In-Situ Phosphatizing Coatings III: A Water-Reducible Alkyd Baking Enamel

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We report the successful formulation of stable and compatible in-situ phosphatizing coatings (ISPCs) for a waterborne alkyd-amino baking enamel applied on bare cold-rolled steel (CRS), iron phosphated Bonderite 1000 (BD), and iron phosphated plus Parcolene 60 chromated (BD+P60) coupons. The enhanced coating adhesion of water-based ISPCs is confirmed by the cathodic delamination measurements. After 100 hr of salt spray (fog) test, the corrosion resistance performance (measured by the corrosion disbondment across the "X" scribe, d in mm) of the water-based ISPC on CRS panel (d = 4.0-7.0 mm) outperformed that of the control alkyd paint on B-1000 (d = 26 mm) and also on BD+P60 (d = 14 mm) coupons. The superior coating performance of water-based ISPCs is believed to result from the in-situ metal surface phosphatization as detected by the reflectance FTIR technique.

INTRODUCTION

The use of waterborne coatings is growing as more finishers see them as the solution to their volatile organic compounds (VOCs) compliance challenges. Users of any and all coatings need to optimize the surface preparation of the metal. Surface pretreatment of metal usually involves a cleaning process and a conversion coating (e.g., phosphate conversion coating)[1] that will transform the metal surface into a metal phosphate thin layer and enhance good adhesion of the applied coating. Typically, conversion coating processes yield water insoluble crystalline hydrate films such as $Zn_3(PO_4)_2{\cdot}4H_2O$ or $2H_2O$, $Zn_2Fe(PO_4)_2{\cdot}4H_2O$, $Fe_3(PO_4)_2{\cdot}8H_2O$ or $4H_2O$, $Mn_3(PO_4)_2{\cdot}3H_2O$, $AlPO_4{\cdot}xH_2O$, and $Mg_3(PO_4)_2{\cdot}xH_2O$. To precipitate these hydrate compounds on the metal surfaces, an aqueous medium at high temperature is required. The problem with the state-of-the-art conversion coating, in particular the use of phosphating bath/line, is the inability to control and maintain the operating parameters and bath compositions. In short, the phosphate pretreatment for preparing the metal surface prior to painting is an error-prone process that represents millions of dollars in time, energy, waste production and reclamation, and chemical expense.

Recently, a novel surface conversion coating technique, namely "in-situ phosphatizing coatings (ISPCs)" has been developed in our laboratory.[2-12] The chemical principle of ISPCs is that phosphate conversion coating and polymer film formation can proceed independently and simultaneously in a single step. The simplicity in the application of a single-coat phosphate/paint over the present multi-step coating practice will make the ISPC paint system attractive to many manufacturers of metal products. It should provide increased quality without the capital and operating expenses of a separate phosphating line/bath. In addition, the disposal of toxic wastes produced from phosphating bath and waste treatment is avoided.

The idea of combining metal phosphate conversion and organic coating application steps has gained a great deal of attention in recent years. Wragg et al. reported[13] an approach of introducing high molecular weight polyacrylic acid to modify the zinc phosphate bath, and significant uniformity in the surface phosphatization products has been reported. Such an approach, although showing the possibility of combining polymer chemistry with metal phosphating chemistry, falls into the subject of optimizing the current multi-step phosphating bath/line. The second approach is to introduce phosphate functional groups into the polymer structure to produce phosphate-modified coating resins. Massingill et al. reported[14-16] the results on the enhanced coating adhesion, flexibility, and corrosion resistance for an epoxy phosphate ester paint, which utilizes mainly phosphate-modified epoxy resins prepared by reacting phosphoric acid with bisphenol A epoxy. A similar approach to that of Massingill et al. has been adopted by Higgins[17] in the commercialization of a series of polymer adhesion promoters for both solventborne and water-based coat-

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ing systems. The phosphate-modified resins give adhesion improvement with organic coatings, but exhibit no sign of detectable metal phosphate layer generation on the surface of a cold-rolled steel substrate.

The novel aspect of ISPCs is that an optimum amount of in-situ phosphatizing reagents (ISPRs) are pre-dispersed in the paint system to form a stable and compatible one-pack coating formualtion.[6] When the single-coat, in-situ self-phosphating paint is applied on a metal substrate, the phosphatizing reagent is available to chemically and/or physically react in-situ with the metal surface to produce a metal phosphate thin layer and, simultaneously, to form a covalent bond of phosphorus-oxygen-carbon (P–O–C) linkage with the polymer resin. The formation of a metal phosphate layer in-situ will essentially eliminate the surface pre-treatment step of employing a phosphating line/bath. The functional groups of ISPRs form chemical bonds with the polymer resin that act to seal and minimize the porosity of the in-situ phosphated substrate. The use of chemical bonds to seal the pores of metal phosphates in-situ will enhance coating adhesion and suppress substrate corrosion without a post-treatment of final rinses containing the carcinogenic chromates (Cr^{6+}).

The technique of ISPCs has been successfully applied in modifications of three commercial paints: a high-solids polyester baking enamel,[10] an air-dried lacquer system,[11] and a VOC-free thermoset acrylic latex system.[12] In this paper, the application of ISPCs is extended to a waterborne alkyd-amino baking enamel. Because of its ease of application and environmental friendliness, water-reducible organic paint has become a popular alternative to the more traditional solvent-based coatings. The challenge in waterborne coating technology is to obtain an adequate water solubility or dispersibility of polymer resin with all of the coating components. Many alkyd, acrylic, and polyester materials are too hydrophobic for the direct incorporation into water-based systems. A common method for improving water dispersibility is by neutralizing some of the carboxylic acid groups on the polymer backbone. This is usually accomplished with amines, and the salts (e.g., alkyd-amine complexes) that are formed help to provide necessary water solubility or dispersibility.

The primary feature of a water-based dispersion system is its inherently pseudo- or non-homogeneity at the molecular level. This is different from the solventborne coatings in which the polymer dispersion is usually homogeneous regardless of the solids content of the paint system. Although the inherent pseudo-homogeneity may affect the introduction of ISPC technique into the waterborne paint systems, the in-situ phosphatizing reagents (ISPRs) are essentially acidic in nature, and should prefer a more polar dispersion environment as in water-based coatings. However, the major challenge in applying the technique of ISPC to water-based coatings lies in the influence of ISPRs toward the polymer dispersion and coating stability in such delicately balanced systems. Moreover, the high surface tension of water molecules should also require the incorporation of dispersion additives (e.g., deformers and anti-settling reagents) in the formula processing procedures.[18,19]

In this study, the stability of water-reducible alkyd ISPC formula is studied by monitoring its rheological behavior change upon aging. Thermal chemical analysis is utilized to ensure the coating's successful crosslinking and film formation. The enhanced coating adhesion of water-based ISPCs is verified by cathodic delamination measurements and water immersion testings in a 3% NaCl solution. Both electrochemical impedance spectroscopy (EIS) and ASTM corrosion test standards (e.g., salt spray (fog) test) were used to evaluate the coating's corrosion resistance performance. The results will be discussed in light of the environmental, economical, and technical advancements of the waterborne alkyd-amino baking ISPCs in comparison to those of the current multi-step coating practice.

EXPERIMENTAL

An organic water-reducible alkyd baking enamel from The Sherwin-Williams Company (Kem Aqua® 1400) was adopted as the control paint formula. This product has a solids content of 30-33% by volume that provides a hard, tough coating at 2.3 VOC compliance without the hazards of flammable solvents. The film formation can be achieved by thermal curing at 163°C (325°F) for 15 min. A pH range of 7.8 to 8.7 is required to maintain the designed storage stability of the paint. An arylphosphonic acid or arylphosphoric acid (designed as ISPR-2, see paper I[11] for the detailed formulation), together with a proper pH-adjusting-agent (e.g., an organic amine) were used as ISPRs to formulate the corresponding water-reducible ISPCs. For the application to water-reducible ISPC formula, a reduction of 40% by weight with water was used to achieve a similar zero-shear viscosity and sprayability of the coating as those of the control alkyd sample (for which a reduction of 10-15% by weight with water before application was recommended). Considering that water is evaporated during thermal curing yet does not contribute to VOC, the water-reducible ISPC maintains its VOC specification as well as achieves coating films of the same dry film thickness by controlling the wet film thickness. The metal coupons tested for the control and ISPC water-reducible paints are the bare (cold-rolled steel, CRS), iron phosphated (Bonderite 1000, BD), and iron phosphated plus Parcolene 60 chromated (BD+P60) mild steel panels (Q-Panel Co., Cleveland, OH and ACT Laboratories, Inc., Hillsdale, MI).

The formulation's stability was monitored by rheological measurements. The experiment was carried out using a cone/plate viscometer, model Brookfield RVDV-IIICP (Brookfield Engineering Laboratories, Inc., Stoughton, MA) with a CP52 cone spindle and operated at a fixed temperature of 25 ± 0.1°C. The shear rate control programming, data acquisition, and processing were conducted by using Brookfield RheoCalc Software version 1.4. For all coating formulations, the viscosity data was obtained for the freshly prepared samples as well as the aged (at room temperature) samples at seven-day intervals for monitoring the coating's stability.

For studying the formation of interfacial metal phosphate layer, the untreated bare CRS panels were mechanically polished to a mirror-finished surface and used

as coating substrates. The water-reducible ISPC on mirror-finished CRS was cured at 325°F for 15 min. The resultant organic coatings had approximately a 1.0 mil dry film thickness. The polymer layer on each panel was removed without damaging the interface by soaking the panel in tetrahydrofuran solvent. The interfacial metal phosphate layer was rinsed with deionized water, dried, and characterized by a Brüker Fourier transform infrared (FTIR) spectrophotometer model Vector 22 equipped with a Spectra Tech FT-80 grazing angle accessory. The absorbance or transmittance spectra of the thin metal phosphate layer are produced by rationing the single-beam spectrum of the same substrate with the thin layer.

The thermal analysis of cured paint films for water-reducible paints was conducted by differential scanning calorimetry (DSC) measurements. All data were obtained on a Seiko DSC 220C (Seiko Scientific Instruments, Inc.) equipped with a Seiko SSC5200H disk station for scanning program manipulation and data analysis, and with a liquid nitrogen auto-cooling unit for an operational temperature range of –150 to 725°C. To erase the thermal history and release the stress resulting from the mechanical peeling and sampling of the cured alkyd paint from the substrate, the paint film specimens were first annealed at 100°C (a temperature well above the glass transition temperature (T_g) of the alkyd resin used and well below the curing temperature of the commercial water-reducible alkyd paint), for two minutes inside the DSC oven and quenched before the actual DSC measurements were taken. The DSC scan was conducted from –100 to 100°C at a heating rate of 10°C/min.

Electrochemical impedance spectroscopy (EIS) offers an approach that promises to reduce the time needed to evaluate the corrosion protective performance of organic coatings and gives insight into the chemical nature of the failure mechanism. AC impedance data were obtained at an open-circuit potential using a PARC 273 potentiostat/galvanostat and PARC 5210 lock-in amplifier (EG&G Princeton Applied Research Corp., Princeton, NJ). A testing area of 10.0 cm^2 in the water-reducible ISPCs panel (as working electrode) was pre-soaked in a 3% NaCl solution for 72 hr and up to 432 hr. The EIS data were collected, stored, and analyzed using an EG&G electrochemical impedance software model 398 installed in an IBM compatible 486/50 computer. The impedance measurements were carried out over the frequency of 100 kHz to 10 mHz. A 5 mV peak-to-peak sinusoidal voltage was used in the frequency range from 100 kHz to 10 Hz. In the multisine mode, a higher applied voltage of 10 mV was used to enhance the sample response and to have good signal to noise data. The experimental results were analyzed by means of computerized Bode and Nyquist plotting routines.

The disbonding resistance of water-reducible paints on metal substrates was conducted by cathodic delamination using the same apparatus as the EIS measurements, and also salt water (3% NaCl) immersion testing. In cathodic delamination, a 20.0 cm^2 area of water-reducible paint film on metal coupon is assembled in a delamination cell as working electrode. The paint film is exposed to a 3% NaCl solution and polarized to –1100 mV versus a saturated calomel electrode (SCE) throughout all testing periods. Initially, a defect (a hole with about 1.0 mm diameter) was drilled through the polymer film to the substrate to observe and measure the coating delamination expanding around the defect. The dynamic control of the applied potential and data acquisition of the delamination rate are done by employing a corrosion measurement software (EG&G model 342C).

RESULTS AND DISCUSSION

Rheology and Water-Reducible ISPC Stability

Because of the chemical principles involved in the alkyd resin synthesis to achieve molecular water-reducibility, the in-can stability of the alkyd ISPC is a concern of considerable importance. The waterborne coatings are prone to changes (e.g., the chemical and physical nature of their polymeric binders) that are not likely to occur in solventborne coatings, and stability can be a problem. *Figure* 1 displays the rheological profile of water-reducible alkyd ISPC formula (curve 1b) and its corresponding control coating sample (curve 1a). The control paint formula gives near-Newtonian flow as shown in *Figure* 1a. A splitting at the low shear end of the shear rate cycle is observed in *Figure* 1a, where up cycle is the top curve and marked as '*,' and down cycle is the bottom curve and marked as 'o.' The observed low shear viscosity is lower after an "up and down" cycle that could result from incomplete rebuilding of the original structure. Curve 1a remains smooth throughout the shear rate range tested, indicating that the control water-based alkyd baking enamel is a homogeneous coating with no significant pigment flocculation.[20]

When an ISPR-amine weak complex is dispersed into the commercial control sample, the resultant water-reducible ISPC formula shows an apparent viscosity in-

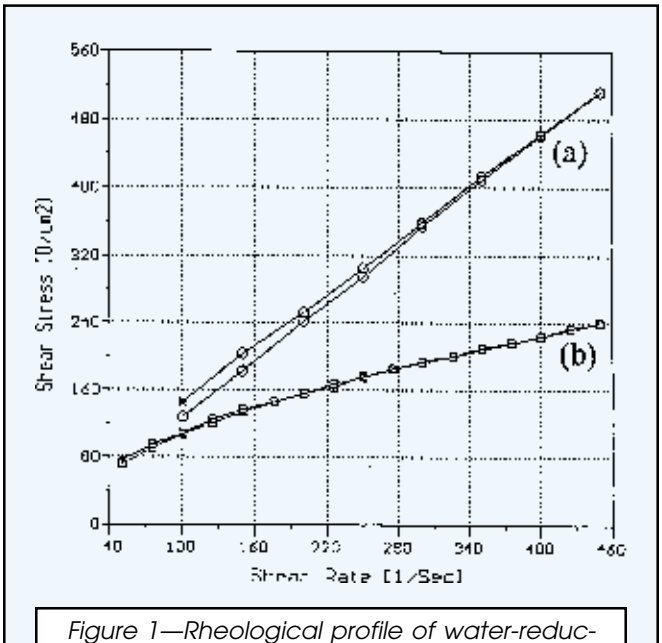

Figure 1—Rheological profile of water-reducible alkyd baking enamel: (a) control sample—Kem Aqua® 1400 from The Sherwin-Williams Company, and (b) ISPC formula.

Table 1—Thermal Chemical Data for the Water-Based Alkyd Baking Enamels

Sample Kem Aqua® 1400	T_g(onset) (°C)	T_g (offset) (°C)	T_g span (°C)	(T_g) (°C)	ΔC_p (mJ/mg·°C)
Alkyd control	18.2	54	35.8	36.1	0.173
Alkyd ISPC	17.6	60.8	43.2	39.2	0.163

crease along with a clear shear thinning effect, while the shear stress-shear rate curve bends from the straight line of "Newtonian" flow. However, no change in the viscosity of the water-reducible ISPC formula was observed during long-term shelf-storage. Apparently, the initial viscosity change in the ISPC formula is not related to a chemical reaction of ISPC with the backbone polymers or oligomers, but rather it is due probably to a physical modification of ionic strength in the water-based coating system by the incorporation of an ISPR-amine complex. The system's ionic strength in water-based paint can normally affect the hydration status of the "hydrophilic" sites or segments of the alkyd resin, altering its molecular conformation, and in turn increasing the apparent viscosity of the paint formula. The conformational change should be larger at the low shear stage, since the alkyd resins can easily relax to their low energy states. At a sufficiently high shear-rate stage, the alkyd ISPC formula can be assumed to have a similar rheological behavior as that of the control sample since the polymer molecules are expected to completely follow the high speed flow. Consequently, the paint system of water-reducible ISPC shows a higher viscosity at the low shear rate range and a normal viscosity at the high-shear region that explains its shear thinning behavior.

Although the alkyd ISPC system is expected to return to the normal viscosity at the sufficiently high shear rate range, water reduction is still utilized in this study to achieve the sprayability without affecting the coating's VOC specification (as water is not counted as VOC). In the ISPC system, a water reduction of 40% by weight is necessary if one wants to achieve as low a zero-shear viscosity in the formula compared to that of the control sample. The paint still remained stable. The rheological profile for such a water-based ISPC formula is shown in *Figure* 1b. A shear-thinning effect is observed with a nonlinear shape of shear stress-shear rate curve. A smooth curve throughout the testing shear rate region in *Figure* 1b is suggestive of a homogeneous coating formula.[20] With the shear thinning effect, spraying, which usually involves a three to four magnitudes higher shear rate, is excellent for the ISPC formula. While the system solids-content has been lowered by water-reduction, a thicker wet film thickness is needed in spray applications for such a reduced system to achieve a dry film thickness equivalent to that of the control coating.

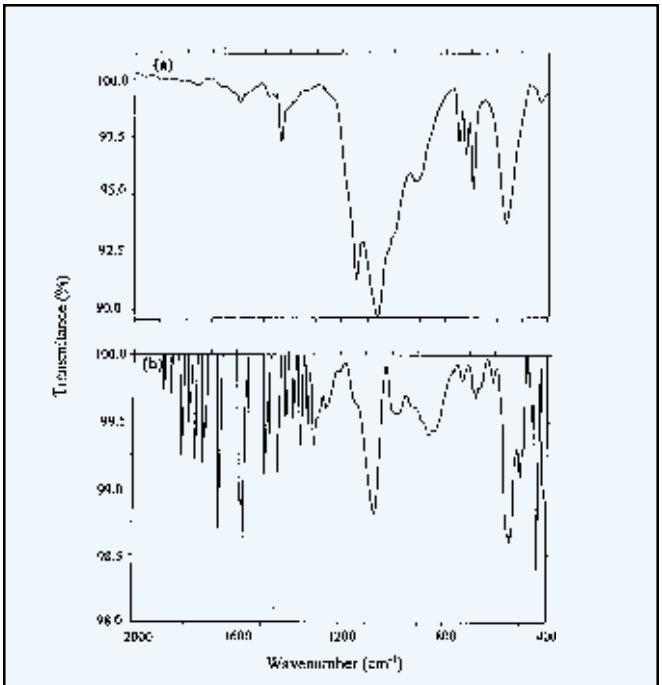

Figure 2—FTIR spectra of iron phosphate thin layer generated on bare CRS coupon by (a) ISPR-amine complex solution, and (b) water-reducible alkyd ISPC formula.

Polymer Chemistry and Paint Film Quality

Crosslinking is one of the most important aspects of polymer film formation in coatings.[21] It influences many paint film properties such as chemical stability, solvent resistance, network morphology, and mechanical properties.[21,22] The degree of crosslinking can be monitored by DSC measurements, wherein T_g, T_g span = T_f (glass transition end point) $-T_i$ (glass transition start point), and specific heat capacity jump (ΔC_p in mJ/mg· °C) are obtained. Qualitatively, the paint film with a higher T_g value and a lower ΔC_p during the glass transition is indicative of a higher crosslinking density.[23]

The thermal properties obtained from the paint film analysis of DSC curves for water-reducible ISPC and control alkyd baking enamels are listed in *Table* 1. A higher T_g value is recorded for the alkyd ISPC formula as compared to the control sample that indicates a relatively higher average polymer crosslinking density for the ISPC paint film. This observation is consistent with a slightly lower heat capacity change (ΔC_p) associated with the glass transition. The T_g span of the water-reducible ISPC film is considerably wider than that of the control formula, suggesting a broader distribution of molecular segment lengths between crosslinks throughout the coating's polymer network. The wider distribution in polymer crosslinking density of water-reducible ISPC is indicative of a coating film with more flexibility, while a higher T_g value indicates a paint film with more physical hardness. The flexibility (not measured) may be caused by ISPR acting as plasticizer. The pencil hardness of the control and ISPC paint films was measured as HB and H, respectively. A harder yet flexible coating film of water-reducible alkyd ISPC is obviously desirable for protective coatings.

In-Situ Phosphatization of Metal Surfaces

The dispersion of phosphatizing reagents in ISPC is designed principally for synthesizing a metal phosphate thin layer in-situ at the interface of metal substrate and

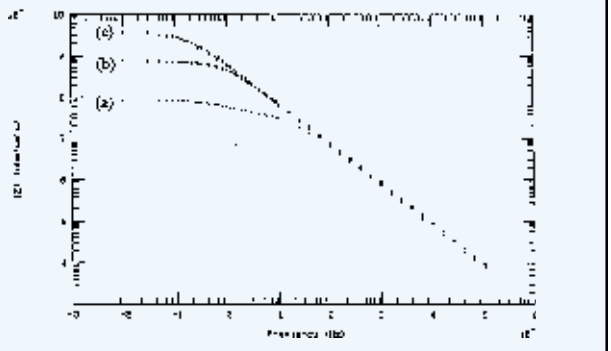

Figure 3—Bode-magnitude plots of EIS measurements for the control water-based alkyd paint coated on (a) bare CRS, (b) iron phosphated, B-1000 and (c) iron phosphated plus Parcolene 60 chromated, BD+P60 coupons.

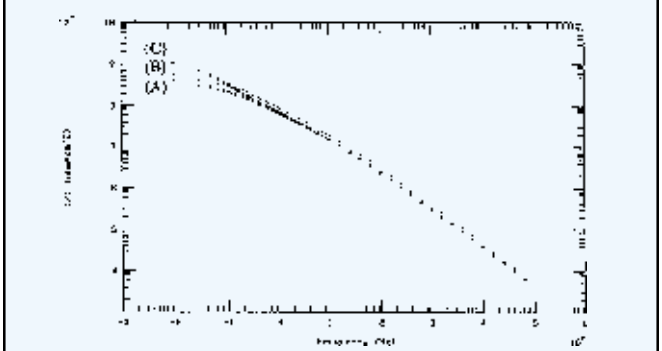

Figure 4—Bode-magnitude plots of EIS measurements for the water-reducible alkyd ISPC coated on (A) bare CRS, (B) B-1000, and (C) BD+P60 coupons.

polymer coating. The nature of metal phosphate bondings in ISPCs was illustrated to have an acid-base type interaction, $P–O^- —M^{n+}$, rather than an induced dipole interaction of P=O/metal complex type.[8] Thus, it is expected that the phosphatizing reagents in waterborne ISPCs, e.g., water-reducible alkyd ISPC should be more effective in achieving the chemical principle of ISPCs and would provide superior protection of metal surfaces. *Figure* 2 shows the FTIR spectra of metal phosphate product synthesized by thermal-cured in-situ phosphatizing reagent (ISPR-amine complex, spectrum 2a) and water-reducible alkyd ISPC (spectrum 2b) on polished bare CRS coupon. The υ_3 (stretching type) and υ_4 (deformation type) vibration modes in PO_4^{3-} centered at 1063 cm^{-1} (ranged from 1000 to 1200 cm^{-1}) and 561 cm^{-1} (ranged from 500 to 600 cm^{-1}), respectively were observed. The spectral intensity in *Figure* 2b is weaker than that in *Figure* 2a, suggesting that ISPR has a slower diffusion rate to and a lower reaction rate with the metal surface when it is dispersed in the ISPC system. In *Figure* 2, the band intensity of υ_4 mode is slightly greater than that of υ_3 vibration, which is in contrast to the observations in thermal-cured solventborne ISPCs.[4] In the reflective mode of FTIR spectrum as shown in *Figure* 2, the higher spectral band intensity corresponds to the larger projection of electric dipole transitions perpendicular to the metal surface.[24] In water-reducible ISPCs, the polarity of ISPRs leads to its preference of incorporating in the hydrophilic phase of pseudo-homogeneous water-based dispersion system to take its action in in-situ phosphatization on CRS panel.

Coating Protective Performance

Electrochemical impedance spectroscopy has been proven to be a powerful tool for the determination of coating protective performance and undercoat metallic corrosion.[25,26] To show the effect of substrate pretreatments on the coating protective performance, the control water-based alkyd baking enamel was applied on three different types of cold-rolled steel panels: (1) untreated bare CRS panel, (2) iron phosphated B-1000 panel, and (3) iron phosphated plus Parcolene 60 chromated (BD+P60) panel. A dry film thickness of about 1.0 mil cured at 325°F for 15 min was used for EIS measurements. *Figure* 3 shows the Bode-magnitude plots for the control coating on bare CRS (curve 3a), B-1000 (curve 3b) and BD+P60 (curve 3c) panels. In the high frequency region, all three curves, 3a-c, are practically unified, as the AC impedance in this region is dominated by the pure capacitor property of the non-conductive organic coating film. This indicates that the alkyd dry film coated on three different types of substrates has a similar dielectric property.

In the low frequency region of *Figure* 3, the three Bode-magnitude curves begin to split, as the impedance ($|Z|$ in ohm·cm^2) is more and more affected by the coating-substrate interface response to the AC signal. In general, all curves deviate from the linear relationship of log $|Z|$ versus log f (f = frequency), and become more frequency independent. A frequency independent horizontal line in the Bode-magnitude diagram is a characteristic of pure resistor. At f = 1.0×10^{-2} Hz, the $|Z|$ value is measured as 8.0×10^7, 7.5×10^8, and 4.1×10^9 ohm·cm^2 for curves 3a-c, respectively. The results follow nicely the expectation that the effect of phosphate pretreatment of CRS increase the $|Z|$ value by an order of magnitude, and that of additional chromate rinse on B-1000 substrate further enhances the impedance value of water-based alkyd coating about five times. It is commonly expected in the paint resistance measurement[27] that in most cases a paint with a measured resistance of 1×10^8 ohm·cm^2 will have good corrosion protection properties, a resistance of 1×10^6 ohm·cm^2 will be poor, and paints with resistance between 1×10^6 and 1×10^8 ohm·cm^2 will be borderline. In short, the control formula of water-reducible alkyd baking enamel coated on pretreated substrates (curves 3b and 3c) give good protective properties, whereas that on untreated panel (curve 3a) is a borderline coating.

Upon the application of single-step water-reducible alkyd ISPC system on a metal substrate, the pre-dispersed phosphatizing reagent can migrate dynamically to and react effectively with the surface of the metal

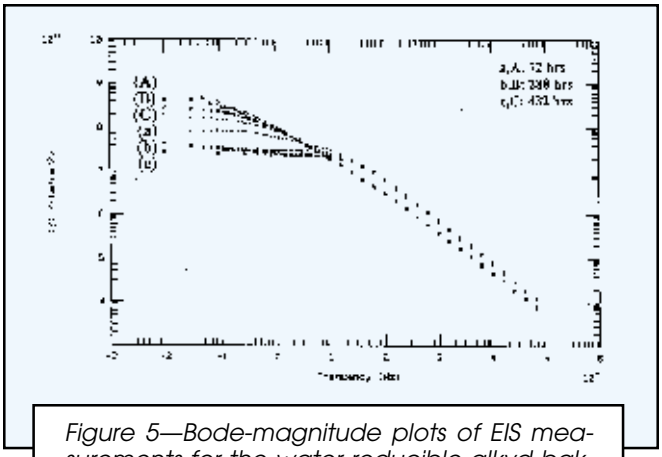

Figure 5—Bode-magnitude plots of EIS measurements for the water-reducible alkyd baking enamel coated on bare CRS coupons after a determined time of exposure to a 3% NaCl aqueous solution. The control sample after (a) 72 hr, (b) 288 hr, and (c) 432 hr; and the ISPC formula after (A) 72 hr, (B) 288 hr, and (C) 432 hr.

substrate. Frequently in the co-existing system reactions, the advantages of the combined system (i.e., a single step in-situ phosphatizing coating process) are greater than the sum of the system's components (i.e., multi-step phosphate conversion paint process).[2] *Figure* 4 shows the Bode-magnitude plots of alkyd ISPCs coated on bare CRS (curve 4A), on iron phosphated B-1000 (curve 4B), and on iron phosphated and chromated BD+P60 (curve 4C) coupons. All three curves are apparently overlapping throughout the experimental frequency range, except a small splitting is noticed in the lower frequency region. At $f = 1.0 \times 10^{-2}$ Hz, the $|Z|$ value is measured as 4.3×10^8, 6.0×10^8, and 1.2×10^9 ohm·cm^2 for curves 4A-C, respectively. This observation clearly indicates that the paint film alkyd ISPC on metal substrates (both untreated and pretreated) can be classified as good in the corrosion protective performance. A five-times increase in paint film resistance $|Z|$ is observed for water-reducible ISPC (curve 4A) as compared to the control alkyd formula (curve 3a) on bare CRS, supporting the successful generation of in-situ metal phosphate layer at the metal/coating interface. In the lower frequency region, the observed $|Z|$ values for the control alkyd formula (*Figure* 3) are quite sensitive to the substrate surface pre-treatment processes, but that is not detected for the ISPC system. The results strongly support that the technique of in-situ phosphatizing coating can be developed into an effective and alternative process for the conventional substrate surface pretreatment which is a costly, error-prone, and environmentally unfriendly process.

Recent studies concerning long-term exposure of coated CRS panels in a saline environment are being investigated for water-reducible ISPC systems as well as for control alkyd samples. The AC impedance values ($|Z|$) are measured using electrochemical impedance spectroscopy. *Figure* 5 shows a comparison of Bode-magnitude plots after 72 hr (curves a and A), 288 hr (curves b and B), and 432 hr (curves c and C) of exposure in a 3% NaCl solution for the control alkyd sample (curves a, b, and c) and the ISPC formula (curves A, B, and C). The $|Z|$ value of curve C is 2.0×10^8 ohm·cm^2 which is higher than that in curve a (8.0×10^7 ohm·cm^2), indicating that the paint film of water-reducible ISPC had a slower rate of deterioration than the control alkyd coating while exposed to a saline solution. At the higher frequency region, the EIS curves a, b, and c are elevated and deviated from the pure capacitive behavior, showing a greater extent in the uptake of electrolytes and water through the control alkyd paint film. Presumably, the ISPR catalyzed ISPC paint film has less defects[28] and forms more bond linkages[4] with the metal phosphate layer that may slow down the transport of water and electrolytes through the paint to the substrate.

In-Situ Phosphatization and Water Disbonding Resistance

The adhesion of many organic coatings (including water-based alkyd enamel) to metal substrates is adversely affected when subjected to an aqueous environment. Even high relative humidity can cause coating disbondment to occur. The mechanism behind the coating adhesion loss[29] is the accumulation of water molecules at small pre-existing unbonded areas at the coating/substrate interface; water diffuses through the coating under a concentration gradient, condenses, and causes them to grow. As these areas grow laterally, they cause stresses to occur at the coating/substrate interface which eventually leads to adhesion loss. The greater the

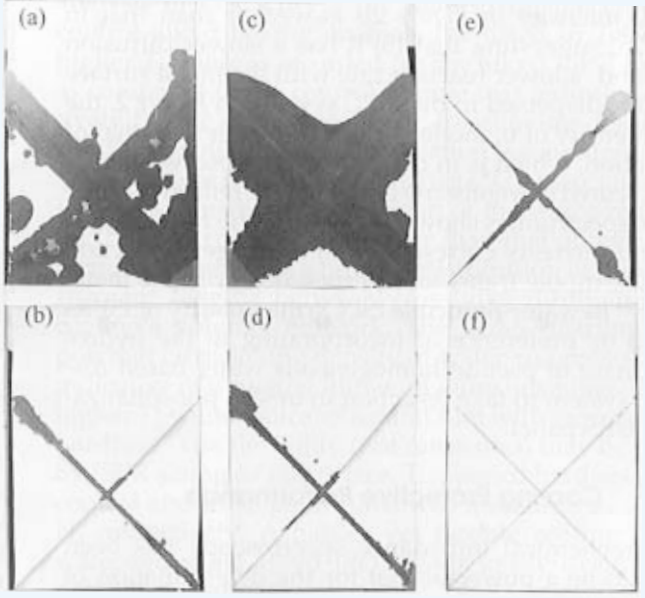

Figure 6—Water disbonding resistance after 100 hr of salt water immersion test. The control water-based alkyd paint coated on (a) bare CRS, (c) B-1000, and (e) BD+P60 coupons. The water-reducible alkyd ISPC coated on (b) bare CRS, (d) B-1000, and (f) BD+P60 coupons.

number of primary chemical adhesive bonds a specific coating makes with the substrate, the more resistant that system is to water disbondment.

In the water-reducible ISPCs, the phosphatizing reagent is available to react in-situ with the metal surface producing a metal phosphate layer and simultaneously forming covalent bonds with alkyd resin. The primary chemical adhesive bonds the in-situ phosphating layer can potentially make with the metal surface is the acid-base type interaction[8] of $P–O^-—M^{n+}$, and with the alkyd resin is the P–O–C chemical linkage.[4] The ISPC system's primary chemical interactions at the coating interface should provide greater resistance to wet adhesion loss than the control alkyd enamels with only secondary interactions.

The salt water immersion test in 3% NaCl solution was conducted for both water-reducible ISPC and control alkyd enamel applied on bare CRS, iron phosphated B-1000, and BD+P60 panels. The painted coupons of about 1.0 mil dry film thickness cured at 325°F for 15 min were X-cut through the film to the substrate and then immersed in a 3% NaCl solution for 100 hr. The specimens were removed from the salt solution, and the coated surface was dried immediately. A pressure-sensitive tape (Duck® brand tape, Manco, Inc., Westlake, OH) was applied over the X-cut and then removed. Adhesion was assessed quantitatively by measuring the distance of the paint disbondment across the X-scribe. The measured disbonding resistance of alkyd ISPC and the control enamel on different surface pre-treated substrates are compared in *Figure* 6 and *Table* 2, according to ASTM D 3359 test method A.[30] The enhancement of paint disbonding resistance in water-reducible alkyd ISPC is self-evident, when one compares the bottom (b, d, and f) relative to the top (a, c, and e) tested coupons in *Figure* 6, and parallel the two columns in *Table* 2. The control alkyd paint films on both bare CRS (panel 6a) and iron phosphated B-1000 (panel 6c) coupons display an extensive paint blistering, i.e., a poor salt water resistance. On the other hand, the water-reducible ISPC formula coated on the bare CRS (i.e., a single-step in-situ phosphatizing coating, panel 6b) is clearly shown to outperform the control alkyd baking enamel on coupons with all pre-treatments (i.e., a state-of-the-art multi-step coating process), with (panel 6e) and without (panel 6c) chromate rinse. These results strongly suggest that with the application of ISPC technique in the water-reducible alkyd enamel, the substrate surface pre-treatment may become an unnecessary step in coating practice. A common phenomena in both coating systems is observed in row 4 of *Table* 2. The chromate rinse (i.e., on the iron phosphated and chromated coupon) is really taking its extra effect on coating adhesion property, which justifies the market value of chromate rinse in surviving the current EPA regulation.

A superior paint disbonding resistance in salt water immersion testings is obtained for the water-reducible ISPC applied on coupons with iron phosphated and chromate rinse (panel 6f). This is attributed to the extra passivating function taken by the chromium (Cr^{6+}) compounds, which reportedly has as high as 100% performance improvement for sealing iron phosphate pretreatment.[1c] However, health and safety concerns are leading to the phasing out of hexavalent chromium (Cr^{6+}) compounds as treatments following phosphating. The comparable coating protective performance between a water-reducible ISPC on a bare CRS panel and the control alkyd formula on a BD+P60 coupon has proven the possibility of using ISPC as a chromate alternative practice.

Table 2—Disbondment from "X" Scribe in Salt Water Immersion Testings for Water-Reducible Alkyd Baking Enamels

Substrate	Control Alkyd Enamel (mm)	Alkyd ISPC (mm)
Bare CRS	22-33	3.0-7.0
Pre-phosphated B-1000	29-32	3.0-5.0
BD+P60	2.0-7.0	0-0.5

Cathodic Delamination

The laboratory accelerated testing method for paint film disbonding resistance on metal substrates is cathodic delamination. The delamination rate of an organic coating under a cathodic potential depends upon the applied potential, electrolyte solution, and metal substrate.[31,32] *Figure* 7 shows the cathodic delamination plots of the control alkyd enamel (delamination area: curve a; and delamination current: curve c) and the water-reducible ISPC (delamination area: curve b; and delamination

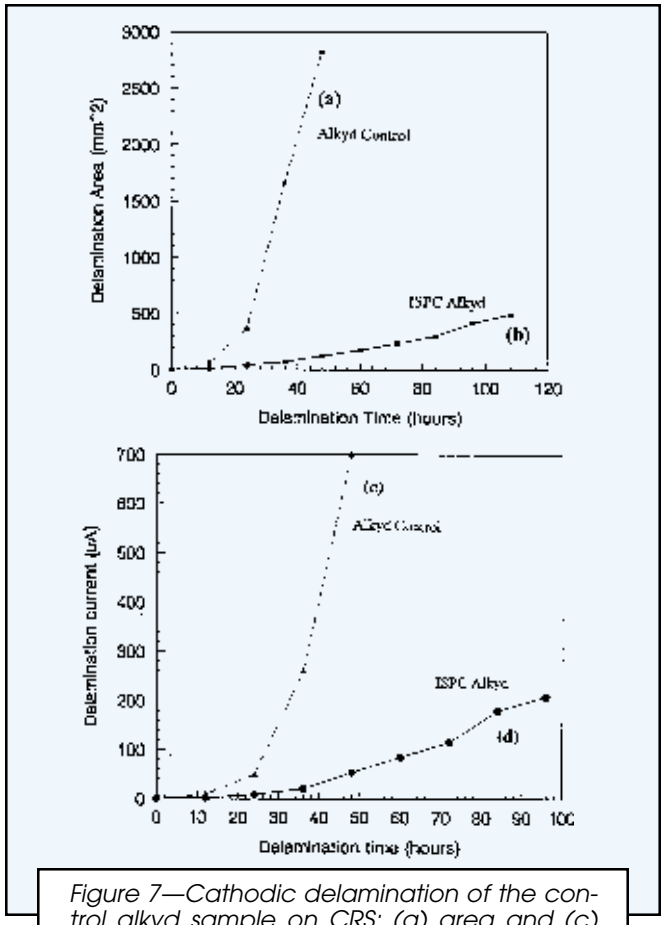

Figure 7—Cathodic delamination of the control alkyd sample on CRS: (a) area and (c) current vs. time; and water-reducible ISPC formula on CRS: (b) area and (d) current vs. time.

Table 3—Disbondment from "X" Scribe in Salt Spray (Fog) Testings for Water-Reducible Alkyd Baking Enamels

Substrate	Control Alkyd Enamel (mm)	Alkyd ISPC (mm)
Bare CRS	Complete failure	4.0-7.0
Pre-phosphated B-1000	26	3.0-4.0
BD+P60	14	0-0.3

current: curve d) coated on bare CRS coupons. The delamination testing was conducted in a 3% NaCl solution; the alkyd coated CRS coupon served as a cathode and was polarized at –1,100 mV versus a saturated calomel electrode. A significant slower delamination rate is obtained for the ISPC formula (curve 7b) as compared to the control alkyd coating (curve 7a). At 44 hr of delamination time, the entire painted area of working electrode (almost 20 cm × 20 cm) for the control alkyd paint has been delaminated, whereas the delamination area of the water-reducible ISPC is measured as small as 1 cm × 1 cm, indicating a considerable coating adhesion property improvement for the alkyd ISPC painted on bare CRS coupon.

The chemical mechanism of cathodic delamination processes has been proposed.[33-35] It is believed that the corrosion process of cathodic delamination in the presence of oxygen and water is the cathodic reaction,

$$H_2O + 1/2O_2 + 2e^- \rightleftharpoons 2OH^- \quad (1)$$

Studies indicate that the pH beneath the organic coating where the cathodic reaction occurs is highly alkaline.[34,35] The in-situ self-phosphating layer on metal surface produced in water-reducible alkyd ISPCs may make the substrate/alkyd film interface more acidic and thus increase the resistance to alkaline attack. The improved adhesion of a metal phosphate layer generated on the substrate surface by ISPC has greatly suppressed the delamination current, reduced the surface activity from the cathodic reaction and thus prevented coating delamination. The bottom portion of *Figure* 7 illustrates a remarkably lowered delamination current as recorded during the entire experimental process for ISPC as compared to the control alkyd formula. The enhanced cathodic delamination resistance of the water-reducible alkyd ISPC paint film on CRS panel represents good coating/substrate adhesion and offers a superior corrosion protective performance as illustrated in the EIS measurements.

ASTM Salt Spray (Fog) Tests

The testing conditions used in the standard salt spray (fog) tests for organic paint films are more aggressive and severe than those employed in the salt water immersion tests. A slightly elevated temperature of 35°C is combined with a continuous salt solution spray. The air flow generated in the salt solution spray can carry fresh oxygen to the test chamber. Following the salt water immersion tests, the alkyd painted coupons of about 1.0 mil dry film thickness cured at 325°F for 15 min were X-cut to the substrate and then 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. With sufficient oxygen supplied during the salt spraying action (unlike the salt water immersion tests where oxygen is limited by its solubility in water and its depletion as a function of time), the corrosion reactions in salt spray (fog) tests are predictably faster than those in the salt water immersion tests. The salt sprayed specimens were removed from the test chamber and the coated surface was immediately dried. A Duck® brand tape was applied over the X-cut and then removed. The paint protective performance was assessed quantitatively by measuring the distance of the coating corrosion across the X-scribe. *Figure* 8 contains the results of 100 hr salt spray (fog) test for the control alkyd formula (top three coupons) and water-reducible ISPC (bottom three coupons) on bare CRS (panels a and b), B-1000 (panels c and d), and BD+P60 (panels e and f). The corresponding distance (in mm) measurements for the surface corrosion across the X scribe are listed in *Table* 3.

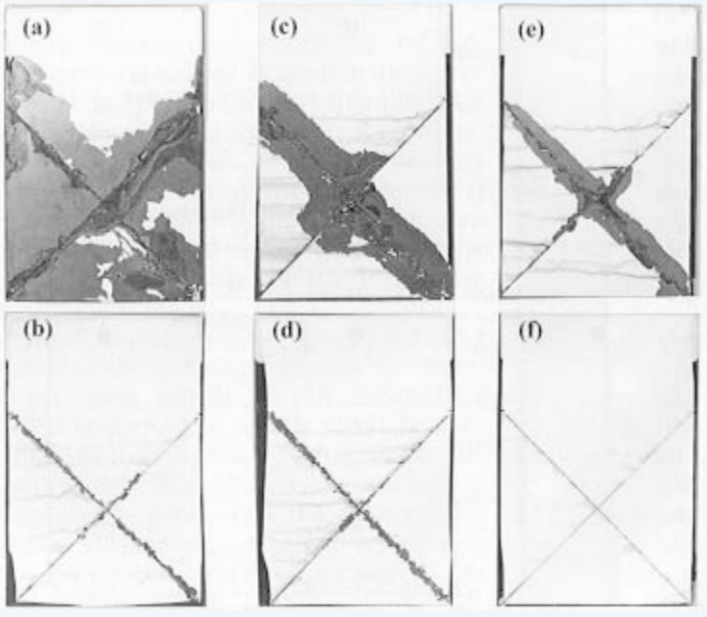

Figure 8—Corrosion protective performance after 100 hr of salt spray (fog) test. The control water-based alkyd paint coated on (a) bare CRS, (c) B-1000, and (e) BD+P60 coupons. The water-reducible alkyd ISPC coated on (b) bare CRS, (d) B-1000, and (f) BD+P60 coupons.

Under the more harsh conditions of the salt spray (fog) test, the results in *Figure* 8 and *Table* 3 differentiate even more than the corrosion resistance performance of the water-reducible ISPC from that of the control alkyd formula. On all three types of substrates, the control alkyd coating provides little corrosion protective effect, whereas protection is evidenced in the water-reducible ISPC for-

mula. The water-reducible ISPC applied on bare CRS panel (*Figure* 8b) has out-performed the control alkyd paint on pre-phosphated and chromated substrate (*Figure* 8e), indicating that the possibility exists for the single-step ISPC technique to substitute the traditional multi-step surface pre-treatment/coating process which could become an unnecessary practice. Similar to that in the salt water immersion test, the best corrosion protective paint film is observed in *Figure* 8f which is a combination of water-reducible ISPC with the BD+P60 substrate to achieve an extra passivation effect.

CONCLUSION

Following the successful application of in-situ phosphatizing coating technique in a high-solids polyester baking enamel,[10] an air-dried lacquer system,[11] and a solvent-free acrylic latex paint,[12] a stable and compatible ISPC of a water-reducible alkyd baking enamel has been formulated. No change in the viscosity of the water-reducible ISPC formula was observed during a long-term shelf storage. By comparison with the paint film of the control alkyd formula, the ISPC polymer film displays a higher T_g value and a lower ΔC_p during the glass transition which are indicative of a higher crosslink density. At 44 hr of cathodic delamination time, the entire coated area of the working electrode for the control alkyd paint (about 3000 mm^2) was delaminated. On the other hand, the delamination area of the water-reducible ISPC was measured as small as 100 mm^2, indicating a considerable coating adhesion property improvement for the alkyd ISPC painted on a bare CRS coupon. The in-situ formation of a phosphate layer between the metal surface and polymer coating functions as an adhesion promoter. Both salt water immersion and salt spray (fog) tests confirmed a comparable coating protective performance between water-reducible ISPC on bare CRS panel and control alkyd formula on BD+P60 coupon, suggesting that a successful application of water-based alkyd ISPC can effectively replace the operation of an iron phosphate/chromate bath/line which is a costly, error-prone, and environmentally unfriendly process. The zero (or low) VOC ISPCs are shown to provide superior protection of metal surfaces, and can eliminate several pretreatment steps, avoid waste generation at the source, and more importantly, act as a chrome (Cr^{6+}) alternative.

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References

(1) (a) Perfetti, B.M., "Metal Surface Characteristics Affecting Organic Coatings," *Federation Series on Coatings Technology*, FSCT, Blue Bell, PA, 1994; (b) Rausch, W., *The Phosphating of Metal*, ASM International, Metal Park, and Finishing Publications Ltd., Teddington, Middlesex, England, 1990; and (c) Freeman, D.B., *Phosphating and Metal Pretreatment: A Guide to Modern Processes and Practice*, Industrial Press Inc., New York, 1986.

(2) Lin, C.T., Lin, P., Hsiao, M.W., Meldrum, D.A., and Martin, F.L., "Chemistry of a Single-Step Phosphate/Paint System," *Ind. Eng. Chem. Res.*, 31, 424 (1992).

(3) Lin, C.T. and Meldrum, D.A., "AC Impedance Analysis and Factorial Designs of an In-Situ Phosphatizing Coating," JOURNAL OF COATINGS TECHNOLOGY, *65*, No. 818, 47 (1993).

(4) 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).

(5) Lin, C.T. and Qvyjt, F., "Chemistry of In-Situ Phosphatizing Coatings," Polymeric Materials: Science and Engineering (ACS, PMSE), 70, 76 (1993).

(6) Lin, C.T., "Additive Package for In-Situ Phosphatizing Paint, Paint and Method," U.S. Patent 5,322,870, June 21, 1994.

(7) Lin, C.T. and Li, L., "SEM-EDS Investigations of Self-Phosphating Coatings," *Ind. Eng. Chem. Res.*, 32, 3241 (1994).

(8) 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).

(9) Yu, T. and Lin, C.T., "The Performance of In-Situ Phosphatizing Reagents in Solventborne Paints," *Ind. Eng. Chem. Res.*, 36, 369 (1997).

(10) Yu, T. and Lin, C.T., "In-Situ Phosphatizing Coatings II: A High-Solids Polyester Baking Enamel," JOURNAL OF COATINGS TECHNOLOGY, *71*, No. 892, 69 (1999).

(11) 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).

(12) Muñoz, C.L., Yu, T., and Lin. C.T., "In-Situ Phosphatizing Coatings: A VOC-Free Thermoset Acrylic Latex System," *Proc. 25th Annual International Waterborne, Higher Solids, and Powder Coatings Symposium*, p. 332-343, New Orleans, LA, 1998.

(13) Wragg, J.L., Chamberlain, J.E., Chann, L., White, H.W., Sugama, T., and Manalis, S., *J. Appl. Polymer Sci.*, 50, 917 (1993).

(14) Massingill, J.L., "Adhesion and Flexibility Contributions to the Performance of Epoxy Phosphate Ester Coatings," JOURNAL OF COATINGS TECHNOLOGY, *63*, No. 797, 47 (1991).

(15) Whiteside, R.C., Sheih, P.S., and Massingill, J.L., "High Performance Epoxy Resins for Container Coating Applications Based on In-Situ Advancement Technology," JOURNAL OF COATINGS TECHNOLOGY, *62*, No. 788, 61 (1990).

(16) Massingill, J.L., Sheih, P.S., Whiteside, R.C., Benton, D.E., and Morisse-Arnold, D.K., "Fundamental Studies of Epoxy Resins for Can and Coil Coatings II: Flexibility and Adhesion of Epoxy Resins," JOURNAL OF COATINGS TECHNOLOGY, *62*, No. 781, 31 (1990).

(17) Higgins, W.A., "Organic Phosphate Substrate Treatments and Coating Additive," Technical Paper Reprint for Lubrizol® 2061/2062/2063 Paint Additives, Lubrizol Corp., Wickliffe, OH, 1992.

(18) van Laere, E.C.L., "Foam Control Agents for Waterborne Coatings," in *Waterborne Coatings and Additives*, Karsa, D.R. and Davies, W.D. (Eds.), The Royal Society of Chemistry, Cambridge, United Kingdom, pp. 133-141, 1995.

(19) Jenness, P.K., "Synthetic Clay Rheology Modifiers for Water-Based Coatings," in *Waterborne Coatings and Additives*, Karsa, D.R. and Davies, W.D. (Eds.), The Royal Society of Chemistry, Cambridge, United Kingdom, pp. 217-231, 1995.

(20) Patton, T.C., *Paint Flow and Pigment Dispersion: A Rheological Approach to Coating and Ink Technology*, 2nd Edition, Wiley-Interscience Inc., New York, pp. 355-375, 1979.

(21) Wicks, Z.W., Jones, F.N., and Pappas, S.P., *Organic Coatings: Science & Technology*, John Wiley & Sons, New York, Vol. 1, Chapter 3, 1992.

(22) Mijovic, J., Fishbain, A., and Wijaya, J., *Macromolecules*, 25, 979 (1992).

(23) Montserrat, S., "Effect of Crosslinking Density on $\Delta Cp(T_g)$ in an Epoxy Network," *Polymer*, 36, 435 (1995).

(24) Carter, R.O., III, Gierczak, C.A., and Dickie, R.A., "The Chemical Interaction of Organic Materials with Metal Substrates. Part II: FTIR Studies of Organic Phosphate Films on Steel," *Appl. Spectrosc*., 40, 649 (1986).

(25) Scantlebury, J.D., Ho, K.N., and Eden, D.A., "Impedance Measurements on Organic Coatings on Mild Steel in Sodium Chloride," in *Electrochemical Corrosion Testing*, Mansfeld, F., Bertocci, U. (Eds.), ASTM, Philadelphia, PA,STP 727, p. 187, 1981.

(26) Strivens, T.A. and Taylor, C.C., "An Assessment of AC Impedance as a Basic Research and Routine Testing Method for Studying Corrosion of Metals under Paint Films," *Mater. Chem.*, 7, 199 (1982).

(27) Leidheiser, H., Jr., "Corrosion of Painted Metals—A Review," *Corrosion*, 38, 374 (1982).

(28) Li, L., Cao, Y. and Lin, C.T., "Environmentally Safe In-Situ Phosphatizing Coating for Corrosion Protection," in *Environmentally Acceptable Inhibitors and Coatings*, Taylor, S.R., Isaacs, H.S. and Brooman, E.W. (Eds.), The Electrochemical Society, Pennington, NJ, Vol. 95-16, pp. 118-132, 1997.

(29) (a) Leidheiser, Jr., H. and Funke, W., *J. of Oil & Colour Chemists' Assoc.*, 70, 121 (1987); and (b) Kaelble, D.H., *Physical Chemistry of Adhesion*, John Wiley & Son, Chap. 5, p. 180, 1971.

(30) Koleske, V.J., Ed., *Paint and Coating Testing Manual, 14th Edition of the Gardner-Sward Handbook*, ASTM Manual Series: MNL 17, ASTM PCN 28-017095-14, Philadelphia, PA, 1995.

(31) Leidheiser, Jr., H., "Cathodic Delamination of Polybutadiene from Steel," *J. Adhesion Sci. Technol.*, 1, 79 (1987).

(32) Sugama, T. and Carciello, N.R., "Cathodic Delaminations of Poly(Phenylether Ether Ketone) (PEEK) Coatings Overlaid on Zinc Phosphate-Deposited Steel," *J. Appl. Polymer Sci.*, 50, 1701 (1993).

(33) Castle, J.E. and Watis, J.F., in *Corrosion Control by Organic Coatings*, Leidheiser, H. Jr., (Ed.), National Association of Corrosion Engineers, Houston, TX, Vol. 28, p. 78, 1981.

(34) Ritter. J.J. and Kruger, J., in *Corrosion Control by Organic Coatings*, Leidheiser, H. Jr., (Ed.), National Association of Corrosion Engineers, Houston, TX, Vol. 28, p. 28-31, 1981.

(35) Dickie, R.A., Hammond, J.S., and Holubka, J.W., *Ind. Eng. Chem. Prod. Res. Dev.*, 20, 339 (1981).