

Replacements for Chromate Pigments in Anticorrosion Primers for Aluminum Alloys

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Aerospace aluminum alloys such as Al alloy 2024-T3 and 7075-T6 are subject to localized corrosion due to the existence of intermetallics containing Cu, Mg or Zn. Chromate is currently widely used in the aerospace industry as the corrosion inhibitor for these alloys. However, chromate needs to be replaced due to its strong carcinogenicity. In this study, an extensive pigment screening has been performed to find replacements for chromates. Different categories of inhibitors were evaluated by immersion tests, DC polarization tests and other methods. Phosphates, zinc salts, cerium salts, vanadates and benzotriazole were found to be effective inhibitors for AA7075. Among those inhibitors, zinc phosphate was found to be the most effective in our novel, silane-based, one-step aqueous primer system. The performance of this primer is comparable to that of currently used chromate primers in accelerated corrosion tests, while it is completely chromate-free and its VOC is about 80% less than that of current primers. Studies by SEM/EDS showed that the unique structure of the superprimer accounts for the strong anti-corrosion performance of the zinc phosphate pigment. The self-assembled stratified double-layer structure of the superprimer is characterized by a less-penetrable hydrophobic layer at the top and a hydrophilic layer accommodating the inhibitors underneath. The top layer functions as the physical barrier against water ingress, while the lower layer functions as a reservoir for the inhibitor, which is leached out only if the coating is damaged by a scratch or scribe. The presence of a silane in the primer further improves the adhesion and anti-corrosion performance of the primer.

Keywords : corrosion, inhibitor, primer, aluminum alloy, zinc phosphate, silane

1. Introduction

Aluminum alloys such as 7075-T6 and 2024-T3 are widely used in aircraft because of their high strength and low weight. The existence of the intermetallics attributes to the superior mechanical properties of the alloys. However, the intermetallics containing Cu, Mg or Zn also cause corrosion problems.^{1),2)}

Chromates as the corrosion inhibitor together with solvent-based primers are used as protection against corrosion on the aircraft. One typical state-of-the art primer currently used on aircraft, MIL-P-23377, contains 25 wt.-% strontium chromate and 340 g/l VOC. Both chromate and high VOC in the primer pose severe environmental issues. Chromate is known as a strong carcinogen. VOCs are negative to human health and contribute to the global warming. Regulations have been put on the use of chromate pigments and VOC level.

Research on finding the replacements for chromate pig-

ments has been going on for decades. The first proposed alternatives are phosphates. Zinc phosphate, for example, has a level of toxicity 50 times lower than chromate.³⁾ However, some authors⁴⁾ found the efficiency of phosphate is not conclusive judging from poor protection in accelerated test but a good performance in outdoor long exposure tests and in industrial environments. And the protection mechanism of zinc phosphate is not well established.⁴⁾ Molybdate is another alternative with which numerous studies have been done. Molybdenum is also in the group VI as Cr and is close to chromium in the periodic table.

Phosphomolybdates and other modified phosphate and molybdates are the newer generation of corrosion inhibitors. They contain more than one anodic or cathodic inhibitive species to achieve synergism or higher solubility. These pigments do demonstrate improved performance, while little interpretations of mechanism were reported.⁴⁾

For aircraft aluminum alloys extensive studies have been done on AA2024 while little has been reported on pigments for AA7075. This study presents an extensive

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and systematic study of pigments for AA7075. Different categories of inhibitors were evaluated by immersion tests, DC polarization tests and accelerating tests. The coating used in this study was a unique waterborne silane-containing primer (named superprimer) which does not require a chromate conversion coating. The detail of superprimer is discussed elsewhere.⁵⁾ The protection mechanism of the pigmented superprimer was studied by using SEM/EDS.

2. Experimental

2.1 Materials

The AA7075 panels used in the study were obtained from Stillwater Steel Supply, Stillwater, OK. The primer L2 used was an epoxy-acrylate based primer developed in the same project. The epoxy EPI-REZ WD510 (bisphenol A epoxy resin) and the acrylate ECO-CRYL 9790 were obtained from Hexion Chemicals, Columbus, OH. Primer L2 also contained bis-sulfur silane and crosslinker. The bis-sulfur silane, i.e., the bis[3-(triethoxysilyl) propyl]tetrasulfide and the crosslink A-Link 25 were obtained from GE Silicones, Wilton, CT.

2.2 Sample preparation

Panels were scrubbed using a maroon "Scotch Brite" pad (approximately 120-grit equivalent), ultrasonically cleaned, rinsed with deionized water and blow-dried.

The ingredients of the primer L2, epoxy, acrylate, silane and crosslinker, were mixed together and high-shear blended. The level of pigment added in the primer was 20 wt.-%. The formulation was applied onto panels by a #28 draw-down bar. The primers coatings were cured at room temperature for 14 days before the tests were done.

2.3 Pigments evaluated

This study investigated over 100 chemicals which covered phosphates, silicates, carbonates, molybdates, vanadates, modified molybdates, modified phosphates, calcium salts, zinc salts, cerium salts, Lanthanum salts, benzotriazole, and hydrotalcite-vanadate (HTV).

2.4 Evaluation and characterization methods

2.4.1 Bare panel immersion test

In order to determine the inhibition of the pigments and also to simulate the working conditions of the pigment in the coatings, water solutions containing 1 wt.-% of each pigment and 3.5 wt.-% NaCl were prepared. The solutions were stirred for 12 hours and then filtered to remove the undissolved pigment. Cleaned AA7075 panels were immersed in the solution at room temperature and the corrosion behaviors were observed.

2.4.2 Electrochemical tests

DC polarization test was carried out on those pigments which performed well in the bare panel immersion test. The electrolytes used in the DC polarization test were prepared in the same way as the solutions used in the bare panel immersion test. Cleaned AA7075 panels were immersed in the electrolyte for 20 hours before the test. DC polarization testing was done on Gamry® CMS100 Corrosion Measurement System. Gamry Echem-Analyst™ software was used to analyze the data. The primer was studied by using electrochemical impedance spectroscopy (EIS). The experimental set-up for EIS has been described elsewhere.⁶⁾ The EIS measurements were performed by using 3.5 wt.-% NaCl as the electrolyte.

2.4.3 Salt water immersion test

Saltwater immersion test was used to evaluate the anti-corrosion ability of the pigment and overall quality of the primer. Primer-coated and cross-scribed panels were immersed 3.5 wt.-% NaCl solution at room temperature and their performance was monitored over time.

2.4.4 SEM/EDS

The scribe and cross-section of coated panels exposed to 30 days of saltwater immersion test were examined by using a Philips XL 30 environmental scanning electron microscope (ESEM). The elementary composition of the scribe and cross-section were analyzed by using energy dispersive x-ray analysis (EDS). For EDS analysis small specimens of scribed panels were sputter-coated with Au-Pd film and analyzed. The cross-sectional samples were prepared in polished epoxy molds. The operating voltage used in SEM analysis was 25 kV.

3. Results and discussion

3.1 Pigment evaluation results

In the bare panel immersion test, excess amount of chemicals (1 wt.-%) were added. Some of the chemicals, e.g., CeCl₃, were quite soluble and dissolved completely. Too soluble chemicals are not suitable for using in the coatings. The purpose of including them in the test was to determine the inhibition of this class of inhibitors on AA7075. In order to simulate the real working condition of the primer the concentration and pH of the solutions were not adjusted to equality.

Among the more than 100 chemicals tested, some categories of corrosion inhibitors were found to be effective on AA7075. Table 1 listed the performance of the typical inhibitors of their categories in the bare panel immersion test for a period of 12 days.

CZPM, zinc phosphate (ZP), silicates, vanadates, zinc

Table 1. Performance of the typical inhibitors in the bare panel immersion test

Pigments	pH	Corrosion Start Time	Corrosion Degree After 12 days
Control	6.5	1hr, medium after 2hrs	severe
MgMoO ₄	7.0	1day, slight	medium
Na ₂ HPO ₄	6.5	2days, medium	medium
CeCl ₃	5.0	2days, slight	medium
HTV	7.0	20hrs, slight	medium
La(OOCCH ₃) ₃	6.5	2hrs, very slight	slight
La(NO ₃) ₃	5.0	4day, slight	slight
ZnSO ₄	5.0	4days, slight	slight
CeVO ₄	6.5	2days, slight	slight
NaSiO ₃	9.0	no corrosion within 12days	very slight
Zn ₃ (PO ₄) ₂	6.0	no corrosion within 12days	no
CZPM*	6.5	no corrosion within 12days	No
BaCrO ₄	6.5	no corrosion within 12days	no

*CZPM: calcium zinc phosphomolybdate

salts, lanthanum salts, cerium salts, phosphates and molybdates were found to be effective on AA7075. Without any inhibitor present corrosion occurred fast on the AA7075 panel immersed in the 3.5 wt-% NaCl solution. Corrosion was visible within an hour and developed to medium after 2 hours. In the solution with strong inhibitors like CZPM and ZP, no corrosion was visible after 12 days of immersion. Images of panels immersed for 40 days are shown in Fig. 1.

DC polarization testing was carried out on pigments listed in Table 1. Fig 2 shows the polarization curves of ZP and CZPM, which demonstrated the strongest inhibition in the immersion test and DC polarization test. Blank and barium chromate were used as control. The cathodic curves of AA7075 in ZP and CZPM solution were depressed compared with AA7075 in the blank solution, indicating a suppression of the cathodic reduction of oxygen to OH⁻. Both anodic and cathodic curves in ZP and CZPM were shifted to the left, i.e., towards lower current density, compared to the blank. The shift resulted in a much lower I_{corr}. Changes were also observed in E_{corr} values, with the shift observed in all inhibitor solution towards cathodic values.

3.2 Performance of coated panels

ZP and CZPM were incorporated into the superprimer L2 that was developed in the same project. Superprimer L2 is an epoxy-acrylate based primer which contains bis-sulfur silane. Bis-sulfur silane helps inhibit corrosion and improves the adhesion between the coating and substrate. To determine the effect of silane and the pigment superprimer L2 without silane (epoxy + acrylate), L2

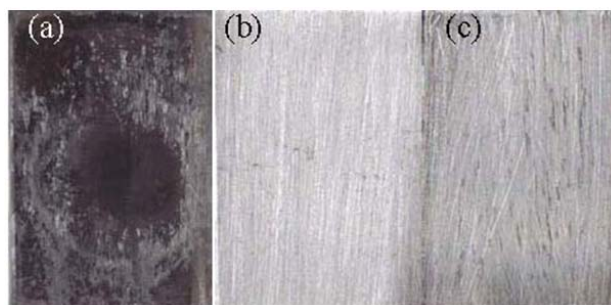


Fig. 1. Bare A A7075 panels immersed in inhibitors extractions for 40 days. (a) Blank, (b) CZPM, (c) ZP

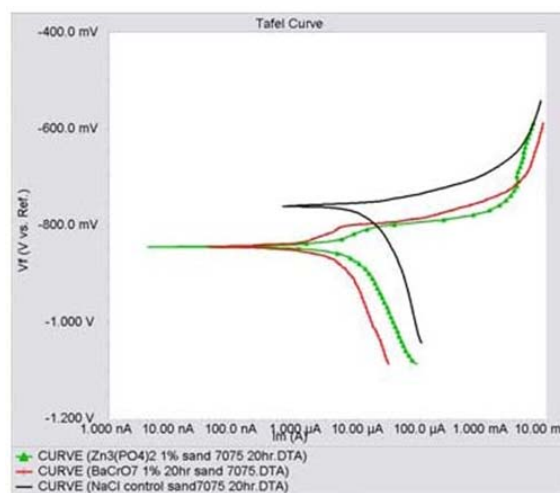
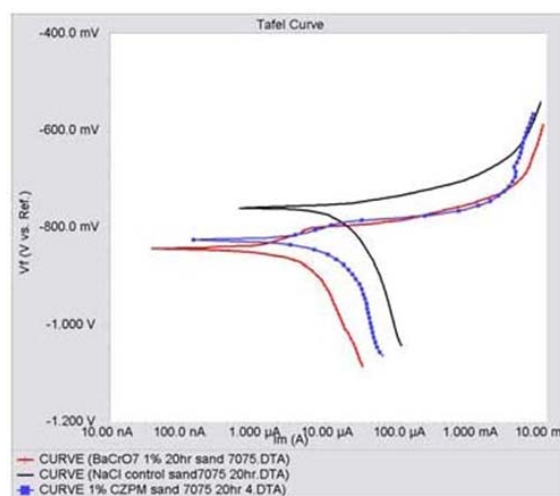


Fig. 2. (a) DC polarization curve of ZP compared to blank and chromate, (b) DC polarization curve of CAPM compared to blank and chromate

(epoxy + acrylate + silane), L2 containing 20 wt-% ZP (epoxy + acrylate + silane + ZP) and L2 containing 20 wt-% CZPM (epoxy + acrylate + silane + CZPM) primers

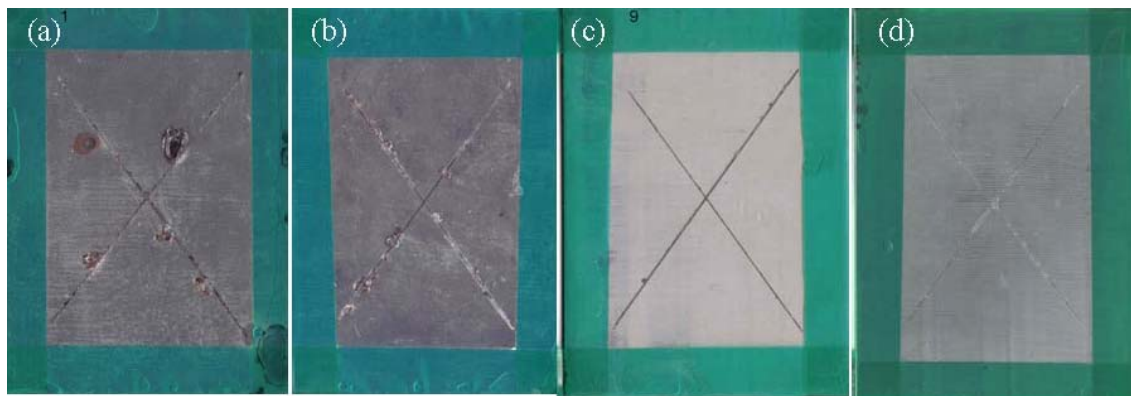


Fig. 3. Coated panels immersed in 3.5% NaCl solution for 40 days. (a) epoxy+acrylate, (b) epoxy+acrylate+silane, (c) epoxy+acrylate+silane+CZPM, (d) epoxy+acrylate+silane+ZP

were prepared and tested in the saltwater immersion test. Images of the panels immersed for 40 days are shown in Fig. 3. Corrosion and blistering occurred on the coating of epoxy + acrylate (panels a) and the coating of epoxy + acrylate + silane (panels b), and corrosion and blistering on the coating without silane is more severe than those on the coating with silane. Pigmented panels (panel c and d) demonstrated good protection against corrosion.

Adhesion tests showed that silane also improved the adhesion between the substrate and superprimer coating. The superprimer containing silane gave results of 5A in the dry condition and 5B in the wet condition in the adhesion test carried out according to ASTM D3359-97 standard. The classification varies from 5A for no peeling or removal to 0A for complete removal. Without silane the results were 4B in the dry condition and 0A in the wet condition.

The 0 ~ 34 days EIS results of L2 pigmented with ZP are shown in Fig. 4. In the period of 34 days, the impedance of the coating showed only minimal shift in all

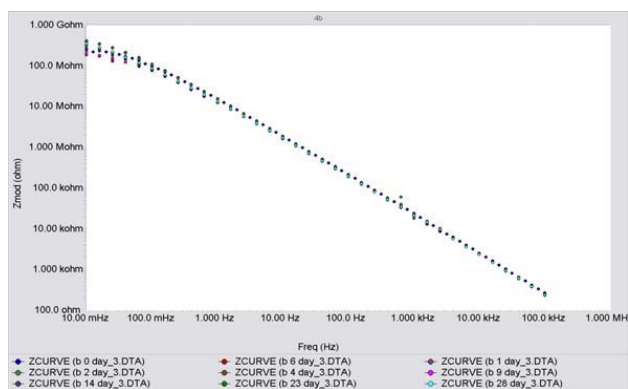


Fig. 4. Impedance spectra for 1-34 days of A A7075 panels coated with superprimer L2 containing ZP

the frequency ranges. This demonstrated that the coating provides good corrosion resistant and good barrier protection.

3.3 Mechanism

Unlike the primers currently used on aircraft, super-primer L2 is a waterborne primer. Zinc phosphate, a hydrophilic pigment, worked well in L2 and some other waterborne superprimers. However, the combination of zinc phosphate and solvent-based primer did not form a satisfactory coating partially due to the low solubility of zinc phosphate. The solubility constant of zinc phosphate is 9.0×10^{-33} . However, as shown in the bare panel immersion test even the very little dissolved zinc phosphate is enough to protect the metal from corrosion. Therefore the leaching rate of the pigments from the coating becomes a more important factor and it may be the reason why zinc phosphate does not work well in solvent-based primers. The cross-section of the pigmented superprimer was examined by using SEM/EDS as shown in Fig. 5. From the SEM image a layered structure can be observed in the cross-section. The apparent layers are the upper dark layer (~10μ

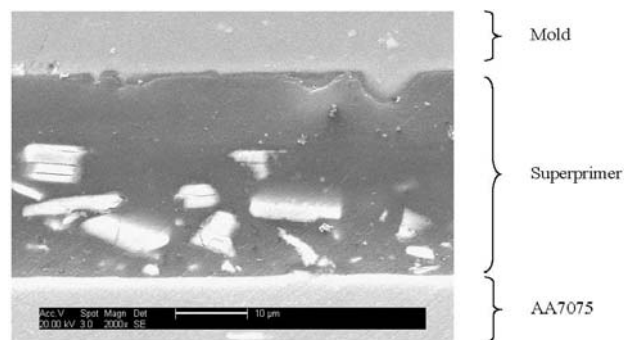


Fig. 5. SEM micrograph of the cross-section of the superprimer L2 pigmented with ZP. The substrate is AA7075

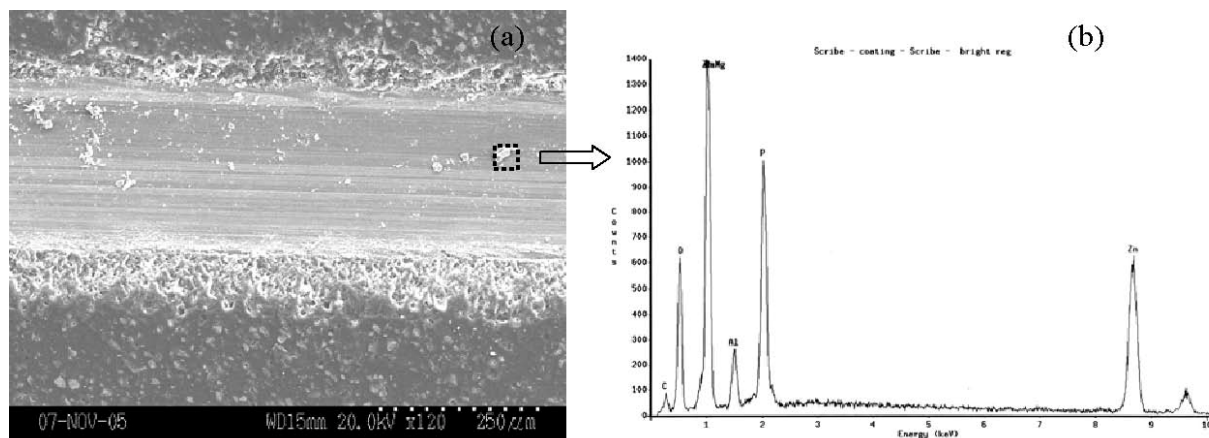


Fig. 6. (a) SEM micrographs of the scribe of AA7075 panels coated with ZP pigmented superprimer L2, (b) EDS spectra of a spot in the scribe shown in (a)

m) which contains no pigments and the lower darker layer (~15 μ m) accommodating all the pigments. It was found that the upper layer is mainly epoxy and the lower layer is acrylate. The level of silane is higher in the lower part of the superprimer.⁵⁾ The epoxy layer is hydrophobic so less water will be absorbed and less water can penetrate it. On the contrary, water can diffuse into the lower hydrophilic layer fast and quickly to release the pigment in the form of a saturated solution when the coating is broken. Therefore, the stratified structure of the superprimer provides good barrier protection with a hydrophobic layer on the top and good corrosion protection with a hydrophilic layer facilitating fast transportation of the pigment underneath. Abundant silane near the interface enhances the corrosion protection and adhesion.

The scribe of the panel coated with ZP-pigmented L2 was found still shining after 30 days immersion in the salt water. The elementary composition of the scribe was analyzed by using EDS. The SEM image of the scribe is shown in Fig. 6a. Trace of zinc and phosphorus were found on the scribe and in some area the level of them are quite high as shown in Fig 6b.

4. Summary

A wide variety of inhibitors were evaluated in a search for chromate-replacing pigments for AA7075. A few categories of inhibitors such as phosphates, zinc salts, cerium salts, and vanadates were found to be effective and zinc phosphate and CZPM were found to be the strongest among them. As demonstrated in the bare panel immersion test the low solubility of zinc phosphate does not impair its corrosion inhibitive ability. DC polarization tests confirmed the inhibitive ability of the pigments.

Epoxy-acrylate based superprimer pigmented with zinc phosphate provides strong protection against corrosion for AA7075. A SEM/EDS investigation showed that the unique structure of the superprimer accounts for the strong anti-corrosion performance of the zinc phosphate pigment. The self-assembled stratified structure of the superprimer is characterized by a less-penetrable hydrophobic layer at the top and a hydrophilic layer accommodating the inhibitors underneath. This structure provides both strong barrier protection and fast pigment leaching out into a scribe, which may be critical for a pigment with very low solubility.

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