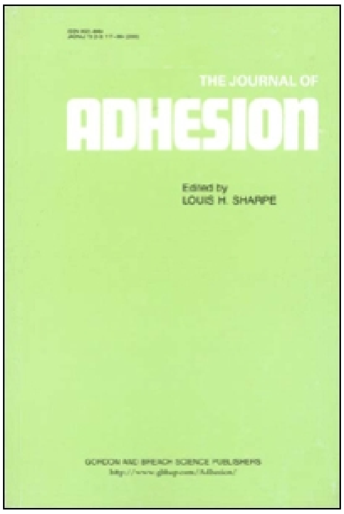

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Cathodic Debonding of Neoprene from Steel†

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X-ray photoelectron spectroscopy (XPS) has been used to determine the failure mechanisms in neoprene/steel adhesive bonds during cathodic delamination or during immersion in aqueous solutions of NaOH to simulate the effects of cathodic delamination at the bondline. Delamination of the rubber from substrates that had been pretreated by acid-etching began at the edges of the bonds and proceeded slowly inward. The centers of the bonds were always intact except for every long times when complete delamination of the rubber was observed. Failure was near the primer/oxide interface but with islands of rubber remaining on the substrate and islands of oxide remaining on the rubber. The failure mechanism was associated with degradation of the phenolic primer and with dehydrohalogenation of chlorinated rubber in the adhesive and primer. Dehydrohalogenation resulted in the formation of inorganic salts which could dissolve during exposure to water at high pH values, leading to large osmotic pressures at the interface. Debonding of rubber from polished substrates was much faster, leaving little rubber on the substrate failure surfaces and little oxide on the rubber failure surfaces, and indicating that mechanical interlocking of the rubber with the substrate has an important effect on the environmental stability of rubber-to-metal bonds.

KEY WORDS Cathodic delamination; chlorinated rubber adhesives; durability; phenolic primers; rubber-to-metal bonding; X-ray photoelectron spectroscopy.

I INTRODUCTION

The acoustical window on wet-end sonar transducers is usually prepared by curing a slab of neoprene in contact with a steel shroud

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and an aluminum head mass that have been pretreated with adhesive systems consisting of metal primers and adhesives. The resulting adhesive bonds must withstand mechanical stresses, temperature extremes, and chemical attack by sea water. Debonding would lead to the entry of water and loss of function in the transducer.

Several investigations concerned with the environmental stability of rubber-to-metal bonds have been reported recently. Ting[1] used the conical button and 90° peel tests to evaluate seven commercial, proprietary adhesive systems for elastomer/metal bonding in transducers. Most of the adhesive systems provided adequate dry strength in the conical button test and failure was usually cohesive within the rubber. However, when 90° peel specimens were statically loaded and immersed in sea water, some attack of the bondline occurred, especially in the presence of oxygen, and failure of the bonds became more interfacial.

Ting[2] subsequently suggested that electrochemical reactions could affect the durability of rubber-to-metal bonds in sonar transducers. The steel shrouds of poorly insulated transducers could become cathodic with respect to sacrificial zinc anodes attached to the hull of a ship and hydroxyl ions generated by the reduction of oxygen at the steel surface could lead to debonding of the rubber. Ting[2] also suggested that chloride ions released during the degradation of adhesives or primers containing chlorinated rubber might lead to corrosion of the steel substrate and to debonding of the acoustical window.

Stevenson[3] has also investigated the durability of rubber-to-steel bonds during immersion in sea water and found that the mechanical properties of most rubbers were not significantly degraded even when they absorbed large amounts of water and that most bonds were stable in electrochemically inert environments. However, when cathodic potentials were applied to the steel, rapid failure of the bonds occurred but without corrosion of the steel. Delamination always proceeded inward from an exposed edge and was not affected by the type of rubber or by the application of shear stresses to the rubber. Stevenson did not determine the failure mechanism for rubber-to-steel bonds undergoing cathodic delamination but speculated that hydroxyl ions resulting from the reduction of hydrogen ions or oxygen at the steel surface were involved.

Several research groups have investigated cathodic delamination of coatings and adhesives from steel and proposed mechanisms to explain their results. Dickie and coworkers[4–6] immersed coated steel panels in 5% NaCl solutions at a potential of −1.05 volts *versus* SCE, measured the delamination of the coatings away from a scribe line as a function of time, and used X-ray photoelectron spectroscopy (XPS) to determine the composition of the "coating" and "substrate" failure surfaces. Derivitization and curve-fitting techniques were used to show that carboxylate groups, which were attributed to hydrolysis of ester groups, were present on the failure surfaces of epoxy-ester coatings and on the surfaces of neat coatings immersed in NaOH solutions but not on the surfaces of the neat coatings. Considering that polymer residues were also detected on the substrate failure surfaces, it was concluded that cathodic delamination involved degradation of the coatings very near the coating/oxide interface.[4]

Similar investigations were carried out for epoxy/amine and epoxy/urethane coatings.[5,6] The failure surfaces of the epoxy/urethane coatings contained more oxygen and less nitrogen than the surface of the neat coating and more sodium than could be explained as NaCl. When the coating failure surface was rinsed with distilled water, the sodium and oxygen concentrations were greatly reduced. It was concluded that a water-soluble salt, sodium carbonate, had formed on the coating failure surface from the hydrolysis products of the urethane groups. Sodium carbonate and small amounts of the epoxy/urethane polymer were found on the substrate failure surface and it was again concluded that cathodic delamination was related to degradation of the coatings near the coating/oxide interface.

The epoxy/amine coatings were more resistant to cathodic delamination than the epoxy/urethane coatings but the failure mechanisms were similar. Sodium carbonate, formed from the hydrolysis products of urea groups in the crosslinking agent, was observed on the coating and substrate failure surfaces and some residual coating was found on the substrate. Once again delamination was attributed to degradation of the resin near the interface.

Watts and Castle[7,8] conducted experiments on the cathodic delamination of polybutadiene and epoxy coatings from steel panels in 3% NaCl at a potential of −1.05 volts *versus* SCE. They measured the delamination away from a circular defect at the center of the panels and used XPS to characterize the coating and substrate failure surfaces. Polybutadiene was a reducing agent when cured against steel.[7] Fe^{+3} ions in the oxide were reduced to Fe^{+2}, providing an interphase with unique composition between the coating and the oxide. Two types of delamination were observed for the polybutadiene coating. Near the circular defect, the interphase itself was attacked and remained attached to the coating failure surface. However, a few millimeters away from the defect the polymer near the interphase was attacked and the interphase remained attached to the substrate.

Somewhat similar results were obtained in the case of epoxy coatings.[8] Near the circular defect, the oxide was reduced and the coating was delaminated. Thereafter, the failure was associated with hydrolysis at the coating/oxide interface. Carbonates were detected on the failure surfaces using XPS but only after an induction time of several weeks. It was concluded that the carbonates were associated with carbon dioxide absorbed by the test solutions and not with degradation of the coatings. Watts and Castle[8] also investigated the effects of substrate surface roughness on cathodic delamination and found that roughness affected the rate of debonding but not the mechanism.

The purpose of this paper is to describe the use of X-ray photoelectron spectroscopy to determine the failure mechanisms in neoprene/steel bonds undergoing cathodic delamination.

II EXPERIMENTAL

Adhesive joints were prepared by curing neoprene in contact with steel in the strip-blister configuration (see Figure 1). Steel coupons (1 × 6 × 0.063″) were cut from large sheets of interstitial-free steel, cleaned in an aqueous solution of a commercial alkaline cleaner (Parko 338, Parker Chemical Co.) at approximately 60°C, rinsed in water, and cleaned again. After the second cleaning step, the coupons were rinsed and then etched in a solution containing 5% nitric acid, 30% phosphoric acid, and 65% distilled water by volume as described by Trawinski.[9] Trawinski recommended that a small amount of fluorinated surfactant also be added to the etching

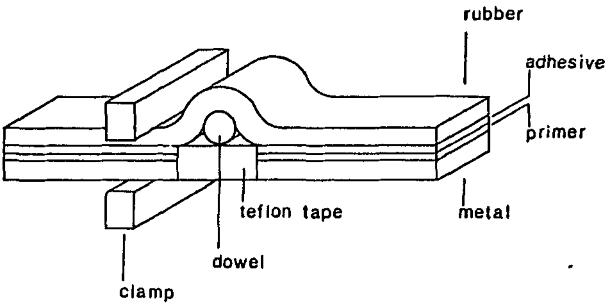

FIGURE 1 Diagram of the strip-blister specimen.

solution but that was omitted here. A metal primer and adhesive (Chemlok 205 and Chemlok 220, Lord Corporation) were applied to the cleaned, etched coupons by brushing and neoprene rubber was cured in contact with the steel by compression molding at 155°C for 45 minutes. The rubber composition is given in Table I.

A debonded region was provided near one end of the specimen by covering the substrate with fluorocarbon tape before the rubber was applied and cured. After curing, a fluorocarbon rod 0.375" in diameter was inserted between the rubber and the fluorocarbon tape to apply a load at the tip of the debonded region. A clamp was applied at one end of the debond to prevent crack propagation in that direction.

The strip-blister specimens were aged in several ways. In some cases, the steel substrates were connected directly to sacrificial zinc anodes in 3.5% aqueous solutions of NaCl. In other cases, the steel substrates were held at a potential of −1.05 volts *vs* SCE in 3.5% NaCl. However, in most cases, the strip-blister specimens

TABLE I

Composition of neoprene rubber

Neoprene GRT	100.0 parts
Stearic acid	1.0
Carbon black	31.0
Red lead dispersion	15.0
Octylated diphenyl amine	2.0
MBTS	1.5
TE-70 processing aid	2.0

were simply immersed in 1N aqueous solutions of NaOH to simulate the conditions obtained at the bondline in the other two types of enviromments.

At appropriate intervals, specimens were removed from the test solutions and examined visually. It was usually observed that delamination progressed slowly inward from the initial debond and from exposed edges of the specimens and that the innermost portions of the bonds remained intact. Delamination was not observed in a few cases where the bondline was covered by rubber during the molding operation and not exposed directly to the test solution. The rate of delamination was decreased when pressure was applied to the faces of the specimens as by the clamps (see Figure 1).

The rubber was removed from the substrate to expose the "rubber" and "substrate" failure surfaces by cutting the intact bonds near the centers of the joints with a sharp blade. Samples for surface analysis were cut from both failure surfaces, rinsed in water, and dried. The rubber samples were usually outgassed at room temperature under vacuum in an oven or a desiccator for a few days before surface analysis.

XPS spectra of the failure surfaces were obtained using a Physical Electronics 5300 X-Ray Photoelectron Spectrometer and Mg K_α radiation. Reference spectra were also obtained from the cured rubber and from films of the adhesive and primer that were cast onto steel substrates and then cured at elevated temperatures. All observed spectra were corrected for the effects of sample charging by referring the C(1s) binding energy for saturated hydrocarbons to a value of 284.6 eV.

III RESULTS AND DISCUSSION

The O(1s), C(1s), Cl(2p), and Pb(4f) spectra observed for the primer, adhesive, and rubber are shown in Figure 2 and summarized in Table II. The XPS results were consistent with results obtained from infrared spectroscopy[10] which showed that the primer was mostly a phenolic polymer blended with a chlorinated rubber and that the adhesive was mostly a chlorinated rubber.

The Cl(2p) spectrum obtained from the adhesive consisted of a

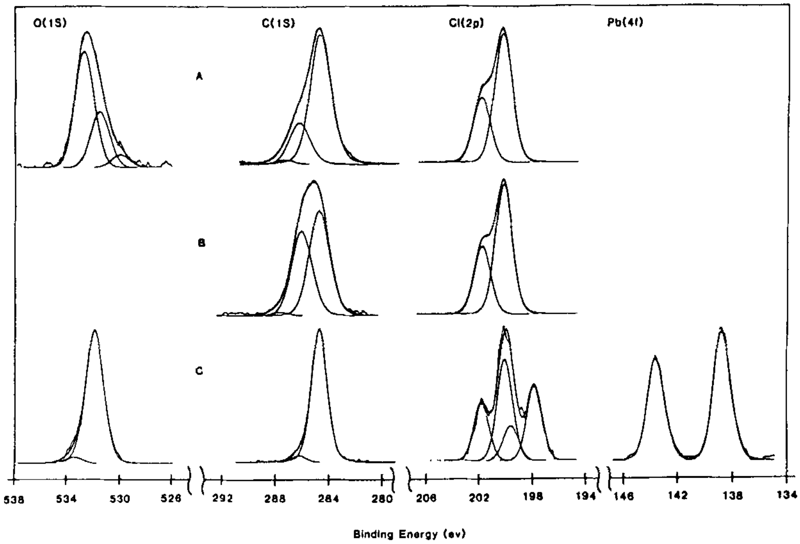

FIGURE 2 XPS spectra observed for (A)-primer, (B)-adhesive, and (C)-neoprene rubber.

doublet near 200.1 and 201.7 eV due to $2p_{1/2}$ and $2p_{3/2}$ electrons and the C(1s) spectrum was a doublet separated by about 1.3 eV due to the primary and secondary substituent effects of chlorine on carbon. Such spectra are very characteristic of chlorinated hydrocarbons.[11] The C(1s) spectrum of the primer consisted mostly of bands near

TABLE II
XPS spectra observed for primer, adhesive, and neoprene

	Pb(4f)	Cl(2p)	C(1s)	O(1s)
Primer		200.1	284.6	530.2
		201.7	286.2	531.7
			287.4	532.9
			291.3	
Adhesive		200.1	284.6	
		201.7	285.9	
Neoprene	138.6	197.8	284.6	531.6
	143.5	199.2		
		200.1		
		201.7		

284.6 and 286.2 eV that are typical of hydrocarbons containing hydroxyl groups[11] and the Cl(2p) spectrum was a doublet near 200.1 and 201.7 eV. O(1s) spectra of the primer consisted of three bands near 530.2, 531.7, and 532.9 eV. The band near 532.9 eV was related to phenolic oxygen while those near 530.2 and 531.7 eV were probably related to inorganic fillers such as TiO_2 and ZnO and aluminosilicates which are known to be present in the primer from infrared spectroscopy[10] and from energy-dispersive X-ray analysis or EDAX.[10,12]

Some interesting features were observed in the spectra of the rubber. A pair of lines related to Pb $4f_{7/2}$ and $4f_{5/2}$ electrons was observed near 138.6 and 143.5 eV. The Cl(2p) spectra consisted of two pairs of lines, attributed to $2p_{3/2}$ and $2p_{1/2}$ electrons from organic (200.1 and 201.7 eV) and inorganic (197.8 and 199.2 eV) chlorides. The inorganic chlorides were presumably lead chlorides formed by the reaction of the red lead (Pb_3O_4) curing agent with tertiary, allylic chlorides in neoprene during the curing reaction and the binding energies of Pb($4f_{7/2}$) and Pb($4f_{5/2}$) electrons in $PbCl_2$ were in fact observed near 138.5 and 143.4 eV. O(1s) spectra from the rubber consisted of a single band near 531.6 eV. The binding energies of oxygen atoms making one or two bonds with carbon are usually higher by at least 1.0 eV.[11] Therefore, the band near 531.6 eV in the O(1s) spectra of the rubber is probably related to unreacted Pb_3O_4 curing agent.

XPS spectra obtained from the "substrate" and "rubber" failure surfaces of a strip-blister specimen that was immersed in 1N NaOH for eight days are shown in Figure 3 and summarized in Table III. Iron was found on both surfaces, implying that the failure was near the interface but partly within the oxide and partly within the organic phase. The O(1s) spectra from the substrate failure surface were complex and contained four main bands, near 529.7, 531.0, 531.8, and 532.9 eV, and weak bands near 534.1 and 535.5 eV. The bands near 529.7 and 531.0 eV were characteristic of oxides and hydroxides on the surface of the substrate but the bands near 531.8 and 532.9 eV were typical of the primer, indicating that failure of the specimens was near the primer/oxide interface. The C(1s) spectrum of the substrate failure surface consisted of the band near 284.6 eV due to saturated hydrocarbons and additional bands that were shifted upwards in binding energy by about 1.6, 3.0, and

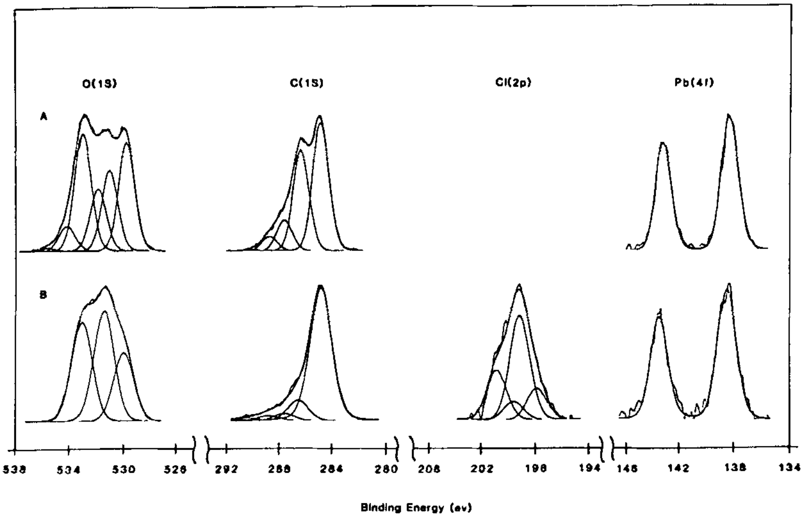

FIGURE 3 XPS spectra observed for (A)-substrate and (B)-rubber failure surfaces of strip-blister specimens prepared from acid-etched steel and then immersed in 1 N NaOH for eight days.

4.1 eV and assigned to carbon forming one, two, or three bonds with oxygen. As described above, carbon forming one bond with oxygen was found in the primer but more highly oxidized forms of carbon were not and it was concluded that carboxylate groups may have been formed in the primer during the debonding reaction.

TABLE III
XPS spectra observed for substrate and rubber failure surfaces of neoprene/steel strip-blister specimens prepared from acid-etched substrates

	Pb(4f)	Cl(2p)	C(1s)	O(1s)
Substrate	138.2		284.6	529.7
	143.0		286.2	531.0
			287.6	531.8
			288.7	532.9
				534.1
				535.5
Rubber	138.3	198.0	284.6	530.1
	143.2	199.1	286.1	531.5
		199.6	287.3	533.0
		200.7	288.7	

Lead was always observed on the substrate failure surfaces. Some of the lead may have come from the lead chlorides formed in the rubber during curing, indicating the presence of small islands of rubber remaining on the substrate failure surface or from diffusion of lead from the rubber into the interface during curing. However, small amounts of lead, which may have diffused to the interface during curing, have also been found in the adhesive.[12]

The O(1s) spectra of the rubber failure surface had bands near 533.0, 531.5, and 530.1 eV which were all typical of the primer. However, the intensity of the band near 531.5 eV was greater than expected for the primer, perhaps due to segregation at the interface of oxide fillers in the primer. Residual NaOH may also have contributed to the intensity of the band near 531.5 eV. C(1s) spectra of the rubber failure consisted of the usual strong band near 284.6 eV that is characteristic of hydrocarbons and weaker bands shifted toward higher energies by 1.5, 2.7, and 4.1 eV that were related to carbon forming one, two, or three bonds with oxygen.

An interesting result concerned the nature of the chlorine present on the rubber failure surfaces. As discussed above, the Cl $2p_{1/2}$ and $2p_{3/2}$ spectra of the primer were observed near 200.1 and 201.7 eV, as expected for chlorinated hydrocarbons. The Cl(2p) spectra obtained from the rubber failure surface contained additional bands near 198.0 and 199.1 eV, perhaps indicating some breakdown of the chlorinated rubber in the primer and the formation of metal chlorides. However, it was also possible that the inorganic chlorides on the rubber failure surfaces simply indicated that the locus of failure was at least partly within the rubber. As discussed above, the formation of a lead chloride during curing was expected and an inorganic chloride was in fact observed on the surface of neoprene that was cured but never exposed to NaOH (see Figure 2).

In order to determine the significance of the lead and the inorganic chlorides found on the rubber and substrate failure surfaces, several strip-blister specimens were prepared as described above except that the steel substrates were mechanically polished before the primer and adhesive were applied. These samples were immersed in 3.5% NaCl and held at a potential of −1.05 volts *vs* SCE. Debonding of the rubber from the polished steel was rapid and complete delamination was observed within a few days. By comparison, debonding from the etched steel substrates was relatively slow and complete delamination sometimes required several months.

The large differences in the rate of delamination from etched and polished substrates may have been related to differences in surface composition or morphology of the substrates. Results obtained from XPS indicated that there were differences in surface composition. A small amount of phosphorous, presumably due to a phosphate, was found on substrates that were etched but not on those that were polished. However, the debonding of neoprene from grit-blasted substrates, with no phosphates present on the surface, was also very slow. Therefore, it seems likely that surface morphology, and not surface composition, was responsible for the difference in the rate at which neoprene debonded from etched and polished substrates and that mechanical interlocking between the rubber and asperities on the surface of the substrate contributed significantly to the bond strength. As described earlier, Watts and Castle[8] reported similar results.

When XPS spectra were obtained from the failure surfaces of joints prepared from polished substrates, some interesting results were obtained (see Figure 4 and Table IV). There was very little

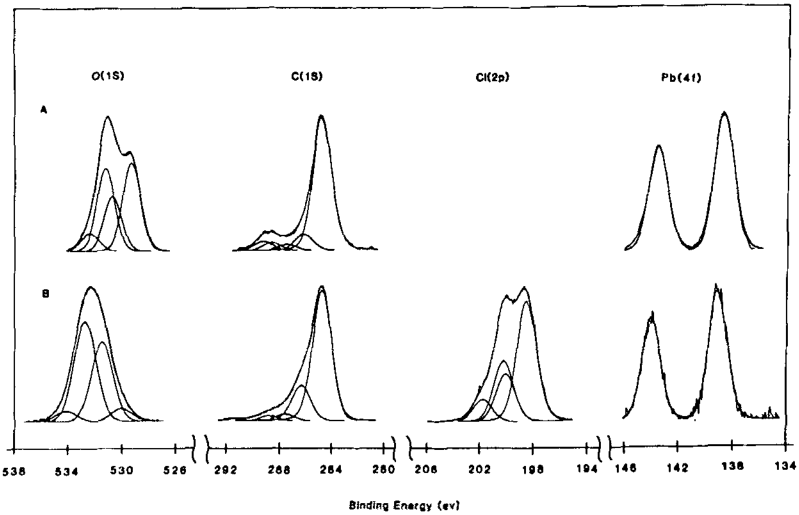

FIGURE 4 XPS spectra observed for (A)-substrate and (B)-rubber failure surfaces of strip-blister specimens prepared from mechanically polished steel and then immersed in 3.5% NaCl at a potential of −1.05 volts *vs* SCE.

TABLE IV
XPS spectra observed for substrate and rubber failure surfaces of neoprene/steel strip-blister specimens prepared from polished substrates

	Pb(4f)	Cl(2p)	C(1s)	O(1s)
Substrate	138.4		284.6	529.4
	143.2		286.1	530.8
			287.4	531.4
			288.6	532.6
			289.2	
Rubber	138.8	198.4	284.6	530.2
	143.6	200.0	286.2	531.7
		200.1	287.4	532.9
		201.7	288.6	534.3
			289.2	
			291.2	

iron on the rubber failure surface and the O(1s) spectra were similar to those of the primer. O(1s) spectra of the steel failure surface were characterized by bands near 531.4, 530.8, and 529.4 eV that were attributed to carbonates, hydroxides, and oxides on the substrate, respectively. Failure was evidently very near the primer/oxide interface and there was little evidence for primer left on the substrate. The Cl(2p) spectra obtained from the rubber failure surface had components near 198.4 and 200.1 eV due to inorganic chlorides and near 200.0 and 201.7 due to organic chlorides. Very similar spectra were obtained from the failure surface of the primer that had delaminated from *beneath* the fluorocarbon tape that was used to provide the initial debond (see Figure 1). Since there was no possibility of rubber remaining on that surface, it was concluded that the inorganic chlorides were formed by dehydrohalogenation of chlorinated rubber in the primer or adhesive and reaction of the chlorine with lead or zinc which are present in the adhesive and primer.

Several experiments were conducted to determine whether dehydrohalogenation occurred during exposure to water at high pH values or during curing. In one case, infrared spectroscopy was used to determine the stability of chlorinated rubber films as a function of immersion time in aqueous solutions of NaOH. Very little change was observed, even after immersion of the films in 2.8 N NaOH for several weeks, indicating that chlorinated rubbers, such as are found in the primer and adhesive, are stable in water at high pH values.[13] In another case, the Cl(2p) XPS spectra of neat films of the primer were examined before and after the surfaces of the films were etched by sputtering briefly with argon ions. Before sputtering only bands attributed to organic chlorides were observed. After sputtering lightly, the bands related to inorganic chlorides appeared, implying that the inorganic chlorides were formed during curing but were covered by a thin polymer layer on the surface of the primer film.

The C(1s) spectra of the substrate failure surface were characterized by the usual band near 284.6 eV but with a component shifted upward in binding energy by about 4.6 eV due to the surface carbonates.[4] Bands characteristic of lead were observed near 138.4 and 143.2 eV, suggesting that the carbonates on the steel surface were lead carbonates. Reflection infrared spectra obtained from the steel failure surface confirmed the presence of lead carbonate.[13] There was a considerable amount of lead on the rubber and steel failure surfaces except from beneath the fluorocarbon tape, implying that lead did diffuse from the rubber into the bondline during curing.

The results described above suggest two possible mechanisms for the debonding of neoprene rubber from steel during cathodic delamination or during exposure to environments, such as aqueous solutions of NaOH, meant to simulate conditions obtained at the bondline during cathodic delamination. They include degradation of the phenolic resin in the primer and the presence of large osmotic pressures at the interface.

Degradation of the primer could occur by oxidation of the methylene linkages between phenol residues to form carboxylic acids and quinones[14] or by alkaline hydrolysis of the methylene linkages to form phenol and carbon dioxide.[15] Some support for each mechanism has been obtained. As discussed above, carboxylate groups have been detected in XPS spectra obtained from the failure surfaces. Carbonates, perhaps formed by carbon dioxide resulting from alkaline hydrolysis, have also been detected. Preliminary results from infrared spectroscopy have verified that the methylene linkages between phenol residues are readily attacked when phenolic polymers are exposed to aqueous solutions of NaOH at room temperature.[13]

As described above, Watts[8] observed carbonates on the failure surfaces of epoxy coatings on steel following cathodic delamination in 0.52 M NaCl for several weeks but attributed them to precipitation of carbon dioxide absorbed by the test solutions. Hammond[6] also observed carbonates on the failure surfaces of epoxy/urethane and epoxy/amine coatings on steel following cathodic delamination for much shorter times. The carbonates were attributed to degradation of urethane and amine groups to form carbon dioxide which combined with metal ions to give carbonates which were detected by XPS. We detected carbonates on the failure surfaces of neoprene/steel strip-blister specimens prepared from polished substrates after cathodic delamination for only two days. Since the carbonates observed on the failure surfaces of the strip-blister specimens formed so quickly, they may have resulted from degradation of the primer.

Formation of salts that were soluble at neutral or high pH values could lead to large osmotic pressures at the interface and to delamination as observed by Ashbee[16] in composites. Inorganic chlorides were found on the rubber failure surfaces of strip-blister specimens that delaminated in aqueous solutions of NaOH or in aqueous solutions of NaCl when the steel substrates were held at cathodic potentials. The chlorides may have formed during delamination or during curing but, as discussed above, present indications are that chlorinated rubbers do not undergo dehydrohalogenation during immersion in concentrated solutions of NaOH.

Delamination was not observed when strip-blister specimens were exposed to aqueous solutions of NaCl without an applied potential or when the bondline was covered by rubber and not exposed directly to the test solution. Thus, diffusion of water and soluble species directly through the rubber were not important. High pH values and, in the case of cathodic delamination, exposed steel where the cathodic reduction of oxygen to form hydroxyl ions could occur, were required for debonding.

The rate of delamination decreased when pressure was applied to the rubber by the clamps that were used to ensure that the starter crack propagated in only one direction. That may indicate that osmotic pressure is an important factor in the delamination process since pressure applied to the rubber would decrease the osmotic pressure at the interface. However, pressure may also reduce the diffusion constant for water along the interface.

The failure mechanism for cathodic delamination of neoprene from steel involves degradation of the primer by hydroxyl ions and, perhaps, large osmotic pressures caused by the presence of lead chlorides at the interface which are soluble at high pH values. Additional work is in progress to determine which mechanism is most important.

IV CONCLUSIONS

Adhesive bonds between neoprene rubber and steel fail near the primer/oxide interface during cathodic delamination or during aging in aqueous solutions at high pH values to simulate the conditions obtained at the bondline during cathodic delamination. The failure mechanism involves dehydrohalogenation of chlorinated rubber in the adhesive and the primer and degradation of the phenolic resin found in the primer.

Degradation of the primer is sufficient to cause failure of the bonds. However, the presence of soluble metal chlorides at the bondline due to dehydrohalogenation could lead to large osmotic pressures at the interface during exposure of the bonds to water at high pH values and contribute to bond failure. Either failure mechanism is consistent with the previous suggestion that failure of rubber-to-metal bonds during cathodic delamination is not dependent on the nature of the rubber.

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