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MAGNESIUM RICH PRIMERS AND RELATED DEVELOPMENTS FOR THE REPLACEMENT OF CHROMIUM CONTAINING AEROSPACE PRIMERS

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ABSTRACT

This paper reports the current development status of magnesium rich primer (MgRP) as a replacement for chromated primers used in aerospace. The current MgRP formula was optimized as part of a Cr-free coating system for the corrosion protection of aircraft and has been observed to match and even exceed the performance of chromated primers in accelerated neutral salt spray testing. This result was achieved after modification of earlier prototype MgRP formulas to ensure consistent performance in accelerated corrosion testing. Adjustments in the formula were directed at controlling the activity of the metallic magnesium in the primer. In a parallel development, the same technology used to modify the MgRP formula was also incorporated into a nonmetallic primer formulation which has been optimized for corrosion inhibition. The ability of this nonmetallic primer to inhibit corrosion of aerospace aluminum alloys implies that the modifications to the MgRP formula have resulted in a secondary inhibition mechanism for the MgRP in addition to the primary galvanic protection mechanism.

Key words: magnesium, aluminum, corrosion, Cr-free, primer, MgRP, magnesium rich primer, corrosion inhibition

INTRODUCTION

In addition to health, safety and regulatory reasons to eliminate chromate (Cr) compounds from primers used in the corrosion protection of aerospace aluminum alloys, the industry has in recent years witnessed a decline in the number of established chromate pigment suppliers in North America and Western Europe. If traditional suppliers of quality chromate pigments continue to leave the market, then a change to chromate-free primer formulations may be forced by supply rather than regulatory means. For suppliers of chromate primers, this is an additional pressure to eliminate chromate formulations from aerospace coatings.

In the search for Cr-free coatings, primers pigmented with magnesium metal have been proposed[1] by researchers at North Dakota State University. The formulation of a magnesium rich primer (MgRP) is directly analogous to the use of zinc metal dust in primers applied to steel. In an MgRP formulation the magnesium metal in the primer behaves as a sacrificial anode to protect the aluminum substrate from corrosion. This sort of sacrificial galvanic coating requires a high loading of pigment to provide the necessary conductivity between Mg metal particles, as well as between the particles and the substrate. Nevertheless, it is possible to formulate a magnesium rich primer formula which is based on resin systems similar to other MIL-PRF-23377 (Performance Specification: Primer Coatings: Epoxy, High-Solids) qualified primers.

A unique perspective of this paper is that the data presented is a result of testing the latest generation of the commercial MgRP development. In comparison, some other recent works[2,3] have relied on prototype formulations which are now approaching five years of age and/or lab-made samples with resins very different from the current commercial system. While the resulting papers are recent, the results may only have partial relevance to the current commercial system. This is because the Aerodur® 2100MgRP(1) system was first conceived in 2008 to address the premature neutral salt spray (NSS) failures which were not consistent with the good outdoor exposure results observed in field tests with earlier MgRP formulations.[4] As the University of Southern Mississippi group ascertained, a significant technology hurdle was to control the activity of the magnesium itself in certain accelerated test environments, such as neutral salt spray, where it was too active due to peculiarities of the test. While the theoretical and experimental reasoning for this position was being developed, concurrent formulation developments at AkzoNobel successfully addressed the same issue. Sampling of the resulting formulation, for commercial and intellectual property reasons, has until now been chiefly limited to qualifying bodies and key customers.

Development of the original concept has resulted in an MgRP formulation which has been tested against MIL-PRF-23377 and MIL-PRF-32239 (Performance Specification: Coating System, Advanced Performance, for Aerospace Applications) requirements and which has now been submitted for evaluation and/or qualification at various entities, including the US Air Force's Coatings Technology Integration Office. Over the course of the development work, a great deal of data was collected on the performance of this particular MgRP formulation. While the galvanic protection mechanism is the main mode of protection, it has been postulated that the protection mechanism may be augmented by secondary effects. The purpose of this paper is to discuss the status of the MgRP development, related developments connected to a proposed secondary protection mechanism and also some general observations on the performance of chromate primers used as controls in the described work.

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(1) Trade name

EXPERIMENTAL PROCEDURE

Substrates included 2024-T3 bare and clad (SAE-AMS-QQ-A-250/4, T3 temper and SAE-AMS-QQ-A-250/5, T3 temper, respectively) as noted in the figures. Panels were cut 3"x6" or 4"x6". Primer formulations were based on 2K epoxy resin systems. In light of the Cr-free system goal, Cr-free pretreatments were used. Unless otherwise noted, the pretreatment was PreKote®(1). Where noted, a sol-gel type pretreatment, AC-®131(1) was also used. Topcoats, were 2K polyurethane systems, including one used for civil aviation and one qualified to MIL-PRF-85285 (Performance Specification: Coating: Polyurethane, Aircraft and Support Equipment). Filiform and neutral salt spray tests were conducted to broadly accepted industry practices, such as those described in MIL-PRF-23377 and MIL-PRF-32239. One deviation from these practices was that specimens were evaluated at multiple time periods, not just at the end of prescribed test duration. Coating systems were tested in triplicate.

Of special note is the preparation of neutral salt spray test panels. All test panels were scribed with a Gravograph IS400 engraver with a targeted minimum scribe width of 0.030" and a minimum depth of approximately 0.009" relative to the surface of the metal substrate. This was done to ensure scribe consistency and in the case of clad panels, complete penetration of the cladding to expose the underlying alloy. All panel edges and backs were sealed with polyester electroplater's tape.

RESULTS

MgRP Performance

The performance of the current MgRP formulation has been tested against commercially available chromate primers many times in ASTM B117 neutral salt spray. Representative results are shown below in Figures 1 and 2.

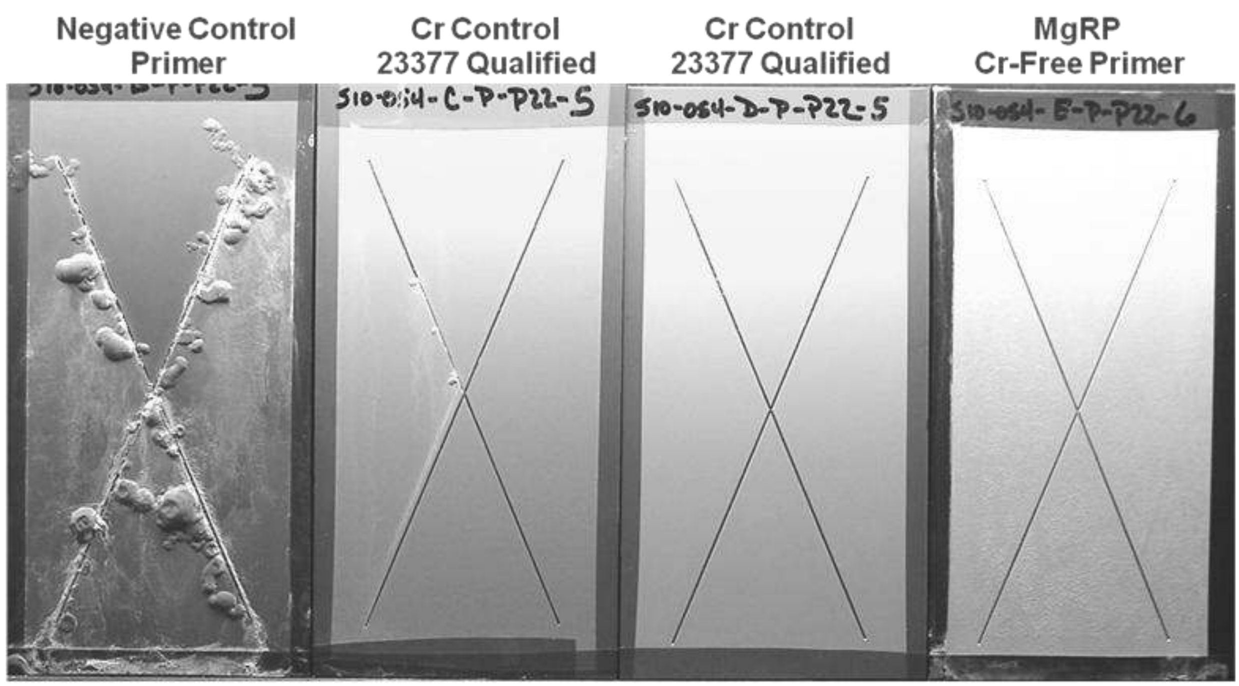

FIGURE 1 - Results at 3000 hours of NSS for primer-only, Cr-free pretreatment, bare 2024-T3

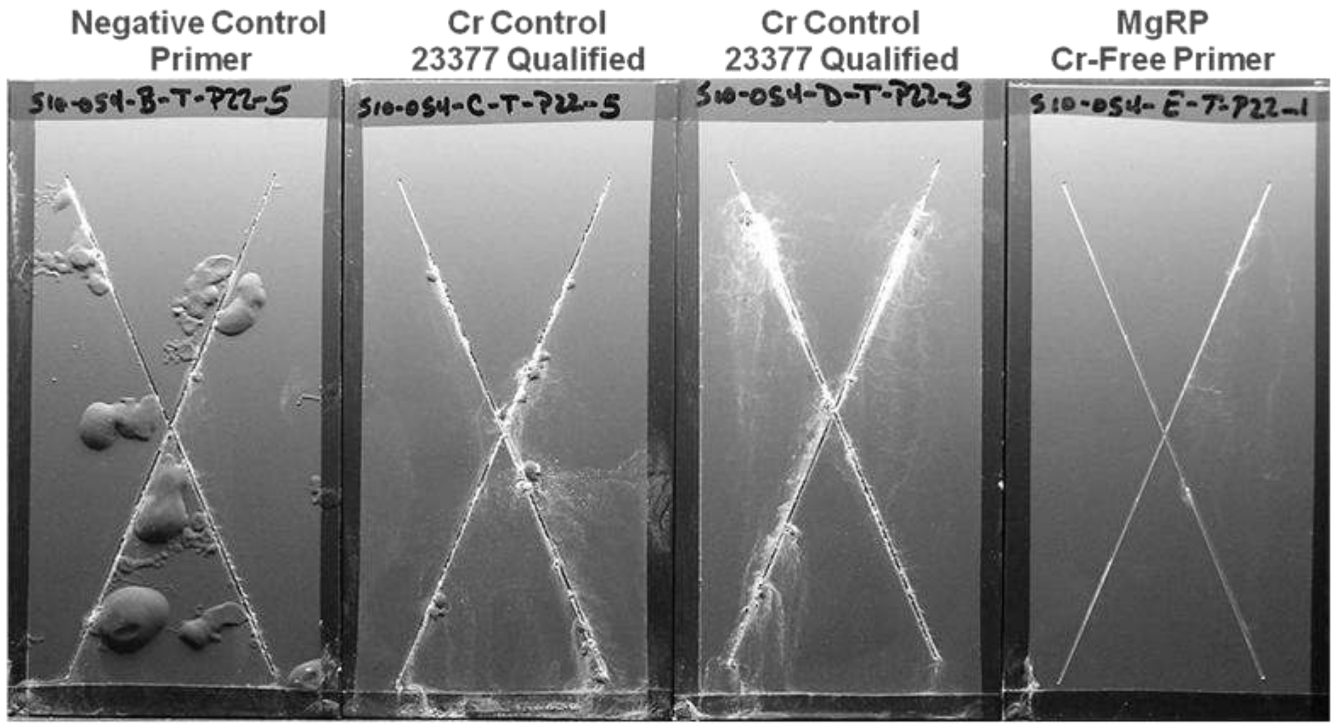

FIGURE 2 - Results at 3000 hours of NSS exposure for topcoated panels, Cr-free pretreatment, bare 2024-T3

An interesting observation from the comparison of Figures 1 and 2 is the negative impact of topcoating on the corrosion performance of the chromate primer. This may be attributable to the fact that the chromate primer depends on solubilization of inhibitor from the primer film, and the topcoat provides a barrier to water which is required for the leaching of chromate from the primer film.[5] While the MgRP requires contact with water to function, the galvanic corrosion protection provided by the MgRP does not require the transport of an active corrosion inhibiting species. It may be that the galvanic protection mechanism is more robust in that there is not a large reduction in performance triggered by topcoating. As might be expected, the negative control primer, without active inhibitor, was not impacted by topcoating either positively or negatively.

Other than a true release-on-demand type system, all inhibitors are going to be “consumed” over time. In the case of chromates and common alternatives, the expectation is that the inhibitor will be leaching out when the coating is wet and that this process will occur whether the inhibitor is needed or not. The MgRP is perhaps a bit different. One part of its behavior is like that of a release-on-demand type inhibitor, while the other part of its behavior is more like a conventional inhibitor.

With regards to the latter, in a process that could be referred to as self-corrosion in the sacrificial anode field, Mg can oxidize independently of the corrosion current driven by coupling it with a more cathodic metal which it is to protect. This self-corrosion, which decreases the current efficiency of the metallic Mg in the coating, is much like the continuous leaching of a conventional inhibitor whenever water is present. Self-corrosion, though, can be reduced by increasing the purity of the Mg or adding in certain beneficial alloying elements.[6] Therefore, self-corrosion can be minimized to some extent in favor of Mg oxidation occurring to protect the substrate when corrosive conditions exist.

Regardless of the mechanism, it has been shown that the MgRP can provide corrosion protection for an extended period of time, even in an accelerated corrosion test without topcoat, as seen in Figure 3. Additionally, MgRP typically exhibits very good filiform corrosion resistance as seen in Figure 4.

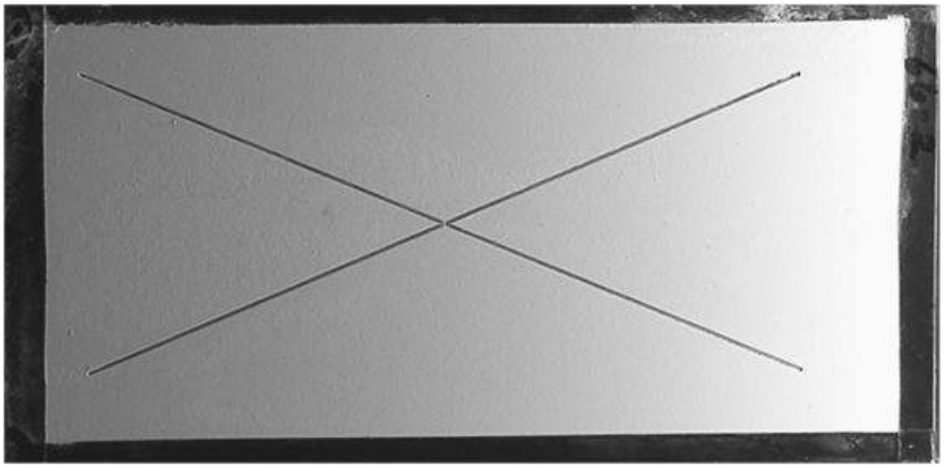

FIGURE 3 - 7000 hours of NSS for MgRP without topcoat, bare 2024-T3

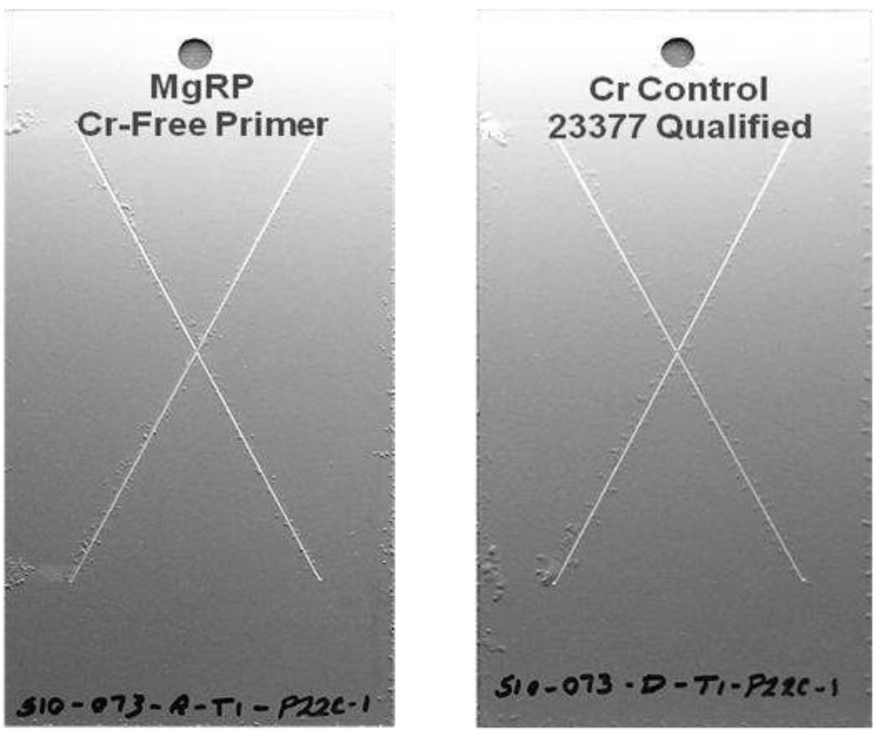

FIGURE 4 - Filiform corrosion resistance of MgRP, clad 2024-T3

As mentioned in the introductory section of this paper, the MgRP formula was modified to provide control of the Mg activity to prevent the occasional early failures seen in neutral salt spray testing. An example of this is seen in Figure 5 below. The two photographs were taken at 500 and 2000 hours of NSS exposure of a topcoated, MgRP prototype without any additive to moderate magnesium metal activity. There are at least three important observations: 1. The blistering along the scribe is odd with some of the blisters not clearly extending to the edge of the scribe. Contrast this to photos of a negative control in Figure 2 which shows something more typical for a system with insufficient corrosion protection. 2. The scribe line is fairly clean, even at 2000 hours, in spite of blistering. 3. The blistering did not seem to worsen significantly from very early in the salt spray test (500 hours) through to 2000 hours.

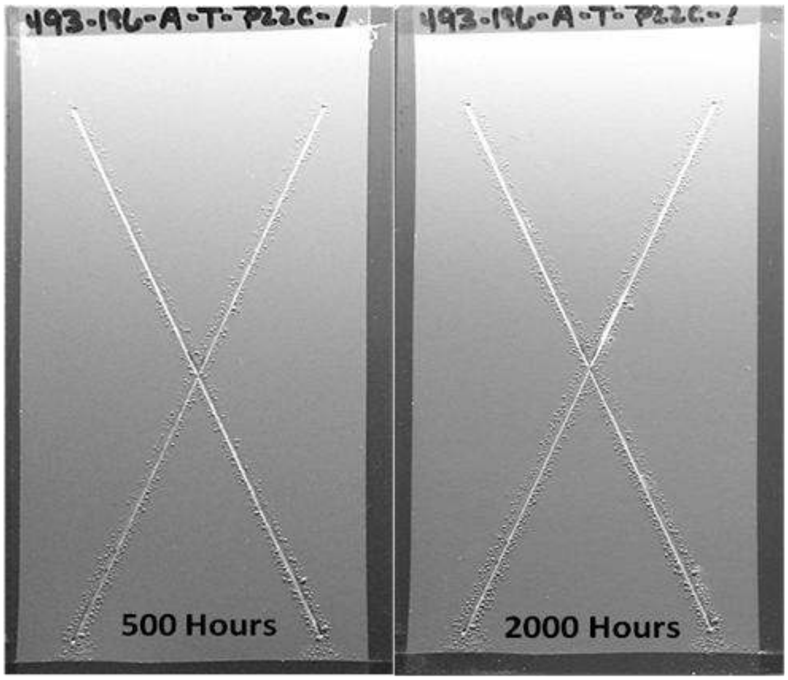

FIGURE 5 - Performance of early prototype in NSS, clad 2024-T3

The three observations above indicated that the MgRP was protecting the scribe, but something clearly was a problem in the early stages of salt spray exposure. (A good review of the possible reasons for this can be found in Reference 4.) Observations related to phenomena seen in Figure 5 pointed to excessive Mg activity as the root cause of the early salt spray failures rather than insufficient corrosion protection from the MgRP. Hence the evolution to the current formula, created by modifications to control the Mg activity to obtain the results seen in Figure 2.

In a parallel product development, the same technology which was used to slow the activity of Mg metal in the MgRP was also used to develop an inhibitive system which would by itself provide corrosion inhibition for aluminum alloys. That there is a relation is not surprising, as some of the same factors which exacerbate corrosion of aluminum alloys are shared with magnesium. An example is the detrimental effect of copper, nickel or iron contamination on the corrosion susceptibility of magnesium metal.[7] These contaminants have an effect on magnesium metal which is similar to the effect of copper rich intermetallics on the corrosion susceptibility of aluminum alloys.

The end result is an MgRP system with a substantial secondary protection mechanism in addition to the primary galvanic protection mechanism. Experimental results are shown below, indicating the potential degree of corrosion protection due to this secondary mechanism which was incidentally included in the current MgRP formulation as a result of the effort to control the magnesium metal activity.

Non-metallic System Performance

A novel, new non-metallic system has been developed which provides insight into the possible secondary protection mechanism for MgRP. The most significant difference between the new system and the MgRP formula is that the metallic Mg is removed. The most significant similarity is that the two formulations share the same technology which is used to moderate the activity of the magnesium pigment. The non-metallic system was tested in salt spray and filiform against control formulations based on strontium chromate and commercially available inhibitors.

Neutral Salt Spray Resistance

As indicated by Figures 6 and 7, in neutral salt spray the chromate control performed best, but the new non-metallic system came closest to matching the performance of the chromate control. The non-metallic system proved superior to the other test primers formulated with commercially available, Cr-free inhibitive pigments based on phosphate compounds.

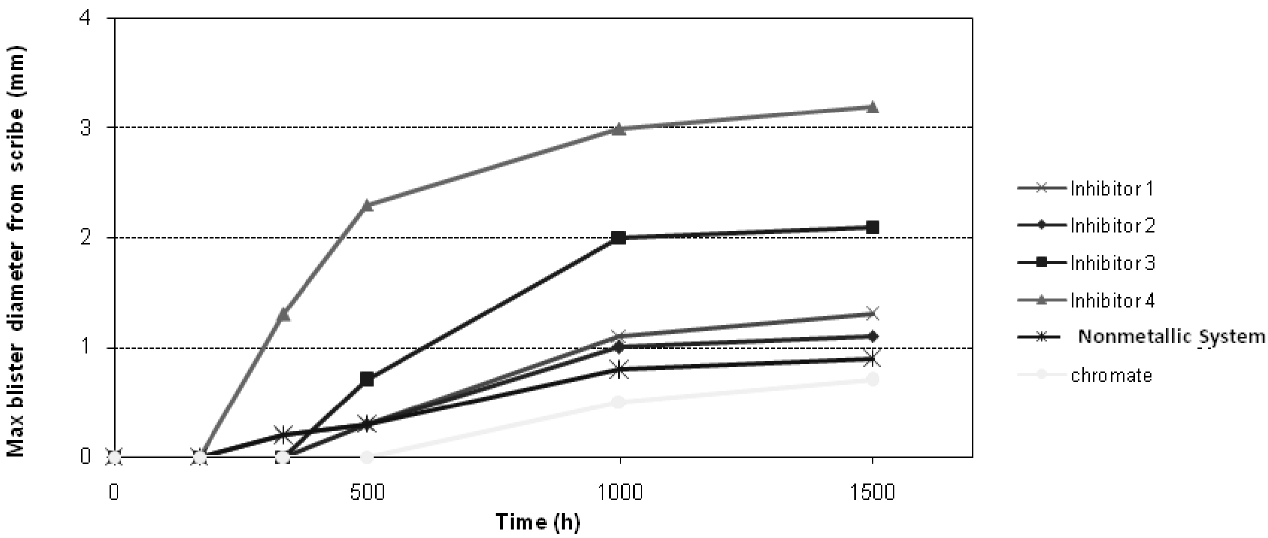

FIGURE 6 - Scribe line blister diameter growth over time in NSS, sol-gel pretreated 2024-T3 clad

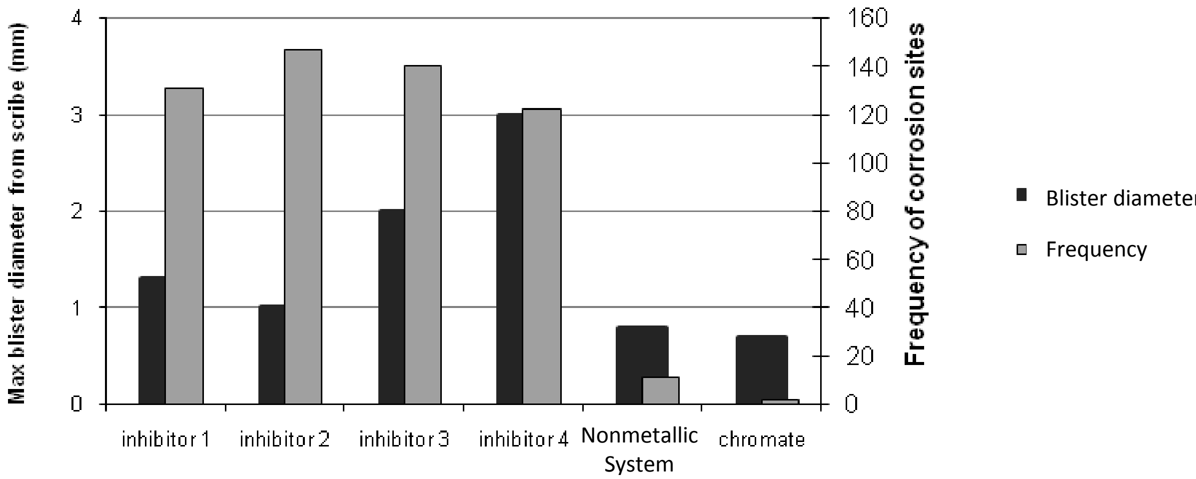

FIGURE 7 - Maximum scribe line blister size and blister frequency after 1500h NSS, sol-gel pretreated 2024-T3 clad

Figure 8, a photo of test panels from another experiment, gives a visual representation of the performance of the new non-metallic system relative to a negative control and the MgRP. While not as good as the MgRP in preventing corrosion in and along the scribe, nevertheless, its performance indicates a great deal of inhibition beyond that which is offered by the negative control primer.

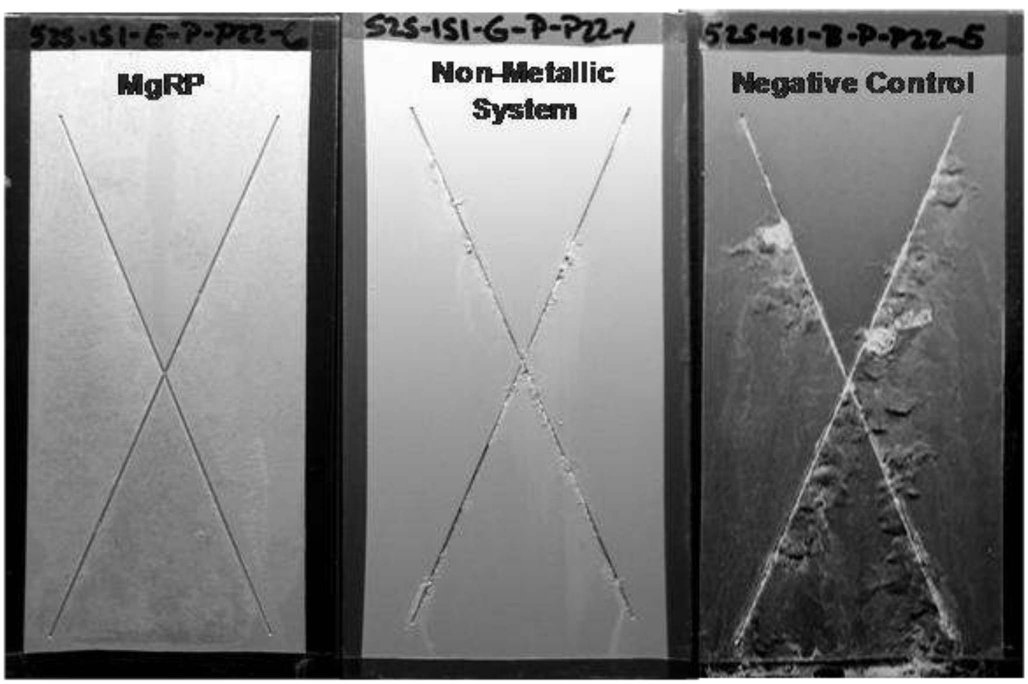

FIGURE 8 - Comparison of 3000 hrs NSS performance for the non-metallic system against the MgRP and the negative control, bare 2024-T3 with Cr-free pretreatment

Figure 9 provides data on the filiform corrosion performance of the non-metallic system. The filiform corrosion resistance has proven to be comparable to the chromate controls, and on the account of this and its good NSS resistance, patent approvals are expected.

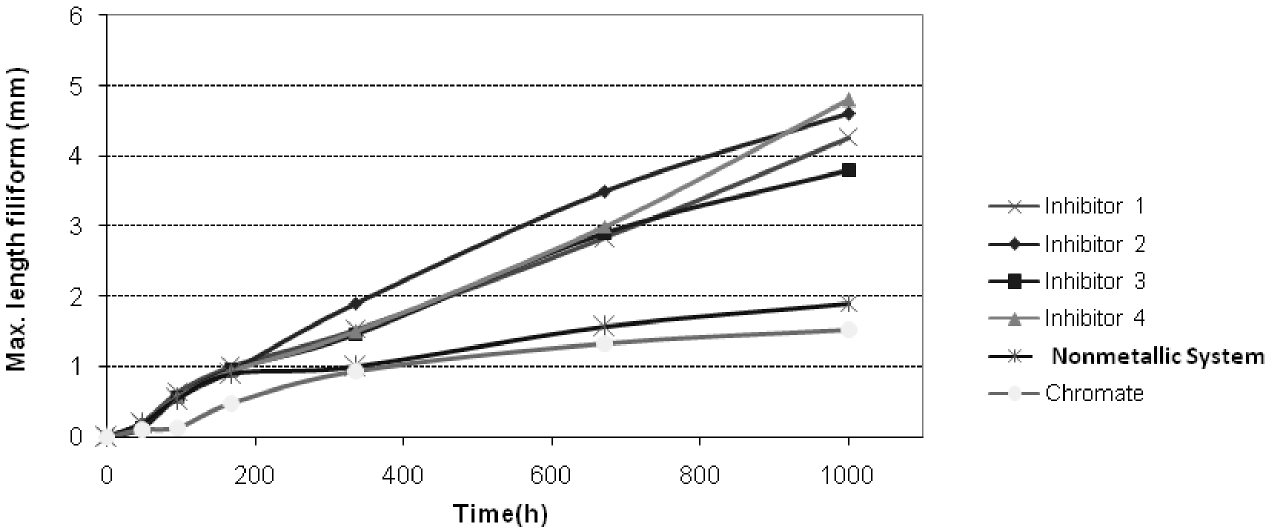

FIGURE 9 - Filiform Corrosion Resistance: Filament growth on sol-gel pretreated 2024-T3

Scanning Electron Microscopy

Analytical work is still in the preliminary stages, but a possible passivating layer morphology has been identified (see Figure 10). It is anticipated that this will be studied in more depth in the future. Data on the composition of this layer is still being developed.

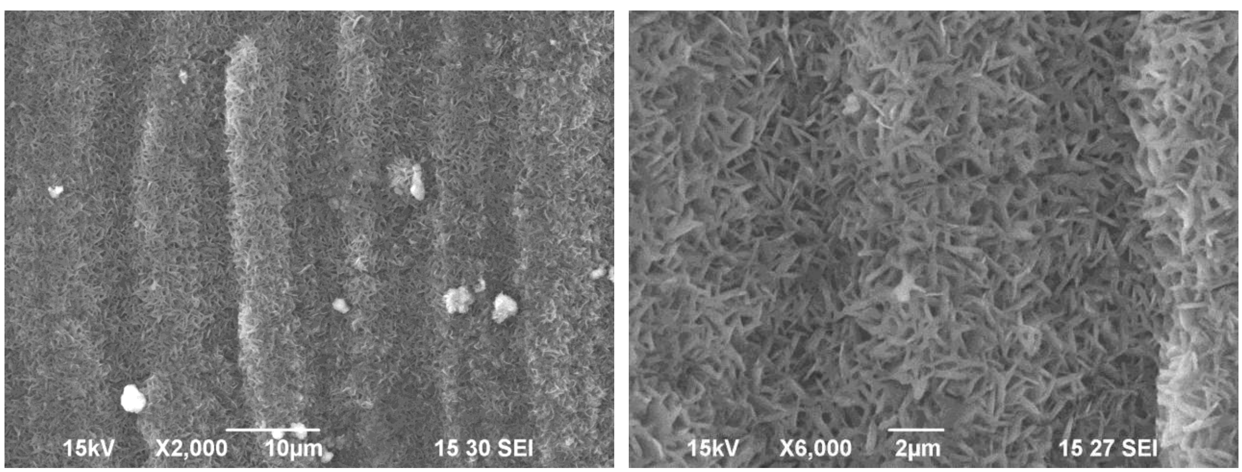

FIGURE 10 - Micrographs showing morphology of possible passivating layer

CONCLUSIONS

A magnesium rich primer (MgRP) has been formulated which can at least equal the neutral salt spray and filiform resistance of chromate based primers. It has been shown to actually exceed the neutral salt spray resistance of chromate primers, which depend on leachability of the chromate-based inhibitor, when all of the primers are topcoated. A major developmental step was taken when the activity of the Mg pigment was controlled by formula modifications. An offshoot of this is that a secondary corrosion protection mechanism has now been built into the current generation of MgRP.

Parallel formula optimization of the related non-metallic system against commercial specifications has resulted in overall product improvement while maintaining overall corrosion resistance. Work has begun to advance the understanding of the secondary corrosion protection mechanism and the proposed passivating layer that may result from it.

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