notable 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 hr after terminating the 120 hr SST. At the higher Λ, no clear advantages were gained under 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 was evident.

Table 2
120 hr 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 D714 blistering	8F	8F	8F	6F	8F	8F	8F	8F
Adhesion on X after 24 hr	4B	5B	5B	4B	4B	3B	5B	5B

Conclusions

• 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.

• 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 magnesium and phosphate ions of the A/C pigment and the calcium ions of the filler.

• Formulation parameters, such 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. *P&SF*

References

1. G. Pipko, U.S. Patents 6,331,202 (2001) and 7,220,297 (2007).
2. S. Tamir, M. Landkof & Z. Miller, Paper 18-C-28,"Corrosion Protection of Al Alloys by using Environmentally-Friendly Pigments", 16th Int'l. Corrosion Conference (16ICC), China International Conference Center for Science and Technology, Beijing, China, 2005.
3. D. Starosvetsky, "Corrosion Protection of Steel and Al in Chloride containing Water with Coatings Filled with different Pigments," unpublished report, Faculty of Material Engineering, Department of Electrochemistry, Technion-Israel Institute of Technology, January 2002.
4. B. Goldie, "New Anticorrosion Pigments Said to be Environmentally Sensitive and Effective", *Journal of Protective Coatings & Linings / Protective Coatings Europe* (JPCL/PCE) (April 2005).
5. D. Engler, Chairman, *Technical Subcommittee on CPVC, Official Digest*, Philadelphia Society For Coatings Technology, November 1961; p. 1437.
6. V.I. Pokhmurskyi, *et al.*, *Materials Science*, **39** (2), 153 (2003).
7. K. Gotzmann, *et al.*, U.S. Patent 5,665,149 (1997).
8. A. Calahorra, *J. Coatings Technology*, **60** (757), 25 (1988).
9. G.P. Bierwagen & T.K. Hay, *Progress in Organic Coatings*, **3** (4), 281 (1975).

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