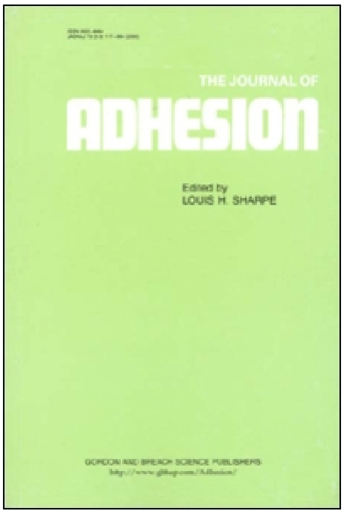

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Cathodic Delamination of an Epoxy/Polyamide Coating from Steel

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X-ray photoelectron spectroscopy (XPS) has been used to determine the mechanism responsible for debonding of an epoxy/polyamide coating from steel during cathodic delamination in 3.5% aqueous NaCl solutions. Coating failure always occurred near the interface between the coating and the oxide. The nitrogen content of the free surface of the prepared coatings was about 10%. However, the nitrogen content of the free surface dropped to only 5% after exposure to 1 N NaOH for four weeks and that of the coating failure surface after cathodic delamination was only about 2%, implying that the failure involved degradation of the polyamide curing agent by hydroxide ions formed at the steel surface by reduction of oxygen. That conclusion was supported by results obtained from curve fitting of C(1s) and O(1s) spectra. The intensity of components in the C(1s) spectra due to C—N and C=O bonds in amide functional groups decreased significantly after coatings were exposed to NaOH or subjected to cathodic delamination. Small amounts of organic materials characteristic of the coating were observed on the substrate failure surface, perhaps indicating that the failure was cohesive within the coating but very close to the interface or that some products from degradation of the curing agent precipitated on the substrate. Use of silane coupling agents to retard cathodic delamination was also investigated. Coupling agents were added directly to the coating or applied to the substrate as a primer before application of the coating. Significant reduction in the rate of cathodic delamination was seen only when the silane coupling agent was applied to the substrate and cured at elevated temperatures before the epoxy/polyamide coating was applied.

KEY WORDS Cathodic delamination; epoxy/polyamide coatings; X-ray photoelectron spectroscopy; silane coupling agents; γ-aminopropyltriethoxysilane.

1 INTRODUCTION

Rapid oxidation of iron-containing metals in humid environments often necessitates use of protective coatings to retard corrosion. Metal parts submerged in water or exposed to splash zones are often cathodically protected by applying a potential below that required for the oxidation of iron. While cathodic polarization will protect the steel from oxidation, it may also produce a high pH environment through reduction of water and dissolved oxygen which diffuse through the film.

$$2H_2O + O_2 + 4e^- \longrightarrow 4OH^- \tag{1}$$

This high pH environment (13 or greater) can quickly degrade many coatings intended to protect the steel substrate.

Cathodic delamination of coatings from steel has been investigated frequently. Leidheiser *et al.*[1] reported on cathodic delamination of polybutadiene from steel and determined that disruption of adhesive-to-substrate bonds was a result of the high concentration of OH^- ions. Delamination was found to initiate at a coating defect and progress laterally outward at the "leading edge." Leidheiser[2] also reported on the cathodic delamination of a fluoropolymer immersed in both a neutral saline solution and an acidic solution. In the neutral solution, cathodically produced OH^- ions disrupted the polymer-to-substrate bonds, causing delamination of the fluoropolymer coating. However, cathodic polarization in an acidic solution resulted in no delamination of the fluoropolymer coating. The acid was believed to have diffused through the coating to neutralize the cathodically produced OH^- ions before delamination occurred.

Koehler *et al.*[3] reported on cathodic delamination of polybutadiene, oleoresinous, and epoxy/phenolic coatings from steel. The principal cause for delamination was found to be displacement of the coatings by a high pH aqueous film found at the coating/substrate interface. OH^- ions were found first to displace the coating from the substrate by disrupting the coating-to-substrate bonds. As delamination proceeded, degradation of the coating was also possible. This was determined by the presence of a residue on substrate failure surfaces which was explained as precipitation of the degraded coating. Koehler's work also included immersion of the above mentioned coatings in an aqueous 2% NH_4OH solution. After 4 hours the oleoresinous and polybutadiene coatings had delaminated. However, no delamination of the epoxy/phenolic coating was detected even after 24 hours. Samples of these coatings on steel were also immersed in pure water. After four days there was no evidence of delamination. This led Koehler to conclude that a high pH environment was necessary for delamination.

Watts *et al.*[4] have investigated cathodic delamination of polybutadiene from steel using X-ray photoelectron spectoscopy (XPS). Delamination initiated within the iron oxide "interphase" region. However, as delamination progressed, the site switched to the coating/substrate interface and delamination was determined to be the result of coating degradation by OH^- ions.

Other work by Watts and coworkers[5] included cathodic delamination of an epoxy/amine coating from steel. XPS analysis of failure surfaces indicated delamination again started from within the iron oxide region (at a coating defect) and was attributed to oxide reduction. As delamination progressed away from an initial defect, the site of delamination passed to within the coating. Coating degradation (hydrolysis) was then responsible for further delamination which took place near the coating/oxide interface. Carbonates were detected on failure surfaces but only after delamination was allowed to continue for several weeks. The presence of carbonates was not attributed to coating degradation but to the reaction of adsorbed CO_2 with the high pH environment.

$$CO_2 + H_2O \longrightarrow H_2CO_3 \qquad (2)$$

$$H_2CO_3 + 2OH^- \longrightarrow CO_3^{-2} + 2H_2O \qquad (3)$$

Boerio *et al.*[6] investigated the mechanism responsible for cathodic delamination of neoprene rubber from steel using IR and XPS. Neoprene was bonded to the steel using a primer (phenolic resin blended with chlorinated rubber) and an adhesive (chlorinated rubber). Two mechanisms were proposed for cathodic delamination. The first involved oxidation of the phenolic resin in the primer. The second involved large osmotic pressures in the bondline due to dissolution of inorganic chlorides. These inorganic chlorides were the result of dehydrohalogenation of the chlorinated rubber in the primer during cure. XPS spectra of failure surfaces showed the presence of carboxylates which were attributed to degradation products of the phenolic resin. Infrared spectra of neat primer films and primer films treated in NaOH solutions indicated that methylene linkages between phenol residues were degraded by the high pH.

The site of delamination was determined to pass back and forth between the outer metal oxide and the coating. Evidence for this was seen by the presence of rubber islands on the substrate failure surface, and islands of iron oxide on the coating failure surface.

Dickie *et al.*[7] also examined cathodic delamination of polybutadiene from steel using XPS. Results showed that an oxidized carbon residue, sodium carboxylate, was present on both the polymer and substrate failure surfaces. This residue was attributed to hydrolysis of ester crosslinks present in the polybutadiene coating. The site of delamination was also determined and found to be near the oxide interface but within the coating.

Additional coatings investigated by Dickie and coworkers[8] included an epoxy/urethane crosslinked with melamine-formaldehyde and an epoxy/amine crosslinked with both melamine-formaldehyde and urea-formaldehyde. XPS analysis of failure surfaces indicated coating degradation was responsible for delamination. Using XPS, the failure surfaces for the epoxy/urethane coating were found to contain less nitrogen than neat surfaces. This was taken as evidence for degradation of the urethane linkage and removal of the nitrogen containing polymer fractions during immersion. Carbonates were also found on the substrate failure surface and attributed to degradation products of the urethane linkages. Results from cathodic delamination of the epoxy/amine coating showed it to be more resistant to the high pH environment than the epoxy/urethane coating. The cause of failure was, however, the same as that for the epoxy/urethane coating. Hydroxide ions were found to degrade the coating by attacking the urea-formaldehyde crosslinking agent. Coating degradation caused delamination and accounted for the decreased nitrogen concentration of coating failure surfaces as compared with a neat surface. Carbonates were detected on the substrate failure surface and were again attributed to degradation products of the coating.

This paper describes an investigation of the cathodic delamination of a commercial epoxy/polyamide coating from mild steel and steel coated with γ-aminopropyltriethoxysilane (γ-APS). Some coatings were also prepared by adding γ-APS directly to the epoxy/polyamide before application to the steel.

XPS was used to examine neat primer films, the "clean" substrate surface, and failure surfaces of cathodically delaminated coatings. XPS survey and multiplex spectra provided information on elemental analysis and chemical states of the epoxy/polyamide coating before and after cathodic delamination. IR and XPS were also used to examine surfaces of the epoxy/polyamide coatings before and after immersion in 1 N NaOH solutions which simulated the high pH conditions encountered at the bondline during cathodic polarization experiments.

II EXPERIMENTAL

The epoxy/polyamide coating (Matcote Paint) was obtained from International Paint Co. and consisted of both a primer and topcoat based on the reaction of an epoxy resin cured with a polyamide hardener. Verification of primer components was performed by separation and analysis using EDAX and infrared spectroscopy. Separation of the primer's inorganic components from the organic epoxy resin was accomplished by Soxhlet extraction using toluene. IR analysis of the curing agent and separated epoxy resin were performed by attenuated total reflection (ATR) IR spectroscopy using a KRS-5 ATR crystal. A KBr pellet was prepared using the separated inorganics and an IR transmission spectrum was obtained for analysis. A Perkin Elmer Model 1800 FT-IR spectrometer equipped with a TGS detector was used to collect all spectra at a nominal resolution of 4 cm^{-1}. EDAX spectra were collected using a Cambridge model 600 SEM.

The steel substrate (interstitial free steel, obtained from Armco, Inc., Middletown, Ohio) was cut on a band saw to 1″ × 1.5″ coupons. The coupons were prepared for coating by immersion (30–35 minutes) in a solution of a commercial alkaline cleaner (Parko 338, Parker Chemical Co.) at 60°C, removed, and rinsed clean with distilled water. Coupons were then polished to a mirror finish by successively grinding with a series of silicon-carbide papers followed by wet polishing with alumina compounds. Between each grinding step the coupons were cleaned using Alconox® detergent, rinsed with distilled water, and blotted dry with a paper towel. Coupons were rinsed free of excess alumina after each polishing step using distilled water and then blown dry in a stream of nitrogen. After final polishing with 0.05 micron alumina, the primer and topcoat were applied as recommended (4 parts/volume epoxy to one part/volume hardner). Coupons were coated by means of a Badger air brush using compressed nitrogen (20 psi). Coated coupons were dried under ambient conditions for 24 hours, and finally cured at 150°C for 1 hour. A dry film thickness of 254 microns (178 microns for the primer plus 76 microns for the topcoat) was measured using a standard micrometer.

Cathodic delamination experiments were carried out in aerated 3.5% NaCl solutions. A Weinking Model ST 72 potentiostat equipped with a platinum counterelectrode was used to maintain the potential at −1.05 volts versus SCE. Electrical contact between potentiostat and coated coupons was made by means of copper wire attached to a small bolt placed through the coupon. All exposed metal surfaces were coated with a quick-setting epoxy to decrease exposed surface area and therefore reduce the risk of overloading the potentiostat. Just prior to immersion in the NaCl solutions, a carbide tipped scribe was used to cut one-inch-long defects (in the form of an X) into the coatings, exposing bare metal along the entire length of the defect. These defects acted as the initial site for cathodic delamination which proceeded laterally outward and near to the substrate surface. After cathodic delamination (approximately 8 weeks), the coupons were removed from the NaCl solution, rinsed with distilled water, blown dry in a stream of nitrogen, and dried over desiccant for 24 hours before either IR or XPS analysis was performed.

In separate experiments, a coated steel substrate (primer only) was immersed in a 1 N NaOH solution in order to simulate the high pH environment found during cathodic polarization. A "clean" steel substrate was also simultaneously immersed in the solution. The primer and substrate surfaces were examined before and after immersion in 1 N NaOH using XPS. After immersion, the samples were removed from the NaOH solution, rinsed with distilled water, blown dry, and dried over desiccant for 24 hours prior to analysis using XPS.

Some of the coatings examined in cathodic delamination experiments were prepared with either 3 or 10% (w/w) γ-APS added directly to the primer 10 minutes after mixing the curing agent with the epoxy resin. Application of the primer then proceeded as outlined above. Still other coatings were prepared where an intermediate layer of γ-APS was applied before the primer. γ-APS was applied by immersing the polished steel substrate in a 1% (v/v) aqueous solution for 30 minutes. The steel coupons were removed, blown dry in a stream of nitrogen, and air-cured for 30 minutes before coating with primer. The intermediate layer of γ-APS was applied from solutions having two pH values, 10.4 (standard pH for a 1% v/v solution) and 8.0 (adjusted using 1 N HCl). In addition, one of the pH 8.0 γ-APS films was post cured at 110°C for 15 minutes before application of primer.

XPS analysis was carried out using a Physical Electronics Model 5300 ESCA system and MgK_α X-rays. The X-ray source had an energy of 1253.6 eV, and was operated at 300 watts and 15 KV dc. Pass energies for survey and high resolution multiplex spectra were 44.75 and 17.90 eV, respectively. Reference data for chemical shifts within C(1s) and O(1s) spectra were obtained from XPS analysis of model compounds and cited literature values.[9,10] Samples for ESCA analysis were either cut (0.5" × 0.25") using a jewelers saw or stamped out by means of a die and press (0.5" dia.).

III RESULTS AND DISCUSSION

A Primer analysis

Using IR analysis we found the epoxy resin to be similar to the diglycidyl ether of bisphenol A and the curing agent to be similar to Versamid 125, a polyamide prepared from a dimer acid[11] and diethylenetriamine. EDAX and infrared analysis of the inorganics separated from the primer by Soxhlet extraction indicated Fe, Mg, Si, Ca, Zn, and Cr were present as Fe_2O_3, $MgSiO_3$, $CaCO_3$, ZnO, and $ZnCr_2O_7$. Material safety data sheets listed the presence of these compounds as fillers and corrosion inhibitors.

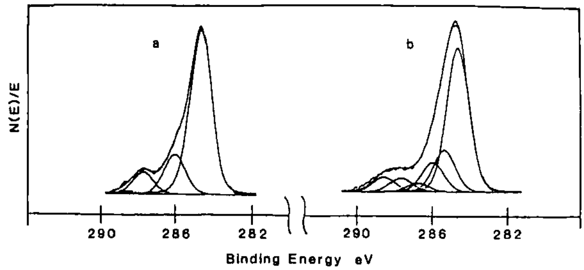


FIGURE 1 C(1s) multiplex spectra obtained from (a) polished steel substrate and (b) substrate after immersion in 1 N NaOH with exposed primer for 2 weeks.

B Substrate characterization

Analysis of the steel substrate was performed prior to application of the primer. The C(1s) spectrum of the polished steel substrate (Figure 1a) had contributions from carbon bound to hydrogen at 284.6 eV (hydrocarbon contaminants), carbon singly bound to oxygen at 286.1 eV, and carbon as bicarbonate at 288.0 eV. The C(1s) spectrum of the polished steel substrate after immersion in 1 N NaOH along with the exposed primer (Figure 1b) will be discussed later. The Fe(2p) spectrum of polished steel (Figure 2) showed the presence of both iron oxide (710.3 eV) and metallic iron at 706.7 eV. The intensity of the metallic iron band indicated the combined film thickness of organic contaminants and iron oxide on the steel surface was less than 50 A.

C Degradation of primer

Degradation of cured primer films immersed in 1 N NaOH solutions (simulating the high pH environment during cathodic polarization) was followed using XPS. XPS survey spectra of primer films before and after immersion in 1 N NaOH were similar and showed bands near 285 (carbon), 400 (nitrogen), and 532 (oxygen) eV (Figure 3). Before immersion in 1 N NaOH, the concentration of nitrogen was

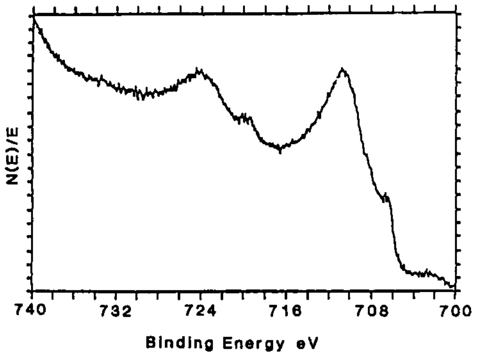


FIGURE 2 Fe(2p) multiplex spectrum of polished steel substrate.

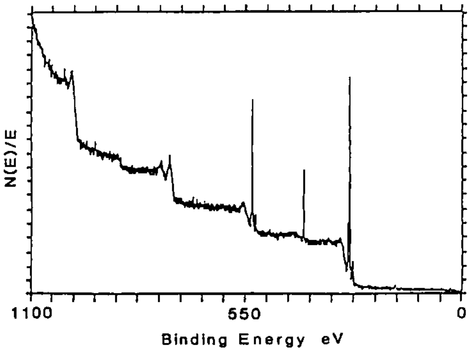


FIGURE 3 XPS survey spectrum of untreated primer.

found to be approximately ten percent. This was higher than calculated (7%) based on primer composition. However, the increased nitrogen concentration may be due to preferential orientation of nitrogen groups towards the outer coating surface. Dickie[8] reported on the preferential orientation of nitrogen-containing groups in an amine-cured epoxy resin where the nitrogen concentration on the outer surface was found to be higher than the theoretical value.

After immersion in 1 N NaOH for periods of two and four weeks, the primer's nitrogen concentration (determined by XPS multiplex spectra) decreased to seven and five percent, respectively (Table I). Sodium was also detected on the exposed primer surface even after vigorous rinsing. The presence of sodium was presumed due to insoluble sodium salts from primer degradation.

The C(1s) spectrum of a neat primer film on steel (Figure 4a) showed contributions from five components: carbon bound to hydrogen at 284.6 eV, carbon bound to nitrogen at 285.5 eV, carbon singly bound to oxygen at 286.1 eV, carbon doubly bound to oxygen (as in an amide functional group) at 287.0 eV, and carbon in the form of carboxylic acid and as carbonate at 288.8 eV. Presence of carbonate was not unexpected since $CaCO_3$ was present in the primer. Commercially available polyamides are a complex mixture of free carboxylic acids, primary and secondary amines, and imidazoline structures.[11] This may then account for the presence of carboxylic acid. However, carboxylic acid may also form by oxidation of the epoxy ring during cure at elevated temperatures as reported by Bell and McCarvill.[12]

The O(1s) spectrum of a neat primer film (Figure 4a) also showed the presence

TABLE I
Composition of primer films before and after immersion in 1 N NaOH for four weeks

Immersion	C(%)	O(%)	N(%)	Fe(%)	Na(%)
None	72.3	16.8	10.1	0.1	0.0
Two weeks	74.9	16.5	7.1	0.0	1.4
Four weeks	73.3	18.4	5.2	0.2	2.9

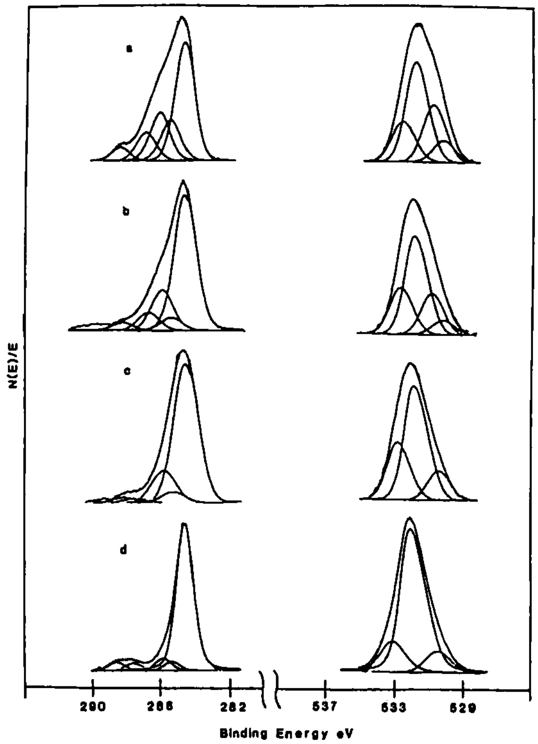


FIGURE 4 C(1s) and O(1s) multiplex spectra obtained from (a) primer before immersion in NaOH, (b) primer after immersion in 1 N NaOH for four weeks, (c) primer failure surface after cathodic delamination from substrate in 3.5% NaCl for 2 months, and (d) substrate failure surface after cathodic delamination of primer in 3.5% NaCl for 2 months.

of a band due to carboxylic acid at 533.6 eV. Existence of an O(1s) carboxyic acid band, 3.8 eV from iron oxide (529.7 eV), has been attributed to an oxygen atom singly bound to a carbon atom doubly bound to a second oxygen atom.[13] Other bands in Figure 4a were assigned to oxygen singly bound to carbon at 532.6 eV (C—O—H), oxygen doubly bound to carbon at 531.6 eV (N—C═O), and oxygen in the form of carbonate at 531.0 eV. A band due to oxygen doubly bound to the carbon of carboxylic acid would be expected at 532.4 eV. However, the presence of this band most likely contributes to the intensity of bands seen at 531.6 and 532.6 eV.

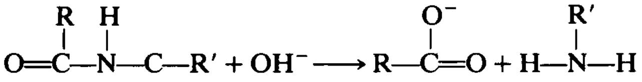
The C(1s) spectrum of the primer film after immersion in 1 N NaOH for four weeks is shown in Figure 4b. The relative concentrations of carbon bound to nitrogen and carbon doubly bound to oxygen (bands 2 and 4, respectively) decreased after immersion. Table II lists the C(1s) components and intensities of the neat primer film (Figure 4a) and the primer film after immersion in 1 N NaOH (Figure 4b). The O(1s) spectrum of the primer film after immersion in 1 N NaOH for four weeks is shown in Figure 4b. The concentration of oxygen doubly bound to carbon at 532.6 eV (amide linkages) has also decreased after immersion.

TABLE II
Components of the carbon (1s) spectra of primer films before and after immersion in 1 N NaOH for four weeks

Band number	1	2	3	4	5
Assignment	CH	CN	CO	NCO	COO/CO_3^{-2}
Shift from 284.6 eV	0	0.9	1.5	2.4	4.2
No immersion	47.5	14.5	18.6	12.9	5.2
Two weeks	59.1	9.5	15.6	11.5	4.3
Four weeks	62.9	6.1	18.8	8.3	3.9

However, an increase in the amount of free carboxylic acid (at 533.6 eV) is apparent.

Degradation of the primer proceeded by hydrolysis of the amide functional groups *via* the same mechanism responsible for hydrolysis of esters. Hydroxide ions hydrolyzed the amide functional groups (from the polyamide curing agent) to yield amines and carboxylates.



$$\mathrm{O{=}\overset{\displaystyle R}{\overset{|}{C}}{-}\overset{\displaystyle H}{\overset{|}{N}}{-}C{-}R' + OH^- \longrightarrow R{-}\overset{\displaystyle O^-}{\overset{|}{C}}{=}O + H{-}\overset{\displaystyle R'}{\overset{|}{N}}{-}H} \qquad (4)$$

This explains the decreased concentration of amide functional groups and increased carboxylate concentration when comparing O(1s) spectra before and after immersion. It also accounts for reduction in carbon bound to nitrogen when comparing C(1s) spectra before and after immersion. Rinsing primer films in distilled water immedately after immersion in 1 N NaOH produced a strong amine odor. This odor was indicative of the low molecular weight amine products from amide hydrolysis and serves as further evidence for polymer degradation. In accounting for these low molecular weight amines we must consider the degree of crosslinking formed between polyamide and epoxide during cure. Their presence would indicate possibly one or even no reactions between an epoxy and a diethylenetriamine unit of the polyamide. When steric hindrance is considered a low degree of crosslinking seems more likely.

As previously mentioned, Dickie and coworkers also saw a decrease in the concentration of nitrogen for cathodically delaminated epoxy/urethane and epoxy/amine coatings from steel. They proposed that OH^- ions attacked the urethane linkage (of the epoxy urethane coating) and the urea-formaldehyde crosslinking agent of the epoxy/amine coating. Cleaved polymer fractions then migrated away during cathodic delamination. The result was a decrease in nitrogen concentration on the failure surfaces, as detected by XPS.

D Cathodic delamination of the primer

Cathodic delamination of the primer progressed very slowly away from the defect and was allowed to continue for 8 weeks before samples of suitable size (approx. 2 cm) for XPS analysis were obtained. XPS survey spectra of substrate and primer failure surfaces were found to be similar to the spectrum shown in Figure 3 in that presence of carbon, nitrogen and oxygen were seen. The nitrogen concentration on the primer failure surface was, however, only 1.2% as compared with that of a neat primer film (10%, Figure 3). A relatively large concentration of sodium was also detected, but there was little evidence for the presence of chloride counterions. Excess sodium was then attributed to organic sodium salts of the degraded primer. Sodium was also detected in the XPS survey spectra of primer films immersed in 1 N NaOH solutions and again there was no evidence of inorganic counterions. This again suggested the excess sodium is present as insoluble organic salts formed by hydroylsis of the primer. Compositions of cathodically delaminated primer and substrate failure surfaces obtained from high resolution multiplex spectra are listed in Table III.

The C(1s) spectra for primer and substrate failure surfaces are shown in Figures 4c and 4d, respectively. Both spectra showed a decrease in concentration of carbon bound to nitrogen (band 2) when compared with the C(1s) spectrum of a neat primer film (Figure 4a). In addition, there was no evidence of intact amide functional groups (band 4 of Figure 4a) in either Figures 4c or 4d. Most or all of the amide linkages have then been hydrolyzed in the high pH environment. Bands due to bicarbonates (288.0 eV) and carbonates/carboxylic acids (288.8 eV) were also seen in Figures 4c and 4d. Their presence was attributed to primer degradation products (organic sodium salts) which again explained the relatively high concentration of sodium detected on failure surfaces.

The O(1s) spectrum of a primer failure surface is shown in Figure 4c. Concentrations of oxidized material, both free carboxylic acid (533.6 eV) and bicarbonate (531.0 eV), increased relative to carbon bound to oxygen (532.6 eV). Relative concentrations of these materials were in contrast to that seen for the O(1s) spectrum of a neat primer film (Figure 4a). No evidence of intact amide functional groups was seen in Figure 4c which was evident by the lack of a band at 531.6 eV. Both C(1s) and O(1s) spectra of primer failure surfaces indicated amide hydrolysis resulted in formation of carboxylates and amines. The smaller nitrogen containing polymer fractions migrated away from the delaminated surface or were rinsed off after delamination. This would account for the drastic

TABLE III

Composition of clean polished substrate, neat primer film, and primer and substrate failure surfaces after cathodic delamination

Sample	C	O	Fe	N	Si	Ca	Cr	Zn	Cl	Na
Clean polished substrate	29.7	56.6	13.8	—	—	—	—	—	—	—
Neat primer film	72.3	16.8	0.1	10.1	—	—	—	—	—	—
Cathod. delam. primer	71.7	20.4	0.1	1.2	3.6	0.1	0.5	0.2	0.3	1.3
Cathod. delam. substrate	62.4	28.6	0.8	1.7	1.3	0.4	1.8	0.4	0.1	2.0
Cathod. delam. primer (post cured pH 8, γ-APS applied to substrate)	79.1	12.4	0.5	4.5	2.3	0.4	0.6	0.3	—	—
Cathod. delam. substrate (post cured pH 8, γ-APS applied to substrate)	80.9	11.4	0.4	5.0	0.6	0.4	0.5	0.3	—	0.6

decrease in nitrogen content detected in the survey spectrum of delaminated primer.

The O(1s) spectrum of the substrate failure surface is shown in Figure 4d. Again, no evidence of intact amide functional groups was seen in Figure 4d. The major component of Figure 4d was carbon bound to oxygen (presumably due to epoxy resin). The relative concentrations of carboxylic acid and bicarbonate were seen to be greatly decreased when compared with Figure 4a.

Residual nitrogen was detected on substrate failure surfaces (a band near 400 eV in the XPS survey spectra) and may indicate that the site of delamination was within the primer, yet very near the substrate surface. However, primer degradation products may deposit onto substrate failure surfaces during delamination giving the false impression that delamination occurs cohesively. Additional evidence for primer degradation and the subsequent precipitation of degraded polymer were obtained by simultaneously immersing a clean polished steel substrate and a primer-coated steel substrate in the same 1 N NaOH solution. As mentioned earlier, after immersion for two weeks the C(1s) spectrum for the steel substrate was obtained (Figure 1b). Figure 1b showed contributions from C—H at 284.6 eV, C—N at 285.5 eV, C—O at 286.1 eV, N—C=O at 287.0 eV, HCO_3^- at 288.0 eV, and CO_3^{-2} at 289.8 eV. Presence of intact amide linkages indicated relatively large polymer fractions were cleaved, and migrated to the steel surface where they were deposited. This may also occur during cathodic delamination experiments where the initial site of delamination is at the steel/coating interface. Further degradation of the coating may then occur, resulting in deposition of polymer fractions on the delaminated steel surface.

E Cathodic delamination of coatings with γ-APS added to the primer

In these experiments γ-APS was added directly to the primer to test its effect on adhesion and resistance to degradation during cathodic polarization. XPS survey spectra of the outer surface of a primer film where γ-APS was added, were found to be similar to Figure 3. However, the surface concentration of nitrogen was seen to decrease with increasing γ-APS content, while the silicon concentration increased. Table IV lists the elemental concentrations for the outer surface of neat primer films and primer films containing γ-APS. Variations in silicon and nitrogen concentrations were taken as evidence for displacement of the nitrogen-containing curing agent (polyamide) from the surface by γ-APS.

The C(1s) spectrum of an outer surface of a primer film containing 10% γ-APS

TABLE IV
Composition of primer films containing γ-APS

Silane concentration	C(%)	O(%)	N(%)	Fe(%)	Si(%)
-0-	72.3	16.8	10.1	0.1	0.0
3%	77.7	16.5	4.0	0.1	1.7
10%	60.6	16.9	4.5	0.0	3.1

was seen to be similar to that of the C(1s) spectrum of a neat primer film (Figure 4a). However, the level of carbon bound to nitrogen (band 2) was seen to be much greater relative to concentrations of both carbon singly and doubly bound to oxygen. The nitrogen present on the surface of the primer film was then predominantly due to γ-APS and not from the polyamide curing agent.

Survey spectra of substrate and primer failure surfaces were found to be similar showing the presence of carbon, nitrogen, oxygen, iron, zinc, and chromium. Levels of these metals were, however, found to be greater in the spectrum of the substrate failure surface. C(1s) spectra of primer and substrate failure surfaces were seen to be very similar to those of failure surfaces (Figures 4c and 4d, respectively) where no γ-APS was added to the primer. No evidence of intact amide groups were seen in the C(1s) spectra indicating delamination proceeded by means of hydrolysis and occurred near or at the substrate interface. A decrease in the amount of carbon bound to nitrogen indicated that cleaved polymer fractions may have been removed from the failure surface during delamination or afterwards while rinsing. There was not as drastic a decrease in the concentration of carbon bound to nitrogen as was detected for the primer failure surface of Figure 4c. Cleaved polymer fractions were then predominantly from degraded polyamide curing agent. Cathodically delaminated coatings containing 3% γ-APS (in the primer) behaved similarly to those containing 10%.

F Cathodic delamination of coatings with an intermediate silane layer between substrate and primer

A γ-APS layer, between the epoxy/polyamide primer and the substrate, greatly increased adhesion of the primer to the substrate during cathodic delamination. The γ-APS layer was applied at pH 8.0 and cured at 110°C for 15 minutes before application of the epoxy/polyamide primer. The rate of cathodic delamination was decreased by a factor of two times that over samples not having this layer. This was attributed to increased adhesion between primer, silane layer, and substrate. For these samples alone, coatings could not be forcibly peeled from the substrate during cathodic delamination. Neither OH^- ions nor H_2O molecules were detected as being able to displace the coating from the substrate.

XPS survey spectra of substrate and primer failure surfaces were nearly identical and showed contributions from only C, N, and O. The C(1s) spectra for primer (Figure 5a) and substrate (Figure 5b) failure surfaces were also nearly identical. This was not true for C(1s) spectra of primer (Figure 4c) and substrate (Figure 4d) failure surfaces where no intermediate layer of γ-APS was applied and post cured. C(1s) spectra of all other cathodically-delaminated substrate failure surfaces were very similar to that of Figure 4d. C(1s) spectra of all other primer failure surfaces were very similar to that of Figure 4c. For this case alone both C(1s) spectra of primer and substrate failure surfaces (Figures 5a and 5b, respectively) were very similar to a C(1s) spectrum of a typical *primer* failure surface (Figure 4c).

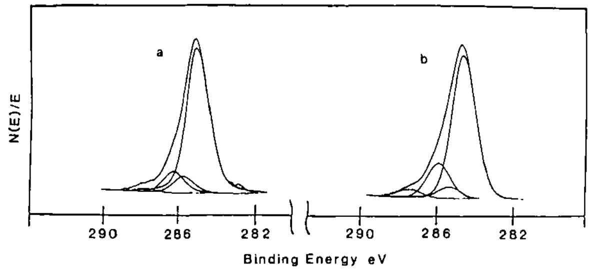


FIGURE 5 C(1s) spectra obtained from (a) primer and (b) substrate failure surfaces after cathodic delamination. A layer of γ-APS was applied to the steel substrate and cured at elevated temperature before the epoxy/polyamide coating was applied.

O(1s) spectra of primer and substrate failure surfaces, where a post-cured pH 8.0 γ-APS layer was applied, were similar. In addition, they were much like those of the O(1s) spectrum for typical primer failure surfaces (Figure 4c). The major contributor to typical primer failure surfaces (Figure 4c) was oxygen singly bound to carbon. Minor contributions from bicarbonate and carboxylic acid were present, but in lower concentrations than for typical primer failure surfaces (Figure 4c).

Similarities between XPS survey, C(1s), and O(1s) spectra indicate the site of delamination was different from that of all other coatings. C(1s) and O(1s) spectra for both failure surfaces (primer *versus* substrate) appear similar to those of typical failed primer spectra where no γ-APS layer was applied and post cured. This led us to conclude that the site of failure for these samples was more cohesive than for other coatings cathodically delaminated. While failure was more cohesive in nature, primer degradation in the high pH environment was still responsible for coating delamination. This was evident from the lack of bands characteristic of intact amide functional groups in either the C(1s) or O(1s) spectra. No band attributable to carbon doubly bound to oxygen, at 288 eV (band 4 of Figure 4a), was detected. Likewise, O(1s) spectra showed no band due to amide oxygen at 531.6 eV (band 2 of Figure 4a). The more cohesive site of failure may indicate the primer was more tightly bound to the substrate and would not allow lifting of the film by the high osmotic pressures at the substrate interface. OH^- ions were then forced to migrate away from the substrate interface into the primer and caused delamination to proceed by means of amide hydrolysis further from the substrate. Compositions of primer and substrate failure surfaces obtained from high resolution multiplex spectra are listed in Table III.

Non post-cured γ-APS layers did not show a remarkable increase in adhesion between coating and substrate for either pH solution studied. The rate for cathodic delamination to occur was comparable with that found for samples which did not have intermediate layers of γ-APS. For both pH solutions studied, silicon was detected on substrate failure surfaces but not on failed primer surfaces. This indicated that part or all of the γ-APS layer remained attached to the substrate, and the site of failure was again within the primer. Degradation of the primer was again evident from the lack of intact amide functional groups.

G Blister formation

In other experiments, coated steel was scored to produce a defect, immersed in an aerated 3.5% NaCl solution, and cathodically protected for a period of two weeks. After removal, the sample was rinsed with distilled water and blown dry in a stream of nitrogen. Coatings treated in this way (not completely dried over desiccant) were easily peeled away from the steel substrate. Detached coatings showed indentations corresponding to formation of blisters at the steel/primer interface. Indentations were only found at the steel/primer interface, indicating that blister formation occurred as a result of cathodic production of hydroxide ions. In addition, blisters were only formed in areas removed from the scribe mark, indicating that delamination proceeded laterally outward from the scribe marks as a result of lateral diffusion of H_2O and O_2 rather than by lifting of the film by blisters which were a result of diffusion of H_2O and O_2 through the film.

A coated steel coupon which was scored and immersed in an aerated 3.5% (w/v) NaCl solution without being cathodically protected did not show signs of blister formation over a period of several months. Only normal corrosion of the exposed metal at the defect was observed. In this case delamination of the coating was a result of corrosion of the metal under the coating. After removal from solution and prior to drying, the coating was found to be easily peeled away from the substrate. The substrate beneath this coating was bright and shiny while that beneath the delaminated region was corroded. After drying, the coating was again found to exhibit good adhesion to the substrate. Presence of water at the substrate interface was believed to disrupt the bonding of the primer to steel substrate.

Formation of blisters was seen to occur beneath all coatings studied by cathodic delamination, except for those samples prepared with an intermediate pH 8.0 layer of γ-APS that had been post cured at elevated temperatures. For those samples prepared with an intermediate layer of γ-APS (both pH 8.0 and 10.4) and not post cured at elevated temperatures, formation of blisters proceeded at a much slower rate than samples not having an intermediate layer of γ-APS. As mentioned earlier, a post cured pH 8.0 layer of γ-APS was believed to increase the adhesion of primer to substrate. This increased adhesion decreased the potential for high osmotic pressures, a result of OH^- ion concentration, to cause blistering or delamination of the coating at the substrate interface.

IV CONCLUSIONS

Cathodic delamination of an epoxy/polyamide primer from steel was the result of degradation of amide linkages by the high pH environment. Our results closely parallel those reported by Dickie for delamination of an epoxy/urethane coating on steel. Dickie saw, as we do, a decrease in the concentration of nitrogen and attributed it to coating degradation. In addition, carbonates were found on their failed surfaces and were attributed to products of coating degradation. We also saw an increase in concentration of carbonate and carboxylate residues in the O(1s) spectrum of failure surfaces and attributed them to build up of primer degradation products.

The site for cathodic delamination was determined to be at or very near the substrate surface. The presence of polymer on the failed substrate surface indicated the site of failure could be within the primer. However, it is also possible for cleaved primer residue to precipitate onto the steel substrate after delamination. This would indicate that the site of delamination was at the primer/substrate interface. Leidheiser and Koehler have also concluded that the site of their coating delamination was at the coating/substrate interface. They attributed delamination to disruption of the coating-substrate bonds by OH^- ions. Any residual coating found on their substrate after delamination was then attributed to precipitation of degradation products onto the surface following coating hydrolysis. The fact that wet primer films can be easily peeled from our substrate surface also indicated that disruption, by H_2O or OH^- ions, of the polymer/substrate bonds was an important step in cathodic delamination.

Blister formation was determined to be a result of cathodic protection of steel. Oxygen and water diffused through the coating and were reduced to OH^- ions. High concentrations of OH^- ions at the substrate surface caused large osmotic pressure differences which subsequently lifted coatings away from the substrate.

Addition of γ-APS directly to the primer did not appear to increase resistance to cathodic delamination. Cathodic delamination proceeded in much the same way as when γ-APS was not added.

Intermediate layers of γ-APS applied directly to the substrate retarded blister formation. However, they did not significantly decrease the rate of cathodic delamination unless they were post cured at elevated temperatures prior to primer application. The site of delamination for a coating with a pH 8.0 post-cured γ-APS layer was more cohesive in nature. Previously the site of delamination was determined to be either at or at least near the substrate interface. Post-cured pH 8.0 γ-APS films were believed to have increased adhesion of the primer to the substrate. Cathodic delamination was then forced to occur more cohesively from within the primer and, therefore, further removed from the substrate interface. This resulted in an increase in the time required for cathodic delamination by approximately a factor of two.

V References

1. H. Leidheiser and W. Wang, *J. Coat. Tech.* **53,** No. 672, 77 (1981).
2. M. L. White, H. Vedage, R. D. Granata and H. Leidheiser, *Ind. Eng. Chem. Prod. Res. Dev.* **25,** 129 (1986).
3. E. L. Koehler, *Corrosion* **40,** 5 (1984).
4. J. F. Watts and J. E. Castle, *J. Mat. Sci.* **18,** 2987 (1983).
5. J. F. Watts and J. E. Castle, *J. Mat. Sci.* **19,** 2259 (1984).
6. F. J. Boerio, S. J. Hudak, M. A. Miller and S. G. Hong, *J. Adhesion* **23,** 99 (1987).
7. R. A. Dickie, J. S. Hammond and J. W. Holubka, *Ind. Eng. Chem. Prod. Res.* **20,** 339 (1981).

8. J. W. Holubka, J. S. Hammond, J. E. Devries and R. A. Dickie, *J. Coat. Tech.* **52,** 63 (1980).
9. A. Dilks, in *Electronic Spectroscopy: Theory Techniques and Applications, Vol.* 4, C. R. Brundle and A. D. Baker, Eds. (Academic Press, N.Y., 1981).
10. D. T. Clark and H. R. Thomas, *J. Poly. Sci.* **16,** 791 (1978).
11. *Encyclopedia of Polymer Science and Engineering, Vol.* 6, J. I. Kroschwitz Ed. (Wiley Interscience, N.Y., 1987), p. 352.
12. J. P. Bell and W. T. McCarvill, *J. Appl. Poly. Sci.* **18,** 2243 (1974).
13. D. T. Clark and H. R. Thomas, *J. Poly. Sci.* **16,** 791 (1978).