* 2001 John A. Gordon Best Paper Award *

Chrome-Free Single-Step In-Situ Phosphatizing Coatings on a Ti-6Al-4V Titanium Alloy

Heather Neuder and Chhiu-Tsu Lin—Northern Illinois University*

Surface pretreatment, such as chromate conversion, is generally required for the organic coating on Ti-6Al-4V titanium alloys. The surface modification process facilitates bond formation between the titanium surface and adhesives or paints. However, the hexavalent chromate used in the conversion coating is carcinogenic and must be eliminated.

Recently, the "green chemistry" technique of in-situ phosphatizing coatings (ISPC) has been developed at Northern Illinois University. In this study, a polyester-melamine coating system catalyzed by p-toluene sulfonic acid is used as a control paint and applied to bare (paint 1) and chromated (paint 3) Ti alloy panels. The arylphosphonic acid employed as an in-situ phosphatizing reagent (ISPR) is used to formulate ISPC polyester-melamine paint and to react in-situ with the metal surface when ISPC paint is applied on bare Ti panels (paint 2) and chromated Ti panels (paint 4). After soaking in 3% NaCl solution for 1500 hr, the electrochemical impedance, $|Z|$, was measured as 10^9, 10^{10}, 10^{10}, and 10^{10} ohm-cm^2 for paints, 1, 2, 3, and 4, respectively. After 1000 hr salt spray (fog) testing, a disbondment from the "X" scribe is observed as 13 and <0.5, <1, <1 mm for paints 1, 2, 3, and 4, respectively. The simultaneous reaction of the ISPR in catalyzing the polymerization of paint film and forming the metal-phosphate layer is the reason for the superior ISPC paint performance.

INTRODUCTION

Titanium and its alloys are truly coming of age and assuming their roles as a cost effective, environmental, and maintenance friendly engineering materials.[1] Titanium is classified as a reactive metal, relying on the formation of a protective oxide film for corrosion resistance. This oxide film is titanium dioxide, a hard, tenacious oxide which forms instantaneously upon contact with air or moisture, and is stable over an extremely wide range of pH and potentials. This passivity yields a noble metal potential in marine environments and thus, in most dissimilar metal couples, titanium will act as the cathode. As the cathode, however, titanium can influence the corrosion of the coupled material, with increases in the rate depending upon surface area ratios and process media. The most practical remedial technique to galvanic corrosion is coating of the cathode (titanium). Metal surface pretreatments prior to the application of organic coatings are used more and more to improve the coating adhesions and to inhibit substrate corrosion.

The current, state-of-the-art process of applying coatings to metal substrates involves many steps. The metal surface must first be cleaned, phosphated and/or chromated, sealed, and dried prior to coating application. This pretreatment process is time-consuming, costly, and generates wastes, which may contain carcinogenic chromates.[2,3] The removal of hexavalent chromium compounds from this process is highly desirable due to environmental concerns. For such a chrome-free technique to be successful, the new process would have to produce a coating that is superior or at least comparable to the current coating practice. In addition, it is desirable that an environmentally friendly application process contains fewer steps, produces less waste, and be cost efficient.

A "green chemistry" approach of single-step, chrome-free in-situ phosphatizing coating has been developed in our laboratory[4-13] and patented.[7] Formulation of an in-situ phosphatizing coating (ISPC) requires predispersal of an in-situ phosphatizing reagent (ISPR) into the paint.[3] The resulting ISPC should be stable. When an ISPC is applied to the metal substrate, the in-situ phosphatizing reagent will chemically and/or physically react with the metal surface

Presented at the 79th Annual Meeting of the Federation of Societies for Coatings Technology, in Atlanta, GA , Nov. 5-7, 2001.

*Department of Chemistry and Biochemistry, DeKalb, IL 60115.

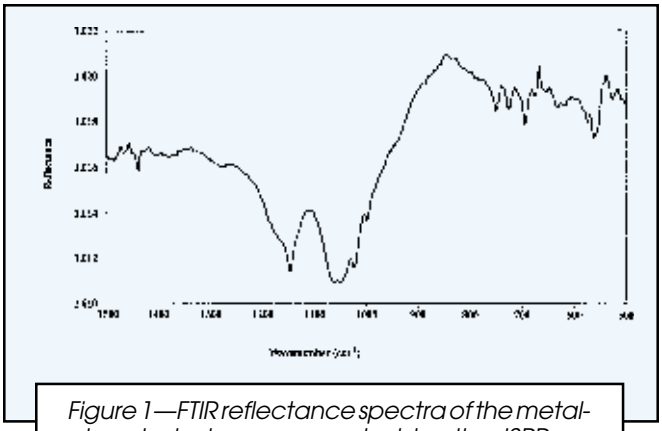

Figure 1—FTIR reflectance spectra of the metal-phosphate layer generated by the ISPR on polished Ti-6Al-4V panel.

to produce a metal-phosphate layer. The active metal-phosphate layer simultaneously forms P–O–C (phosphorous-oxygen-carbon) linkages with the polymer resin, sealing any pores which may be present in the layer.[6,9] Not only does this improve the coating's adhesion to the surface, it also reduces the corrosion of the substrate without using deleterious hexavalent chromium (Cr^{6+}) compounds.

Catalysis of polyester-melamine paints usually requires the presence of an organic acid, such as *para*-toluenesulfonic acid (*p*-TSA). Since the ISPR employed in this study is acidic, its presence will also aid in catalyzing the polymer crosslinking reaction. Previous studies have indicated the ISPR's ability to catalyze polyester-melamine systems.[14] The ISPR's dual function could lead to better coating adhesion due to the ISPR's promotion of co-condensation reactions between the melamine and the polyester polyols. The *p*-TSA catalyzed polyester-melamine system allows for *p*-TSA to remain after curing, since it does not serve a dual purpose like an ISPR. The underuse of *p*-TSA after curing could lessen the stability of the resulting film over time.[14]

Electrochemical impedance spectroscopy (EIS) is an important tool for predicting the relative performance of organic coatings on metal. Corrosion parameters such as charge transfer resistance and coating parameters such as coating capacitance, can be derived from EIS data. EIS data can also predict the effects of long-term salt fog exposure.[15]

Past studies have been performed using ISPCs on ferrous substrates and aluminum.[16,17] In this paper, the focus is on the behavior of two different paint systems on Ti-6Al-4V titanium alloy. Alloy strengthening of Ti-6Al-4V is achieved via solid-solution alloying and the stabilization of the two-phase (α and β) structures.[18] The first system is the ISPC coating formulated by addition of an arylphosphonic acid ISPR, which is used to form the metal-phosphate layer in-situ and to catalyze the polyester melamine paint. The second system uses *p*-TSA as the acid catalyst in the polyester melamine paint system. Both paints were applied to bare and chromated titanium alloy coupons. The integrities of the coatings were evaluated by physical tests and EIS.

MATERIALS AND EXPERIMENTAL

Materials

The in-situ phosphatizing reagent employed for this study was an arylphosphonic acid. The polyester melamine paint system was composed of the following; Akzo resin 26-1612, Rheox MPA 2000X, Aerosil R972, Cymel 303, Tioxide TR90 titanium dioxide, and solvents (2-butoxyethanol, 2-butanone, xylenes and *n*-butanol). The two catalysts used were the *p*-TSA (Cycat 4040) and the ISPR. An initial stock paint solution was made. The stock was divided into two containers. The first aliquot of stock had 1% Cycat 4040 added by weight and is referred to as control paint. The second half of the stock solution had 1.5% ISPR added by weight and is referred to as the ISPC paint. The panels used were bare Ti-6Al-4V and chromated Ti-6Al-4V coupons. The panels had been cleaned prior to paint application. Chromated panels were treated with alodine solution (MIL-C-5541). Painted panels were cured at 120°C for 20 min. These panels were used for the EIS, salt (fog) spray (ASTM B-117), and physical testing.

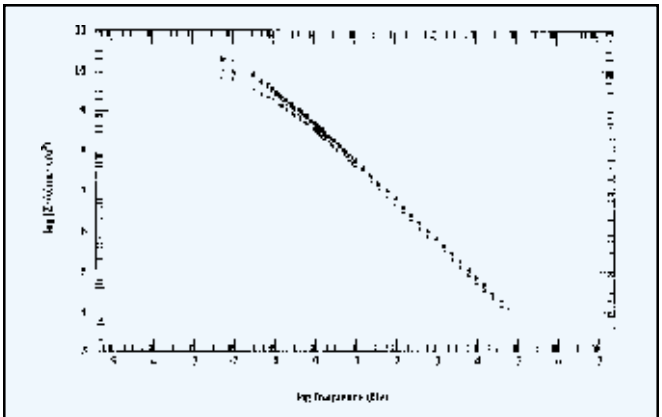

Figure 2—Bode-magnitude plot (log impedance vs log frequency) after soaking the painted panels in a 3% salt solution for three days: (a) control paint on bare Ti, (b) ISPC paint on bare Ti, (c) control paint on chromated Ti, and (d) ISPC paint on chromated Ti.

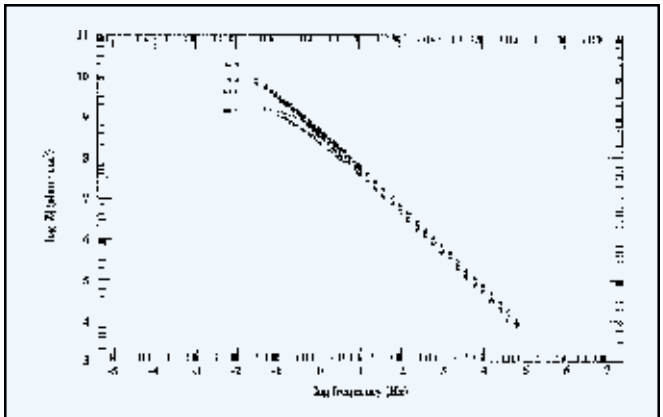

Figure 3—Bode-magnitude plot (log impedance vs log frequency) after soaking the painted panels in a 3% salt solution for 500 hr: (a) control paint on bare Ti, (b) ISPC paint on bare Ti, (c) control paint on chromated Ti, and (d) ISPC paint on chromated Ti.

Fourier transform infrared (FTIR) samples were prepared as follows. The Ti-6Al-4V panels were polished to a mirror finish. Ten percent by weight of the ISPR was dissolved in the solvents used in the paint formulation. The ISPR was applied to the polished panel and allowed to soak for 24 hr at room temperature. The panel was then rinsed with acetone and ethanol to ensure that the ISPR had reacted with the metal surface to form the metal-phosphate layer. The phosphate layer that formed on the Ti-6Al-4V surface was used to acquire the reflectance FTIR data.

Instrumentation

The FTIR reflectance spectra was acquired using a Bruker Vector 22 equipped with a grazing angle accessory (Spectra Tech FT-80). Prior to acquisition, the sample chamber was purged with nitrogen. The computer software used for data acquisition was OPUS/IR version 2.2. A background of a bare titanium alloy panel was acquired. After running sample panels, the background subtraction was performed by dividing the sample spectrum by the background spectrum.

EIS data were obtained from the coated panels using a potientiostat/galvanostat (PARC 273) and a lock-in amplifier (PARC 5210). The experimental parameters were input and controlled by an IBM-compatible 486/50 computer with EG&G software (Model 398) for EIS. A platinum electrode was used as a counter electrode. An Ag/AgCl electrode was used as a reference electrode. The coated panel served as the working electrode. A 10.0 cm^2 area of the panel was exposed to 3% NaCl aqueous solution. AC impedance measurements were performed over a 100kHz-10mHz frequency range with a 5mV peak-to-peak sinusoidal voltage in the high frequency range. At lower frequencies, a multisine technique was used with an applied voltage of ±10 mV. The coated panels were soaked for 72 hr in 3% NaCl prior to acquiring EIS data. Subsequent EIS analyses of the panels were performed after 500 and 1500 hours of soaking.

Salt (fog) spray tests were performed according to American Society for Testing and Materials (ASTM) method B117. The panels were scribed with an "X" and placed in a corrosion test cabinet (Type 411 ACD1 from Industrial Filter & Pump Mfg. Co.). The panels were removed after 1000 hr of exposure to a 5% NaCl fog.

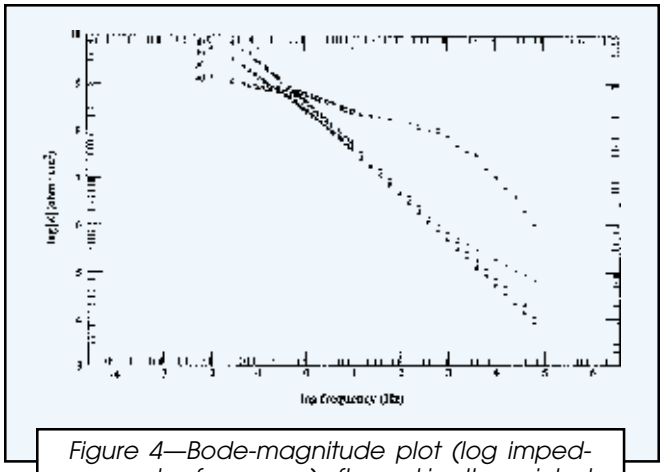

Figure 4—Bode-magnitude plot (log impedance vs log frequency) after soaking the painted panels in a 3% salt solution for 1500 hr: (a) control paint on bare Ti, (b) ISPC paint on bare Ti, (c) control paint on chromated Ti, and (d) ISPC paint on chromated Ti.

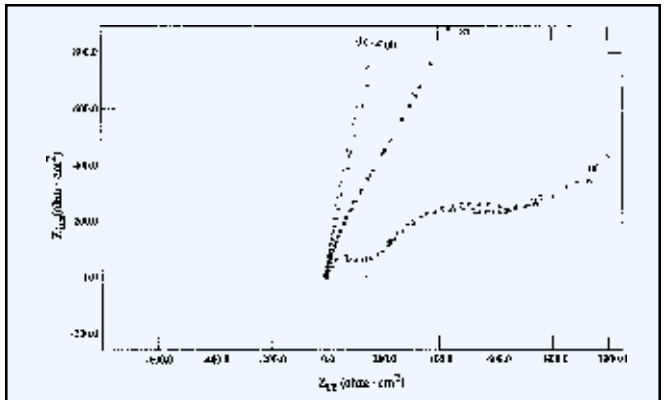

Figure 5—Nyquist plot after soaking the painted panels in a 3% salt solution for 1500 hr: (a) control paint on bare Ti, (b) ISPC paint on bare Ti, (c) control paint on chromated Ti, and (d) ISPC paint on chromated Ti.

Saltwater immersion studies were performed using ASTM method D 3359A. Panels were scribed with an "X" and submerged in 3% NaCl for six days. Upon removal, the panels were dried. Duck brand tape was applied to the scribed area and then removed. The panels were then evaluated.

RESULTS

Verification of ISPR Ability to Form Metal-Phosphate Layer on Ti Alloy

Figure 1 shows the FTIR spectra of the titanium-phosphate layer on polished titanium alloy coated with ISPR. The peaks at 1150/1054/1041 cm^{-1} are attributed to the P=O absorption band ν_3.[9] Absorption of O–P–O bond, ν_4, gives the bands at 564/545 cm^{-1}.[9] The other peaks at 700-750 cm^{-1} are from C–H out-of-plane and in-plane bending.[19] The splitting of the degeneracy of the ν_3 and ν_4 absorption bands is an indication that the metal-phosphate layer produced on the Ti-6Al-4V surface is possibly crystalline.[20] It is important to note that the Ti-phosphate layer shows ν_3 absorption bands at 1150/1054/1041 cm^{-1}, while the steel-phosphate layer's absorption band is at 1195/1147/1105 cm^{-1},[9] and the Al-phosphate layer's absorption band is at 1230/1196/1166 cm^{-1}.[17] This shift to lower frequencies can be attributed to a lower bond order of the P–O bond due to smaller ionicity of the Ti–O bond compared to the Fe–O bond or the Al–O bond.[20] The appearance of the peaks in the FTIR spectrum of the ISPR on the polished Ti-6Al-4V coupon shows that an in-situ phosphate layer has been produced on the surface of the Ti alloy. Furthermore, since the phosphate layer was not removed when the sample was rinsed with deionized water, acetone, and ethanol, the ISPR has reacted and bonded with the surface.

Electrochemical Impedance Spectroscopy

The EIS data are displayed as Bode-magnitude plots in *Figures* 2-4. *Figure* 2 displays the results after panels were

soaked for 72 hr in 3% NaCl. All spectra for the four paint systems overlap: (a) control paint on bare Ti, (b) ISPC paint on bare Ti, (c) control paint on chromated Ti, and (d) ISPC paint on chromated Ti. Having impedance values, $|Z|$, greater than 1×10^9 ohm•cm^2, all coatings are considered excellent.[21] The high frequency portion has a slope of –1, which indicates a pure capacitor.[21] The impedance at higher frequencies is due to the presence of the organic coating. The ISPC paint on bare Ti performs comparably to the control paint on the chromated Ti alloy.

In *Figure* 3, all coatings still possess impedance values greater than or equal to 10^9 ohm•cm^2 after 500 hr of soaking in 3% NaCl solution. However, the control paint, on both bare and chromated Ti, shows a lower $|Z|$ value than the ISPC paint on bare Ti alloy in the low-frequency range. In this frequency range, the control paint on bare Ti (spectrum 3a) has begun to level off. Although it still has a very good $|Z|$ value, there is indication of corrosion-related activity at the metal-paint interface for the control paint on bare Ti panel. At the high frequency range, all samples show a slope of –1 which still indicates a pure capacitance behavior of paint films.

Figure 4 displays EIS results after the paint films have been subjected to 1500 hr of soaking in 3% NaCl solution. The ISPC paint on both bare and chromated Ti panels (spectra 4b and 4d) now have $|Z|$ values exceeding the control paint on the chromated Ti panel (spectrum 4c). At the higher frequencies, the control paint on the bare panel has a slope deviating greatly from –1, which indicates the system is no longer acting as a pure capacitor. The coating in *Figure* 4a is beginning to suffer from the effects of salt solution exposure. The ISPC paint on bare Ti (spectrum 4b) is also showing a slight deviation from a –1 slope in this frequency range. Both the control and ISPC paints on chromated Ti panels (spectra 4c and 4d) still possess a –1 slope within this region. Thus, the presence of the chromate conversion provides additional protection for the organic paint films on Ti-6Al-4V alloys. There is no visible breakdown of any of the coatings at this test point.

To illustrate the corrosion protective barrier at the metal-coating interface, *Figure* 5 shows Nyquist plots of Z_{im} vs Z_{re} based on the EIS data from *Figure* 4. Without a complete analysis of the electrical equivalent circuits for paint films applied on Ti-6Al-4V alloy, curves 5b(ISPC paint on bare Ti coupon), 5c (control paint on chromated Ti coupon) and 5d (ISPC paint on chromated Ti coupon) demonstrate the presence of only a high frequency response, indicative of a purely capacitive dielectric for these paint films. On the other hand, curve 5a (control paint on bare Ti coupon after exposure to a 3% salt solution for 1500 hr) shows two semicircles at low frequencies and a Warburg impedance, Z_W, describing the diffusion-related impedance of the rate-limiting species. The results indicate that the chemical bonds generated in ISPCs are capable of providing coating adhesion enhancement and substrate corrosion inhibition of Ti-6Al-4V alloys.

Figure 6—Painted panels subjected to the salt water immersion test and followed by the tape test: (a) control paint on bare Ti, (b) ISPC paint on bare Ti, (c) control paint on chromated Ti, and (d) ISPC paint on chromated Ti.

Salt Water Immersion

The adhesion of many organic coatings to metal substrates (such as Ti-6Al-4V alloy) is adversely affected by exposure to an aqueous environment. Even high relative humidities can cause coating disbondment to occur. In general, the greater number of primary chemical adhesive bonds a specific coating makes with a substrate, the more resistant the coating system is to water disbondment. In ISPCs, the phosphatizing reagent is available to react in-situ with the Ti-6Al-4V surface; producing a Ti-phosphate layer, and simultaneously forming covalent bonds with polymer resin. The ISPC system's primary chemical interaction at the interface should provide greater resistance to wet adhesion loss than the control paint on bare Ti-6AL-4V substrates with only secondary interactions.

Figure 6 displays the saltwater immersion results for the four painted coupons after six days of soaking in 3% NaCl solution. For both the control paint (panel C) and ISPC paint (panel D) coated on chromated panels, less than 0.5 mm was removed from each side of the "X" scribe. The ISPC on bare titanium (panel B) paint has approximately 1 mm of paint removed from the scribe, which classifies it as a very good coating. The control paint on a bare Ti panel (panel A) shows complete failure, with virtually all paint removed from the scribed area. Obviously, the presence of the chromated layer improves the adhesion performance of the paints under these testing conditions. More importantly, the Ti-phosphate layer generated by ISPC gives a comparable paint adhesion performance to that of the chromate conversion process.

Salt Fog Test

Verification of the performance of coating meant to endure for long periods of time under various environmental conditions represents a major technical challenge. The testing conditions used in the standard salt (fog) spray tests (ASTM B 117) for organic paint films are more aggressive and severe than those employed in the saltwater immersion tests. A slightly elevated temperature of 35°C is combined with a continuous salt solution spray. The airflow generated in the salt solution spray can carry fresh oxygen to the test chamber. The painted coupons are subjected to a 100% humidity environment along with the 5% salt mist that serves as a conductive circuit for the electrochemical reactions during the corrosion process.

Figure 7 displays the results of the salt (fog) spray test after the coated Ti-6Al-4V panels have been subject to 1000 hr in an ASTM B 117 chamber. The control paint on a chromated Ti coupon (panel C) gave the best result, having less than 0.5 mm of paint removed from either side of the "X" scribe. Both the ISPC paint on the bare Ti coupon (panel B) and the ISPC paint on the chromated coupon (panel D) still gave excellent results, having approximately 1 mm of paint removed from each side of the scribe. Once again, the control paint on a bare Ti coupon (panel A) gave the poorest performance, having about 13 mm of paint removed from the scribed area. Moreover, panel 7A shows tiny blisters on the areas which are subject to the salt fog test.

Figure 7—Painted panels subjected to the salt (fog) spray test for 1000 hr: (a) control paint on bare Ti, (b) ISPC paint on bare Ti, (c) control paint on chromated Ti, and (d) ISPC paint on chromated Ti.

Table 1—Pencil Hardness of ISPC and Control on TI and Al Alloys

Paint System	Pencil Hardness Ti-6Al-4V	Pencil Hardness Al 2024 T3
ISPC on bare coupon	4H	2H
ISPC on chromated coupon	4H	2H
Control paint on bare coupon	3H	H-2H
Control paint on chromated coupon	4H	H-2H

Pencil Hardness

The manufacturer's paint description provided by Akzo Resins includes a pencil hardness of F–H for Akzo resin 26-1612. *Table* 1 shows the results of the pencil hardness test conducted on the four coating systems on Ti-6Al-4V alloys. For comparison, *Table* 1 lists also the pencil hardness test for the same four coating systems on Al 2024 T3 alloys.[17]

The ISPC paint on both bare and chromated Ti substrates gives a pencil hardness of 4H, which is the same as the control paint on chromated Ti substrate. The control paint on bare Ti substrate yielded a pencil hardness of 3H, which is not a significant deviation from the other three paint systems. The same observations are also noted for those four paint systems on Al 2024 T3 substrate. However, the same paint systems on Ti-6Al-4V alloy have higher pencil hardness than those on Al 2024 T3 substrate.

CONCLUSIONS

Titanium is immune to general corrosion attack in all natural environments to temperatures in excess of 300°C. Titanium needs a good organic coating or electrical insulation coating for interrupting the metal connectivity, i.e., a good coating of the cathode (titanium). The coating adhesion to the metal substrate is particularly important for Ti alloys. The control paint on untreated Ti panels gave a poor paint film adhesion, as shown in the water immersion test, and substrate corrosion inhibition, as illustrated by the EIS and salt (fog) spray experiments. The presence of a Ti-phosphate layer in the FTIR spectrum of ISPR-treated Ti-6Al-4V substrate provides the needed chemical bonds at the metal-coating interface. After 1500 hr of soaking in 3% NaCl solution, the ISPC paint films on bare and chromated Ti-6Al-4V coupons gave an AC impedance, $|Z| = 1 \times 10^{10} \text{ohm} \bullet \text{cm}^2$ at low frequency and a pure capacitance behavior at high frequency. In water immersion and salt (fog) spray tests, the ISPC paint films also gave an excellent barrier with good adhesion and corrosion resistance properties. These protective performances are similar to those of the control paint on chromated Ti-6Al-4V alloy, indicating that a one-step self-phosphating process may be developed as a "green chemistry" chrome-free technique to replace the current multi-step coating practice.

ACKNOWLEDGMENTS

Financial support is acknowledged from ChemNova Technologies, Inc. The authors thank Akzo Resins and Dupont Ti-Pure for their donations of some paint materials.

References

(1) Grauman, J.S. and Barber, J., in *International Workshop on Corrosion Control for Marine Structures and Pipelines*, Edward, G.R., Hanzalek, W., Liu, S., Olson, D.L., and Smith, C. (Eds.), American Bureau of Shipping, Houston, 2000.
(2) Freeman, D.B., *Phosphating and Metal Pretreatment*, Industrial Press, Inc., New York, 1986.
(3) Spadafora, S.J., Hegedus, C.R., Hirst, D.J., and Eng, A.T., "Primerless Finishing Systems for Aluminum Substrates," *Mod. Paint Coat.*, 36 (1990).
(4) Lin, C.T., Lin, P.,Hsiao, M.W., Meldrum, D.A., and Martin, F.L., "Chemistry of Single-Step Phosphate/Paint System," *Ind. Eng. Chem. Res.*, 31, 424 (1992).
(5) Meldrum, D.A. and Lin, C.T., "AC Impedance Analysis and Factorial Designs of an In-Situ Phosphatizing Coating," JOURNAL OF COATINGS TECHNOLOGY, *65*, No. 818, 47 (1993).
(6) Lin, C.T., Lin, P., and Quitian-Puello, F., "Interfacial Chemistry of a Single-Step Phosphate/Paint System," *Ind. Eng. Chem. Res.*, 32, 818 (1993).
(7) Lin, C.T., "Additive Package for In Situ Phosphatizing Paint," Paint Method. U.S. Patent, 5,322,870, 1994.
(8) Li, L. and Lin, C.T., "SEM-EDS Investigation of Self-Phosphating Coatings," *Ind. Eng. Chem. Res.*, 33, 3241 (1994).
(9) Yu, T., Li, L., and Lin, C.T., "Chemical Affinity of In Situ Phosphatizing Reagents on Cold-Rolled Steel," *J. Phys. Chem.*, 99, 7613 (1995).
(10) Yu, T. and Lin, C.T., "The Performance of In Situ Phosphatizing Reagents in Solvent-Borne Paints," *Ind. Eng. Chem. Res.*, 36, 368 (1997).
(11) Yu, T. and Lin, C.T., "In Situ Phosphatizing Coatings: A High-Solids Polyester Baking Enamel," *Proc. 24th Annual Waterborne, High-Solids, and Powder Coatings Symp.*, New Orleans, LA, Feb. 5-7, 1997, pp 56-69, 1997.
(12) Wang, C.H., Chuang, Y.Y., and Lin, C.T., "In-Situ Phosphatizing Coatings I: An Air-Dried Lacquer System," JOURNAL OF COATINGS TECHNOLOGY, *71*, No. 892, 61 (1999).
(13) Li, L., Cao, Y., and Lin, C.T., "Environmentally Safe In Situ Phosphatizing Coatings for Corrosion Protection," *Environmentally Acceptable Inhibitors and Coatings*, Taylor, S.R., Isaacs, H.S., and Brooman, E.W. (Eds.), The Electrochemical Society, Inc., Pennington, NJ, Proc. vol. 95-16, pp 118-132, 1997.
(14) Whitten, M.C., Lin, C.T, in: *Proc. 25th Annual Waterborne, High-Solids, and Powder Coatings Symp.*, New Orleans, LA, Feb. 18-20, pp. 458-471, 1998.
(15) Kendig, M., Jeanjaquet, S., Brown, R., and Thomas, F., "Rapid Electrochemical Assessment to Paint (REAP)," JOURNAL OF COATINGS TECHNOLOGY, *68*, No. 863, 39 (1996).
(16) Whitten, M.C. and Lin, C.T., "An In Situ Phosphatizing Coating on 2024 T3 Aluminum Coupons," *Prog. Org. Coat.*, 38, pp. 151-162 (2000).
(17) Whitten, M.C and Lin, C.T., "Coating Performance of Polyester-Melamine Enamels Catalyzed by an In Situ Phosphatizing Reagent on Aluminum," *Ind. Eng. Chem. Res.*, 38, pp. 3903-3910 (1999).
(18) *Titanium—A Technical Guide*, Donachie, M.J. Jr. (Ed.), ASM International, Metal Park, OH, 1998.
(19) Silverstein, R.M., Bassler, G.C., and Morrill, T.C., *Spectrometric Identification of Organic Compounds*, 4th ed., John Wiley and Sons, Inc., New York, 1981.
(20) Akiyoshi, O., Takahashi, K., and Ikeda, M., "Infrared Study of Trivalent Cations B and Fe in Amorphous and Crystalline Phosphates," *J. Mater. Sci. Lett.*, 3, 36 (1984).
(21) Leidheiser, H. Jr., *Corrosion.*, 39, 5 pp. 189 (1983).