NOVEL, ONE-STEP, CHROMATE-FREE COATINGS CONTAINING ANTICORROSION PIGMENTS FOR METALS THAT CAN BE USED IN A VARIETY OF INDUSTRIES

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Abstract

The concept of superprimers, i.e., primers for metals with the conversion coating built in, has proven to be feasible. Such primers can be applied on any bare metal, provided it is reasonably clean. These primers are based on water-dispersed organic resins and organofunctional silanes, which assure good adhesion both to the substrate and the overcoat. In this paper we will discuss an epoxy-novolac based system for AA20242-T3, but we will also present an overview of other coatings. The corrosion protection performance of these coatings has been evaluated using electrochemical methods and performance tests. All of the developed coatings survive 2000 hrs in ASTM B117 salt spray test. The systems have also been extensively characterized. The characterization methods have provided information on the formation of the coatings and the mechanism by which the coatings protect the metal substrates.

Keywords: silane, superprimer, pigment, chromate, aluminum alloy

1. Introduction

Chromate performs two major applications in corrosion control. The first is conversion sealing pretreatments for metal alloys of iron, aluminum, zinc, copper, and magnesium. The second application is as leachable inhibitive pigments in many primer formulations. Both of these uses of chromate compounds produce strong corrosion inhibiting effects. Trialkoxysilanes and similar silicon compounds are currently the subject of intensive research due to the need of “green” technology in the metal-finishing and the adhesive industries. Chromate and similar hexavalent chromium compounds have been reported to be toxic and carcinogenic, and thus their use and waste are regulated heavily by most environmental legislation [1,2]. Volatile organic carbon (VOC) in coatings and other sources have been linked to smog formation [3]. The proposed lower emission levels have forced many companies to look for water-based solutions to their corrosion prevention needs. Research has progressed into investigating the modification of silane technology with conventional paint coating methodology. This has been accomplished through resin and/or pigment additions to sol-gel processes or direct network formation of siloxane using large silane precursor additions to paint formulations [4-6].

When it comes to protecting metals from corrosion, all our research is focused to solve the chromate and the VOC problem. Recently we have formulated and studied several chromate-free, water-borne primers based on organic resins, crosslinkers, bis-silanes and pigments for substrates like aluminum alloys, hot-dip galvanized (HDG) steel and cold-rolled steel (CRS) [7-11]. This study focuses on the development of an epoxy-novolac based superprimer coating system for AA2024-T3, but our other formulations on other substrates will also be briefly presented.

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Epoxy-novolac resins are produced by acid catalyzed condensation of a phenolic precursor with formaldehyde, followed by glycidation with epichlorohydrin. The relatively high epoxide functionality of epoxy-novolac resins leads to an increased cross-linking density, which results in better chemical resistance and thermal properties compared to that achieved with standard Bisphenol A or Bisphenol F resins in parallel primer systems. Epoxy-novolac resins are therefore seen as high performance products for a broad range of applications [12].

2. Experimental

2.1 Materials, chemicals and sample preparation

Aluminum AA 2024-T3 alloy substrates of 0.032 inch thickness were acquired from Stillwater Steel and Supply, Stillwater, OK. The other substrates were also obtained from this supplier.

The epoxy-novolac resin and its curing agent were acquired from Hexion Chemicals, Houston, TX. The polyurethane dispersions were obtained from DSM Neo-Resins, Wilmington, MA. Silquest® A-1289 bis-[3-(triethoxysilyl) propyl] tetrasulfide or bis-sulfur silane (BS), $(OC_2H_5)_3Si(CH_2)_3S_4(CH_2)_3Si(OC_2H_5)_3$, Silquest® Y 9805 bis-[triethoxysilyl] ethane or BTSE, $(OC_2H_5)_3Si(CH_2)_2Si(OC_2H_5)_3$ and Silquest® A-1170 bis-(trimethoxysilylpropyl) amine or bis-amino silane, $OCH_3)_3Si(CH_2)_3NH(CH_2)_3Si(OCH_3)_3$, were obtained from GE Silicones, South Charleston, WV. Vinyltriacetoxysilane (VTAS) was procured from Gelest Inc., Tullytown, PA. The resins and silanes for the other formulations have been presented elsewhere [13].

Non-chromate inhibitors were used in this study to impart self-healing or corrosion inhibiting properties to the superprimer. Corrostain 228, a corrosion inhibitor pigment containing Ca, Zn, P, Si and O, was procured from Wayne Pigment Corp., Milwaukee, WI. Alfa Aesar zinc phosphate, a technical grade zinc phosphate corrosion inhibitor was procured from Johnson Mathey, Ward Hill, MA. Phosguard J0806, a micronized zinc phosphate/molybdate corrosion inhibitor from Rockwood Pigments, Beltsville, MD. Sodium meta-vanadate of chemical grade was procured from Fluka industries, Switzerland.

The metal panels were thoroughly cleaned, rinsed with DI water and blow-dried. The formulation ingredients were mixed together and high shear blended. The formulations were applied onto panels by draw-down bar. The epoxy novolac primers coated onto AA2024-T3 were cured at room temperature (RT) for 14 days or at 70°C. The chromate controls were prepared from the CA 7233 High solids chromated epoxy standard military primer and its activator component CA 7233 B, mixed in the ratio 1:1 by volume, applied on chromate-pretreated AA 2024-T3 panels and cured at RT.

2.2 Tests and characterization methods

Corrosion resistance of the superprimed metals was studied by electrochemical impedance spectroscopy (EIS). The experimental setup for EIS has been described elsewhere [14-15]. The EIS measurements were performed by using 3.5 wt.-% NaCl as the electrolyte. The following ASTM standard tests were performed on the coating systems:

- ASTM B-117 salt spray test

- ASTM D 714 3.5 wt.-% NaCl solution immersion test
- ASTM D 3359-97 tape adhesion test
- ASTM D 3912 chemical resistance (6 N HCl and 6 N NaOH)
- ASTM D 4752 MEK double rub test
- ASTM D 3363-00 pencil hardness test

The superprimer liquid dispersions and/or the resulting coatings were also characterized by using the following methods; Nuclear Magnetic Resonance (NMR) Spectroscopy, Fourier Transform Infrared (FTIR) Spectroscopy, X-ray reflection methods, Scanning Electron Microscopy combined with Energy Dispersive X-ray analysis (SEM/EDX).

4. Results and discussion

The amount of water absorbed or diffusing through a coating depends on the amine content which can affect the corrosion-inhibiting properties of the coating [12]. Hence, the ratio of epoxy-novolac resin and amine adduct curing agent had first to be sought out for this particular superprimer. Formulations with different ratios ranging from 90:10 to 50:50 were prepared. These were cured both at room temperature (RT) and at 70°C. The best ratio was selected by comparing the results of water contact angle, MEK double rub value and pencil hardness. The formulation containing 80 wt.-% of epoxy-novolac resin and 20 wt.-% of curing agent had the best values. Therefore, the 80:20 novolac:crosslinker formulation was chosen as the base ratio.

The 80:20 formulation formed, however, a hard coating after curing and was brittle at low temperatures. It is known that silanes can affect film properties such as hardness, flexibility, hydrophobicity, solvent and chemical resistance [14]. Therefore, three silanes were separately added into the 80:20 epoxy-novolac formulation and several coating properties were determined. The coating formulations are shown in Table 1. All three silanes; the bis-sulfur silane, the BTSE and the AV5 mixture solution were chosen because these silanes had already been used successfully in other primer formulations [7-11]. The bis-sulfur silane was the strongest candidate, because neutron reflectivity studies of bis-sulfur films had shown that they are hydrophobic, resistant to the action of boiling water and show a tendency of reconstruction of the siloxane and metallo-siloxane bonds upon drying [16]. Both bis-sulfur silane and BTSE were added into the formulation in unhydrolyzed form.

The AV5 mixture solution consists of bis-amino silane and VTAS (5:1 by volume). It is known to have unique properties and better performance than the individual silanes [15]. In this study, AV5 was used only along with the novolac resin (Table 1). Both polyurethane resins were highly reactive towards the AV5 mixture and hence, they were not used in formulations containing AV5.

For aircraft applications coatings need to sustain cyclic stresses at low temperatures during flights. One aim of this study was to develop a coating with good flexibility at a wide range of temperatures. This particular goal was achieved by incorporating a small amount of polyurethane into the 80:20 epoxy-novolac formulation both with and without silane as shown in Table 1. The amount of polyurethane addition was, however, limited to 15 wt.-%, because of the reactivity between the epoxy-novolac and the polyurethane. The water contact angle, MEK double rub and pencil hardness values of the coatings shown in Table 1 are presented in Table 2.

Table 1 Additions of silane and/or polyurethane to the base formulation of epoxy-novolac resin + crosslinker

Formulation	Silane	Polyurethane 1 (g)	Polyurethane 2 (g)
BS	BS	-	-
AV5-1	AV5	-	-
AV5-2	AV5	-	-
BS P15	BS	15	-
BS P20	BS	20	-
BS P10	BS	10	-
BTSE P15	BTSE	-	15

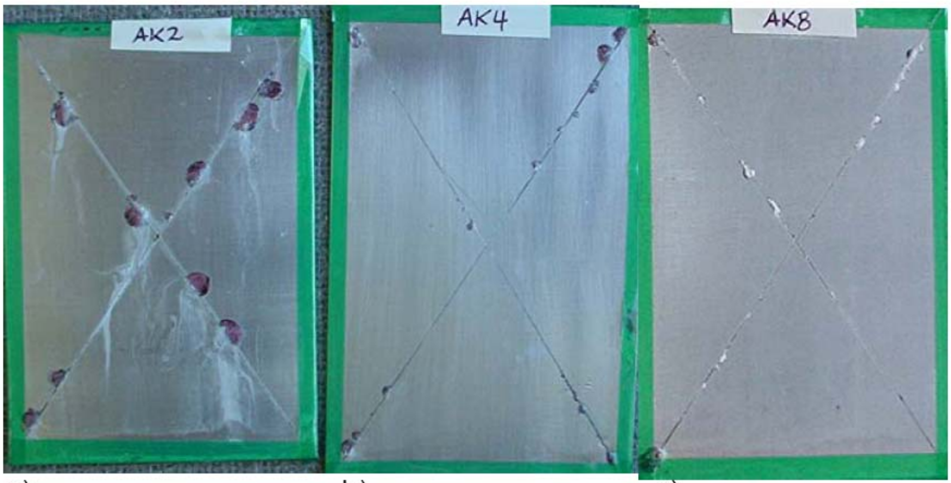
Table 2. Properties for the coatings presented in Table 1.

Formulation	Water contact angle, (°) (cured at RT)	MEK double rub value (cured at RT)	MEK double rub value (cured at 70°C)	Pencil Hardness (cured at RT)
BS	76	60	300	1B
AV5-1	65	25	250	1H
AV5-2	60	15	150	2H
BSP15	79	100	300	2H
BSP20	76	90	-	HB
BSP10	73	10	-	2B
BTSE P15	81	70	-	2B

Of the silane containing epoxy-novolac coatings the coating containing bis-sulfur silane performed overall best (Table 2). The high contact angle can be explained by the fact that coatings containing bis-sulfur silane are more hydrophobic than coatings containing bis-amino silane [16]. The MEK values indicate that the bis-sulfur silane was more able to interact and crosslink with the epoxy-novolac formulation compared to the AV5 mixture. One would, however, have expected a higher pencil hardness than 1B for the bis-sulfur containing coating.

Among the coatings containing both silane and polyurethane the coating containing an intermediate amount of polyurethane (15 wt.-%) performed best, also the pencil hardness of this coating had improved compared to the corresponding coating without polyurethane. Apparently, the bis-sulfur silane and the polyurethane together had a synergistic effect in enhancing the hardness of the resulting coating. The effect of the substantial increase in the MEK values with temperature could be observed for all coatings that were cured at both RT and at 70°C. This indicates that curing at a slightly elevated temperature really enhances crosslinking of the resins and results in more chemically resistant coatings.

Figure 1 shows the images of the epoxy-novolac base coating without bis-sulfur silane after 1000 hrs, with bis-sulfur silane after 1500 hrs and with bis-sulfur silane + polyurethane after 2000 hours of exposure in salt spray test. All results such as the salt spray test results (Figure 1), the EIS low impedance spectra of these coatings, the ASTM D 3359 adhesion results as well as the salt immersion test results showed the same trend; the performance of the coating improved with the addition of bis-sulfur silane and further improved with the addition of bis-sulfur silane and polyurethane.



a) b) c)

Figure 1. The epoxy-novolac base coating a) without bis-sulfur silane after 1000 hrs, b) with bis-sulfur silane after 1500 hrs and c) with bis-sulfur silane and polyurethane after 2000 hrs of exposure in ASTM B-117 salt spray test.

In order to investigate the flexibility of the coatings the three coatings shown in Figure 1 were subjected to a bend test. After bending the specimens were immersed in 3.5 wt.-% NaCl for 30 days. The coating without silane showed huge cracks after bending because of its brittleness. It also suffered from extensive corrosion on the cracks as well as the rest of the coating. The coating containing silane was slightly less brittle after bending and only the cracked part of the coating suffered from corrosion. The BSP15 formulation showed no cracking at room temperature bending and remained intact even after exposure to salt water. These results confirmed the role of silane in providing corrosion protection and the flexibility and resistance to cracking imparted by the addition of polyurethane to the novolac-based superprimer. The BSP15 coating was also bent at -70°C. It cracked slightly, but still performed well in salt immersion test.

The results presented above clearly show that the epoxy-novolac coating containing both bis-sulfur and polyurethane performed quite convincingly. Instead of BSP15 this formulation was named NP-1. Small amounts of three different pigments were separately added to this formulation. The sample containing zinc phosphate was named NP-1 +ZP, the one containing Corrostain 228 was termed NP-1 + CORR and the one containing sodium metavanadate was designated NP-1 + NaVO3. The performance of these coatings was compared with the chromate containing control coatings C1 and C2. Figure 2 shows the low frequency impedance values of these coatings measured during the exposure of these coatings in ASTM B117 salt spray test.

As can be observed from Figure 2, the impedance values for the superprimer coatings containing inhibitors dropped initially but stabilized later on. For the chromate controls the impedance values remain very high throughout the depicted time. This is in consistency with our previous results with other superprimer coatings [11]. The EIS low frequency impedance is mainly an indicator of the electrolyte absorption tendency of the coating. As the superprimer coatings were made from a water-based formulation, it is evident that these samples are more hydrophilic than the control coatings prepared from solvent-borne coatings.

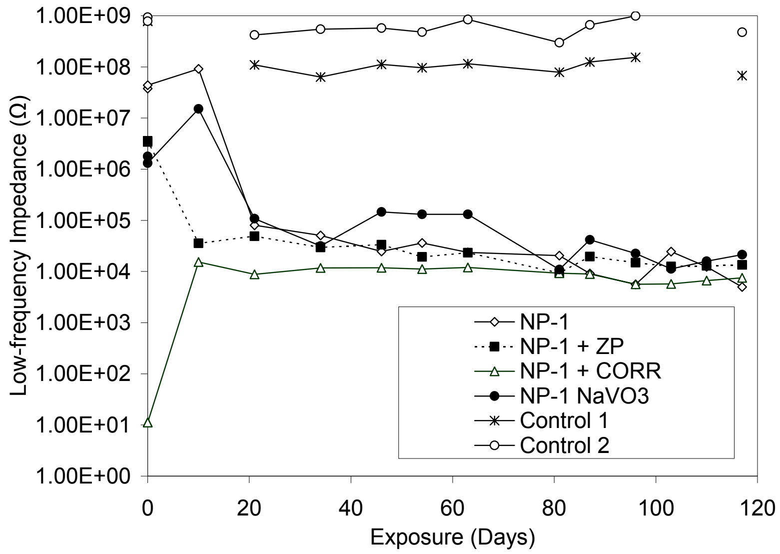


Figure 2. The low frequency impedance values of the inhibitor containing coatings measured during the exposure of these coatings in ASTM B117 salt spray test.

The images of the inhibitor containing samples after 2500 hrs of salt spray test showed, however, that an effect of scribe protection or defect healing was generated by all three corrosion inhibitors. A hint of corrosion on scribes was observed but large parts of the scribes remained clean and free from white rust. Thus, the water absorption of the coatings can also be turned into an advantage in combination with suitable inhibitors, provided that an appropriate water-resistant film is still present in the coating. SEM/EDX studies of coatings exposed to 30 days of salt immersion testing have shown that due to the hydrophilic nature of the superprimer coating the chromate-free inhibitors of the coating are able to leach out on demand and protect the scribes of the coating in corrosive environments. The EIS and performance test results of the coatings indicates the phenomenon described, i.e., the low-frequency impedance value of the coatings drops at the beginning of the tests but the scribes on the panel remain nearly clean and no blistering and delamination is observed.

The FTIR and NMR results of this epoxy-novolac based coating have shown that the epoxy groups of the resin react with the amines of the crosslinker. The silanol groups of the hydrolyzed silane react with each other forming siloxane Si-O-Si and the OH groups of the resin forming C-O-Si. The polyurethane also reacts with the other ingredients and is incorporated into the network, i.e., an interpenetrating water-resistant network is present in the coating, which assures the degradation resistance of the coating upon water penetration.

Table 3 shows an overview of the properties of the different superprimer formulations and Figure 3 presents the images of the superprimer samples after ASTM B117 salt spray testing of 2000 hrs or more. The results of the NP-1 coating is shown in column three in Table 3 and the image of this coating is presented as Figure 3c.

Table 3. Properties of the superprimer formulations

Property	Chromate Control	NP-1 for AA2024-T3	Acrylate-epoxy for Al-alloys	Polyurethane for Al-alloys	Epoxy for HDG steel
VOC (g/L)	~ 340	~ 30	~ 40	~ 150	~ 40
Pot-life (hr)	4-5	3-4	3-4	6 months	3
Dry-to-touch (hr)	3-4	6	7-8	6	1-2
MEK double rub	300	100	98	> 100	> 300*
Pencil hardness	3H	2H	3H	1H	4H

*step-cured; 14 days RT + 30 minutes 135°C

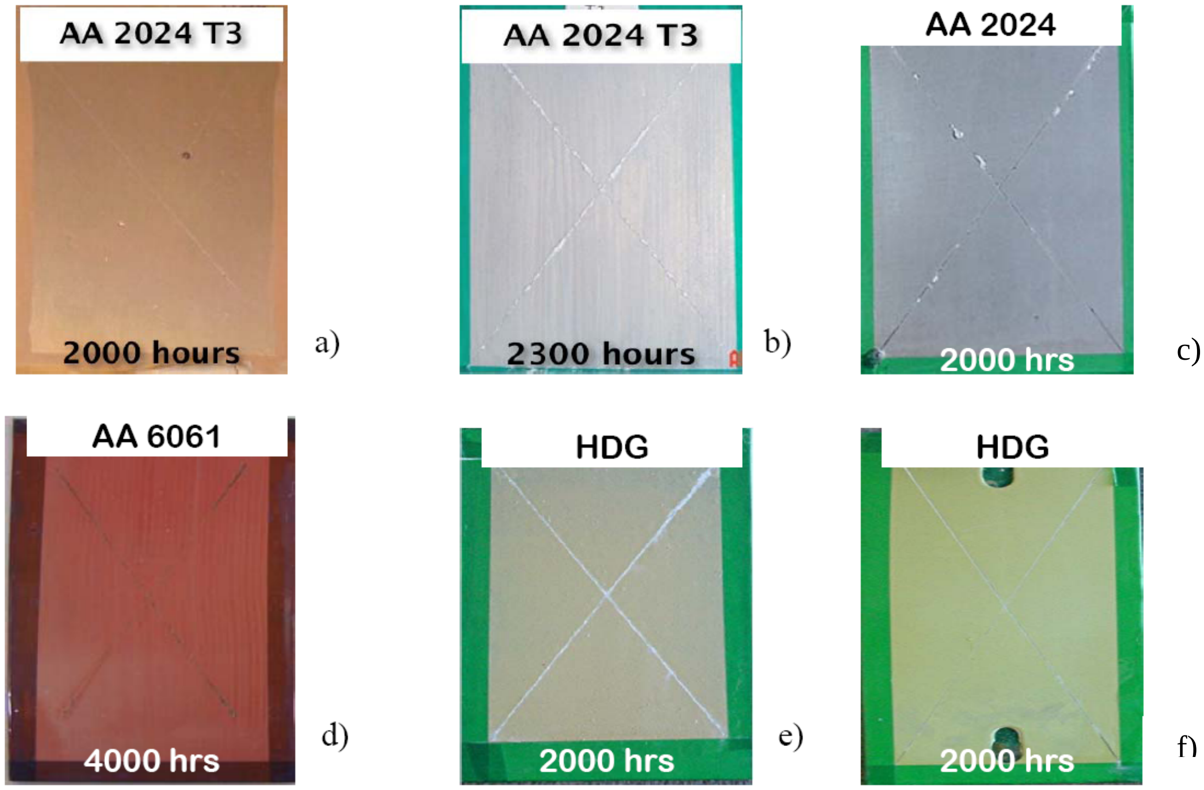


Figure 3. ASTM B-117 salt spray test results of a) the chromate control on AA2024-T3, b) the acrylate-epoxy based system on AA2024-T3, c) the novolac-epoxy-polyurethane based coating on AA2024-T3, d) the polyurethane based coating on AA6061, e) the epoxy based system on HDG and f) the chromate control on HDG

As can be seen from the results in Table 3 and Figure 3 the superprimer coatings perform fairly well compared with the chromate controls.

4. Conclusions

The results of the development of an epoxy-novolac based superprimer coating for AA2024-T3 has been discussed in this paper along with a short overview of the performance results of our other superprimers. Regarding the novolac based coating, the following can be concluded:

- Incorporation of silane such as bis-sulfur silane, improves the anti-corrosion performance, water-barrier properties and adhesion characteristics of the novolac-based superprimer coating.
- Corrostain 228, zinc phosphate and sodium metavanadate have been effective in corrosion inhibition in this coating on AA 2024-T3.

- The polyurethane resin enhances flexibility and low-temperature behavior of the novolac-based superprimer while further improving solvent resistance and adhesion.

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References

1. Toxicological Profile for Chromium. Agency for Toxic Substances, U.S. Public Health Service, Report No. ATSDR/TP-88/10, July 1989.
2. EPA website. Toxicological review of hexavalent chromium. CAS No. 18540-29-9, U.S. Environmental Protection Agency, Washington DC, 1998.
3. EPA Clean Air Act. http: //www.epa.gov.
4. Osborne J. H., Joshua D. Y., Damron M. *Prog. Org. Coat.*, 41 (2001) 226-232.
5. Metroke T L, Kachurina O, Knobbe E T. *Prog. Org. Coat.*, 44 (2002) 295.
6. Van Ooij W. J., Seth A., Mugada T., Pan G. and Schaefer D. W. *A novel self priming coating for corrosion control*. In: International Surface Engineering Congress and Exposition, ASM International, Orlando Florida, August 2-4, 2004.
7. Seth A. and Van Ooij W. J., *J. Mat. Eng. Perf.* 13 (2004) 292.
8. Seth A. and Van Ooij W. J., *Submitted for publication in the ACS Volume based on New Developments in Coatings Tech*., P. Zarras, B. C. Benicewicz, T. Wood, B. Richey, Eds., (2005).
9. Mugada T., *M.S. Thesis*, University of Cincinnati, Chemical and Materials Engineering (CME) (2006).
10. Suryanarayanan K.., Metroke T., Van Ooij W. J., *submitted for publication in the Silane and Other Coupling Agents*, Vol 4., K. L. Mittal, Ed., (2005).
11. Shivane C., *M.S. Thesis*, University of Cincinnati, CME (2006).
12. Bauer R.S., *Epoxy Resin Chemistry II*, ACS Symposium Series 221, Washington D.C. (1983)
13. Seth, A., Van Ooij, W.J., Puomi P., Yin, Z., Ashirgade A., Bafna S. and Shivane C., *Novel, one-step, chromate-free coatings containing anticorrosion pigments for metals – an overview and a mechanistic study*, submitted for publication in Prog. Org. Coat. (2006)
14. Zhu D., *Ph.D. Thesis,* University of Cincinnati, CME (2002).
15. Van Ooij W. J. and Zhu D. *Prog. Org. Coat.*, 49 (2004) 42-53.
16. Pan G. and Schaefer D.W., submitted for publication in the *Silanes and Other Coupling Agents*, Vol 4., K. L. Mittal, eds., 2005, Canada; June 22- 24, 2005.