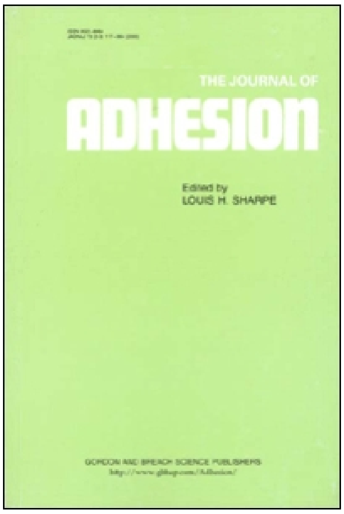

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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F. J. Boerio[a]; S. G. Hong[a]
[a] Department of Materials Science and Engineering, University of Cincinnati, Cincinnati, Ohio, U.S.A.

To cite this Article Boerio, F. J. and Hong, S. G.(1989) 'Degradation of Rubber-to-Metal Bonds During Simulated Cathodic Delamination', The Journal of Adhesion, 30: 1, 119 — 134
To link to this Article: DOI: 10.1080/00218468908048201
URL: http://dx.doi.org/10.1080/00218468908048201

J. Adhesion, 1989, Vol. 30, pp. 119–134
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Printed in the United Kingdom

Degradation of Rubber-to-Metal Bonds During Simulated Cathodic Delamination

F. J. BOERIO and S. G. HONG

Department of Materials Science and Engineering, University of Cincinnati, Cincinnati, Ohio 45221, U.S.A.

(Received November 5, 1988; in final form April 6, 1989)

Cathodic delamination of neoprene-to-steel adhesive bonds prepared using a proprietary vulcanizing adhesive and primer was investigated using Fourier-transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). Chlorinated rubber in the adhesive and primer was stable during immersion in NaOH solutions simulating the high pH conditions obtained at the bondline during cathodic delamination. However, methylene groups linking phenol moieties in phenolic resins in the primer were rapidly oxidized during immersion in NaOH solutions to form benzophenone linkages which were oxidized further to carboxylic acids and quinones. Chlorine produced by dehydrohalogenation of chlorinated rubber in the adhesive and primer during curing of the neoprene reacted with ZnO in the primer to form $ZnCl_2$ in the bondline. Failure of adhesive bonds between neoprene and steel during cathodic delamination is probably related to oxidation of the phenolic resins in the primer and to osmotic effects related to the high solubility of $ZnCl_2$.

KEY WORDS Rubber-to-metal bonding; Durability; Cathodic delamination; Oxidation; Infrared spectroscopy; X-ray photoelectron spectroscopy.

I INTRODUCTION

Adhesive systems for rubber-to-metal bonding are widely used in industry and the military. Tire manufacturers use adhesive systems for bonding rubber to steel cord in radial tires. In the offshore oil industry, pipelines are coated with rubber for corrosion protection of steel under seawater.[1] In military applications, rubber is bonded to metal substrates in acoustic absorbers, sound reflectors, and sonar transducers.[2]

Rubber-to-metal bonds are expected to last for many years in sonar transducers and oil pipelines but, because of the aggressive environments to which these bonds are exposed, it is very difficult to obtain such excellent durability. During use in seawater, rubber-to-metal bonds may suffer different kinds of rigorous adverse conditions such as chemical attack by seawater, temperature extremes, pressure cycling, and mechancial stresses. Perhaps the most detrimental condition is the highly alkaline environment which results from cathodic contact of steel substrates with other metals such as zinc and aluminum.[2] It has been reported[3] that the pH beneath a film undergoing cathodic delamination from steel can be nearly as high as 14 due to the generation of OH^- ions on the steel surface by the reduction of oxygen:

$$2H_2O + O_2 + 4e^- \longrightarrow 4OH^-$$

Many different mechanisms have been proposed to explain how the bond between a polymeric coating and a metal substrate is broken by OH^- ions at the interface. Koehler[4] stated that development of a high pH at the coating/substrate interface should have an increased effect in physically displacing the coating, just as a high pH cleaning solution is more effective than neutral water in displacing foreign substances from a metal. Koehler reported that polybutadiene coatings debonded from steel at a pH of only 11.7, which was thought to be too low to cause effective attack of the coating or the metal oxide.[4]

Hammond, Holubka, and Dickie[5] used X-ray photoelectron spectroscopy (XPS) to investigate polyethylene terephthalate and a melamine-crosslinked epoxy ester primer on steel and showed that both systems underwent surface hydrolysis to form sodium carboxylates when treated with sodium hydroxide. Hydrolysis was also observed when crosslinked epoxy ester primers on steel were exposed to cathodically-generated hydroxide ions by coupling the coated steel sample to zinc in 5% sodium chloride solution.[5] Hammond *et al.* concluded that a significant path for adhesion loss was hydrolysis of the primer resin adjacent to the coating/steel interface by cathodically-produced hydroxide ions followed by cohesive failures of the primer film.

Castle and Watts[6] also reported that alkaline degradation of the polymer was a major factor in cathodic delamination. They used XPS to study cathodic debonding of polybutadiene coatings from steel by an impressed potential of −1.5 volts *vs.* SCE in 0.52 M sodium chloride solution and found a clear separation of the coating from the metal surface. Castle and Watts suggested that alkaline hydrolysis affected the interface bond. They observed that oxide reduction occurred at the advancing edge of the debonding crevice but, owing to the random nature of this process, did not consider this an important factor causing delamination in their samples.

Ritter and Kruger speculated that dissolution of the oxide film beneath the coating was a major factor in the cathodic delamination of polybutadiene from steel.[3] Leidheiser suggested that oxide dissolution was more important than coating degradation since oxidized organic species observed on the metal failure surface could result from redeposition of oxidized species from the test solutions or from islands of organic left on the surface in the debonding process.[7]

Relatively little work has been done on cathodic debonding of rubber-to-metal bonds. Stevenson[8] reported that electrochemical potentials involved in the cathodic reaction played a dominant role in limiting durability. He found that rubber-to-metal bonds were very stable in electrochemically inert conditions and that the type of rubber, the application of shear stresses, and the amount of water absorbed did not greatly affect the rate of delamination. However, rapid failure of the bonds occurred when cathodic potentials were applied to the steel.

Stevenson suggested that hydroxyl ions resulting from the reduction of oxygen on the steel surface were reponsible for this rapid delamination but did not determine the actual failure mechanisms.

Recently, we began an investigation of cathodic delamination of adhesive bonds prepared by compression molding neoprene to steel using a proprietary primer and adhesive.[9,10] It was found that diffusion of water and soluble species directly through the rubber were not important since delamination was not observed when specimens were immersed in NaCl solutions without an applied potential or when bondlines were covered by rubber and not exposed directly to the test solutions. However, debonding of rubber from the substrates began at the edges of the bonds and proceeded slowly inward in NaOH solutions or in NaCl solutions when the steel substrate was held at cathodic potential.[9]

Results obtained from infrared spectroscopy and X-ray diffraction showed that the adhesive was mostly chlorinated rubber and carbon black dispersed in solvent. The primer consisted of chlorinated rubber, phenolic resins, carbon black, ZnO, and TiO_2 dispersed in solvents.[10] Degradation of the phenolic resin in the primer by cathodically generated OH^- ions was found to be the most important factor in the failure of these bonds.[9] Inorganic chlorides were found on the "rubber" failure surfaces using XPS. It was suggested that the inorganic chlorides were formed by dehydrohalogenation of chlorinated rubber during the curing reaction and could lead to large osmotic pressures at the interface during exposure of the bonds to water at high pH values, thus contributing to bond failure.

Hamadeh, van Ooij, and Dillard[11] investigated cathodic delamination of similar neoprene-to-steel bonds and reached somewhat different conclusions. They used XPS to determine the surface composition of neat films of primer as a function of immersion time in NaOH solutions. Organic chlorides were observed on the surfaces of as-prepared primer films but there was no evidence of shake-up satellites characteristic of the aromatic groups in the phenolic resin in the primer, indicating a tendency for chlorinated rubber to segregate to the surface of the primer films. Inorganic chlorides were observed on the surfaces of neat primer films that were immersed in NaOH for twenty hours or for one week. It was concluded that chlorinated rubber was unstable during exposure to alkaline solutions and that chlorides evolved could cause corrosion of the substrate, thus contributing to delamination. Evidence was observed in XPS spectra of neat primer films exposed to NaOH solutions for the formation of carboxylate and carbonate species by hydrolysis of ether linkages in the phenolic resin.

Phenolic resins are usually considered to be stable in alkaline solutions at room temperature. Allen investigated alkaline hydrolysis of phenolic resins in caustic solutions at high temperature.[12] Phenol, cresols, xylenols, and hydrogen were obtained by heating cured phenolic resins in 10% to 15% NaOH solutions in an autoclave for several hours at 300°C. It was suggested that hydrogenolysis and hydrolysis of methylene linkages resulted in degradation. Summer reported that novolac resins could be obtained from cured phenolic resins by a short alkaline hydrolysis at 280–320°C but did not propose a mechanism.[13]

The objective of the present research was to reconsider the causes of cathodic delamination in neoprene/steel adhesive bonds prepared using the proprietary adhesive and primer referred to above. Results obtained show that the chlorinated rubber in the adhesive and primer is stable during exposure to alkaline solutions but the phenolic resin is rapidly attacked. However, inorganic chlorides are formed in the bondline during curing by dehydrohalogenation of the chlorinated rubber. Cathodic delamination is mostly attributed to degradation of the phenolic resin. However, dissolution of inorganic chlorides may lead to large osmotic pressures at the bondline, contributing to cathodic delamination.

II EXPERIMENTAL

The adhesive system used here consisted of Chemlok 205 primer and Chemlok 220 adhesive (Lord Corporation). As indicated above, the adhesive was mostly chlorinated rubber and carbon black dispersed in solvent while the primer was mostly chlorinated rubber, phenolic resin, ZnO, TiO_2, and carbon black dispersed in solvent. A specially formulated neoprene rubber (5109S) having the composition shown in Table I was provided by Dr Corley Thompson, Naval Research Laboratory, Orlando, FL. Interstitial-free steel was obtained from Armco, Inc, Middletown, OH.

The adhesive was centrifuged at a speed of 8000 rpm for 20 hours to separate the solids from the polymer solution. Samples for infrared spectroscopy were prepared by spin-coating the polymer solution onto 3″ × 2″ steel substrates that were polished using successively finer grits of sand paper and polishing compounds. 0.05 micron-alumina was used in the final polishing step. The films were dried in a hood at room temperature for one hour and cured in an oven at 155°C for 45 minutes. Reflection-absorption infrared spectroscopy (RAIR) was used to analyze the films before and after curing.

After the films were cured, samples were immersed in 1 N NaOH solutions to observe the degradation process. At selected intervals, samples were removed from the solutions, rinsed with deionized water, dried in a vacuum oven, and examined using RAIR. After 216 hours in 1 N NaOH solutions, some samples were put in 2.8 N NaOH solutions to accelerate the degradation process. When the polymer films delaminated from the polished steel substrates, transmission

TABLE I
Composition of 5109S neoprene

Compound	Quantity
Neoprene GRT	100 parts by weight
Stearic Acid	1 part
Octylated diphenylamine	2 parts
Benzothiazyl disulfide	1.5 parts
Carbon black	31 parts
Red lead dispersion	15 parts
TE-70 processing aid	2 parts

infrared spectroscopy was used to examine the films instead of RAIR. Similar procedures were used to prepare and analyze films of the primer.

Three different kinds of fracture surfaces were analyzed in this investigation. "Bulk" fracture surfaces of the primer were obtained by coating two steel substrates, which were cleaned and etched as described previously,[9] with primer, drying the primer films in a hood for an hour, and compression molding the steel substrates together at 155°C for 45 minutes. A wedge was then driven between the substrates to obtain "bulk" fracture surfaces which were analyzed by XPS to obtain structural information for the bulk primer. Similar techniques were used to prepare and analyze "bulk" fracture surfaces of the adhesive.

Fracture surfaces of "as-prepared" neoprene/steel adhesive joints were obtained as follows. Steel substrates were cleaned and etched as explained before. Primer was applied to substrates and dried in a hood at room temperature for one hour. Adhesive was then applied on top of the primer surface and dried in the hood. Neoprene rubber was bonded to the steel by compression molding at 155°C for 45 minutes. The joint was then immersed in liquid nitrogen, causing the rubber to delaminate from the steel near the primer/steel interface. The failure surfaces were then analyzed by XPS. In a few cases, neat primer (primer without fillers) was used in the preparation of similar samples.

The failure surfaces of adhesive joints that had been immersed in NaOH solutions to simulate conditions at the bondline during cathodic delamination were also examined. "Strip-blister" specimens (see Figure 1) were prepared by the procedures described previously.[9] Primer and adhesive were applied to cleaned, etched steel substrates and allowed to dry. A piece of fluorocarbon tape one inch in length was placed over the adhesive at the center of the substrate to serve as a starter crack and neoprene rubber was bonded to the steel by compression molding at 155°C for 45 minutes. After molding, a fluorocarbon rod was inserted between the tape and the rubber to apply a load to the starter crack. The specimens were then immersed in a 1 N NaOH solution and the rubber was allowed to delaminate. After delamination, the "rubber" and "metal" failure surfaces were rinsed with deionized water, dried, and analyzed by XPS.

A Perkin–Elmer Model 1800 Fourier-transform infrared spectrophotometer

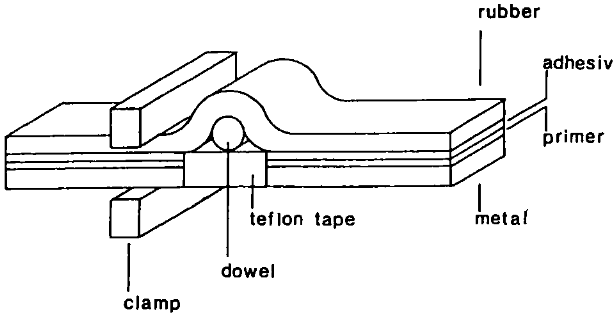

FIGURE 1 "Strip-blister" specimen used for investigating simulated cathodic delamination.

was used for IR analyses. All RAIR and transmission spectra were taken at 4 cm^{-1} resolution using the quantitative mode for 16 cycles. Each cycle consisted of 8 sample scans and 4 reference scans. RAIR spectra were obtained using one reflection at 78° angle of incidence with external reflection accessories provided by Harrick Scientific Co. The absorbance of the bands was calculated by the methods of Wright.[14]

A Perkin-Elmer Model 5300 system was used for XPS analyses. The Mg anode was used to generate X-ray photons with energy of 1253.6 eV. In the survey mode, a pass energy of 44.75 eV and 0.5 eV/step were used to scan the region from 0 eV to 1100 eV. In the multiplex mode, a pass energy of 17.9 eV and 0.05 eV/step were used. The elemental compositions of various failure surfaces were obtained from the multiplex spectra using sensitivity factors supplied with the software. "Angle-resolved" XPS spectra were obtained by varying the "take-off" angle, defined as the angle between the surface of the sample and the axis of the electron energy analyzer.

III RESULTS AND DISCUSSION

A Infrared spectroscopy of polymer films

The infrared spectra of thin films spin-coated onto steel mirrors from polymer solutions separated from the adhesive were similar to those of chlorinated isoprene (see Figure 2A). After curing at 145°C for 45 minutes, a few bands

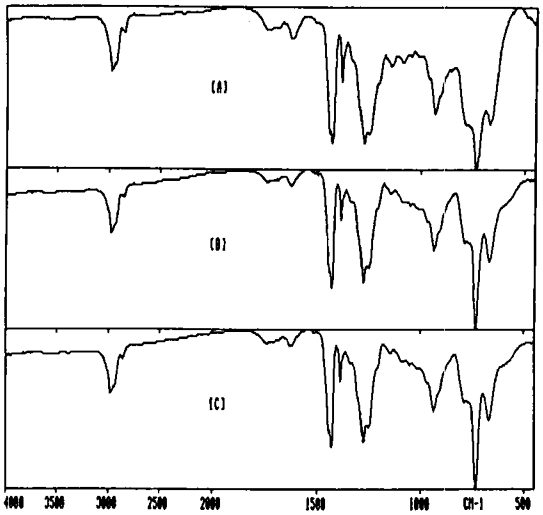

FIGURE 2 Infrared spectra of thin films cast from polymer solutions separated from the adhesive. The RAIR spectra of the polymer spin-coated onto a steel mirror and cured are shown in (A). When the mirror was immersed in 1 N NaOH, the polymer film debonded after 24 hours. The transmission spectra shown in (B) and (C) were obtained after the detached films were immersed in 1 N NaOH for 216 hours and in 2.8 N NaOH for an additional 360 hours, respectively.

attributed to solvent decreased in intensity but there were no changes observed in bands assigned to the adhesive, indicating that the bulk adhesive was stable during curing.

When similar samples were immersed in NaOH for twenty-four hours, the films debonded from the steel substrates. Thereafter, the detached films were immersed in NaOH solutions and examined periodically using infrared spectroscopy. Even after 216 hours in 1 N NAOH and 360 hours in 2.8 N NaOH solution, hardly any changes were observed in the spectra, indicating that the chlorinated rubber in the adhesive was also stable during exposure to concentrated alkaline solutions (see Figures 2B and 2C). Since the primer contained a blend of phenolic resins and a similar chlorinated rubber, it was inferred that changes in the infrared spectra of primer films during immersion in NaOH solutions could be attributed to degradation of the phenolic resins.

RAIR spectra of thin films spin-coated onto steel mirrors from polymer solutions separated from the primer are shown in Figure 3 before and after curing. Bands near 1700, 1590, 1365, 760 and 690 cm^{-1}, which were related to solvents, decreased in intensity after curing. A band near 1650 cm^{-1} increased due to formation of benzophenone groups during oxidative degradation of the phenolic resin, and bands near 1000 cm^{-1} due to aliphatic hydroxyl groups decreased in intensity. Bands characteristic of chlorinated rubber, such as those near 730 and 666 cm^{-1}, remained the same.

Infrared spectra obtained before and after films of the polymers separated from the primer were immersed in NaOH solutions are shown in Figure 4. The first change observed in the spectra was the rapid increase in intensity of the band near 1650 cm^{-1} which was related to benzophenone groups resulting from oxidation of the methylene groups between substituted phenols as discussed above. Formation of benzophenone groups during oxidative degradation of phenolic resins has also been observed by Conley.[15] At the same time, the intensity of the band near 1482 cm^{-1}, which is related to methylene groups linking

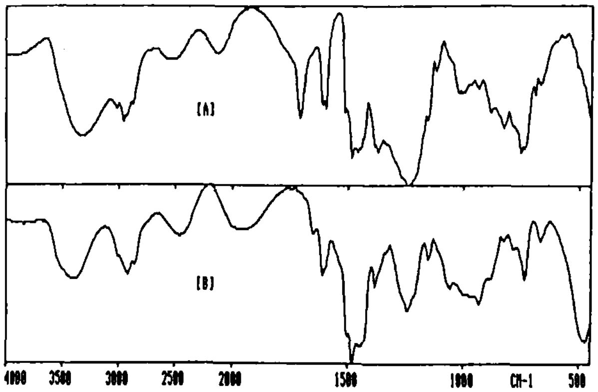

FIGURE 3 RAIR spectra of thin films spin-coated onto steel mirrors from solutions separated from the primer (A)—before and (B)—after curing for 45 minutes at 155°C.

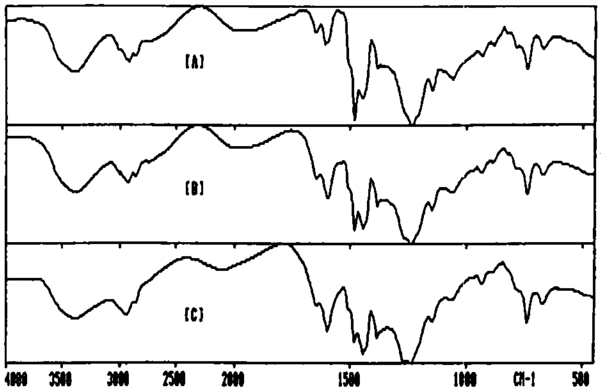

FIGURE 4 FTIR spectra obtained after polymer films cast from solutions separated from the primer were immersed in 1 N NaOH for 216 hours and 2.8 N NaOH for an additional (A)—24 hours, (B)—600 hours, and (C)—2040 hours.

phenol moieties, decreased in intensity. Bands near 1609 and 1598 cm^{-1}, which are related to aromatic ring stretching modes, increased in intensity, and bands near 1149, 1059, 888, 823, and 782 cm^{-1} decreased in intensity. The band near 1149 cm^{-1} is related to CO attached to the benzene ring.[16] The band near 1059 cm^{-1} is related to methylol groups on aromatic rings and the bands near 888, 823 and 782 cm^{-1} are characteristic bands of 2,4,6-trisubstituted phenol, 2,4-

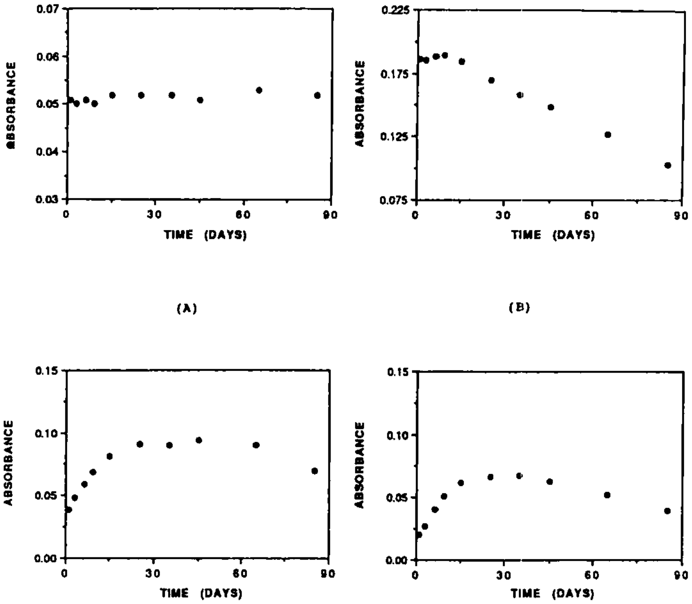

FIGURE 5 Absorbance as a function of immersion time in 2.8 N NaOH for bands near (A)—730, (B)—1482, (C)—1609, and (D)—1650 cm^{-1} in the infrared spectra of the polymer separated from the primer.

disubstituted phenol and 2,6-disubstituted phenol, respectively.[16,17] All these bands are related to the phenolic resin in the primer. The bands near 935, 730 and 666 cm^{-1}, which are related to the chlorinated rubber, did not change.[18,19] This result is consistent with the earlier observation that the chlorinated rubber in the adhesive did not degrade in strong alkaline conditions. Bands of phenolic resins and chlorinated rubber overlapped in the region from 1450 to 1200 cm^{-1} and changed irregularly during immersion of primer films in NaOH solutions. Changes in absorbance during immersion in NaOH are shown in Figure 5 for some characteristic bands in infrared spectra of films cast from solutions of polymers separated from the primer.

Primer films turned deep red in color during immersion in NaOH solutions but the color disappeared after the films were removed from the solutions and rinsed. Compounds with conjugated ring structures may have been formed along with the carbonyl groups.[20] However, the reactions involved are very complicated and the structure of such intermediate compounds could not be determined.

B X-ray photoelectron spectroscopy of "Bulk" failure surfaces

"Bulk" fracture surfaces of the primer and adhesive were analyzed by XPS in order to determine the differences in composition between the bulk and surface regions. The elemental composition of these surfaces, as well as all others examined, are summarized in Table II. The bulk region of the primer contained 72.7% C, 8.4% O, 18.3% Cl, and small amounts of Zn and Ti. The Cl(2p) XPS spectra of the primer are shown in Figure 6. After the binding energies were

TABLE II

Composition of various failure surfaces as determined by X-ray photoelectron spectroscopy[a]

Sample	Atomic concentration (%)									
	C	O	Cl	Pb	Zn	Fe	Br	Ti	Si	Al
Bulk adhesive	67.0	3.2	28.7	<1			1.0			
Bulk primer	72.7	8.4	18.3		<1			<1		
As-prepared strip blister joints										
Substrate–										
15° take off	68.1	2.6	29.2		<1					
45° take off	76.2	1.7	22.0		<1					
75° take off	80.3	2.1	17.5		<1					
Rubber–										
15° take off	74.3	2.7	23.1							
45° take off	80.4	2.3	17.3							
As-prepared strip blister joints, no solids in primer:										
Substrate	84.1	10.7	2.9	2.4						
Rubber	83.7	7.4	3.9	<1			<1		3.2	
Strip-blister joints after immersion in 1 N NaOH for ten days:										
Substrate	55.7	33.9		<1		9.9				
rubber	78.5	17.0	2.4	<1				<1	<1	1.5

[a] The take off angle was 45° unless otherwise indicated.

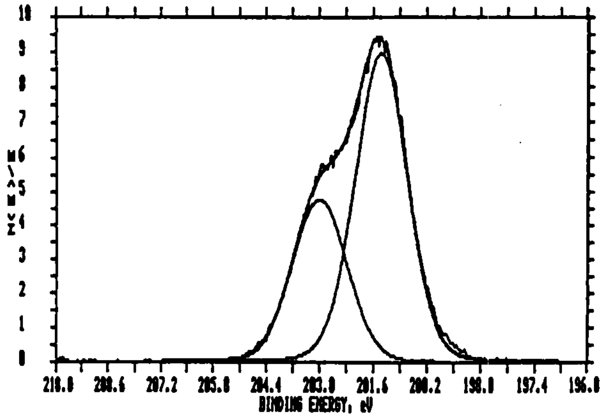

FIGURE 6 Cl(2p) XPS spectra obtained from the bulk failure surface of the primer.

corrected for charging, the Cl($2p_{3/2}$) and Cl($2p_{1/2}$) bands were near 200.1 and 201.7 eV, respectively, which are the binding energies of organic chlorides such as polyvinyl chloride. There was no evidence for formation of inorganic chlorides in the bulk primer.

The bulk region of the adhesive contained 67.0% C, 3.2% O, 28.7% Cl, and small amounts of Br and Pb. A similar composition was obtained from the neat adhesive which contained no fillers. The shapes of the chlorine 2p peaks of the adhesive were very similar to those from the primer (see Figure 6), indicating that there were no inorganic chlorides formed in the bulk adhesive during curing.

C X-ray photoelectron spectroscopy of failure surfaces of "As-prepared" strip blister specimens

The failure surfaces of strip-blister specimens after cathodic delamination or immersion in NaOH solutions have previously been characterized.[9] However, no information has been obtained about the composition of the steel/primer interphase region in "as-prepared" strip-blister specimens. Accordingly, "as-prepared" specimens were fractured by being immersed in liquid nitrogen and the "substrate" and "rubber" fracture surfaces were analyzed by XPS and SEM. The results were compared with those obtained previously for samples after cathodic delamination or immersion in NaOH to determine the changes in the interphase region after bond degradation.

Failure of the as-prepared specimens was near the primer/substrate interface. The Cl(2p) XPS spectrum from the "substrate" failure surface consisted of four bands, near 199.6, 200.9, 201.2 and 202.5 eV, each with a full width at half maximum (FWMH) equal to 1.7 eV (see Figure 7). The bands near 200.9 and 202.5 eV were assigned to Cl $2p_{3/2}$ and $2p_{1/2}$ spectra of organic chlorides while those near 199.6 and 201.2 eV were assigned to the Cl $2p_{3/2}$ and $2p_{1/2}$ spectra of inorganic chlorides. Since zinc was detected on the substrate failure surfaces of as-prepared strip-blister specimens but other metals such as lead or iron were not,

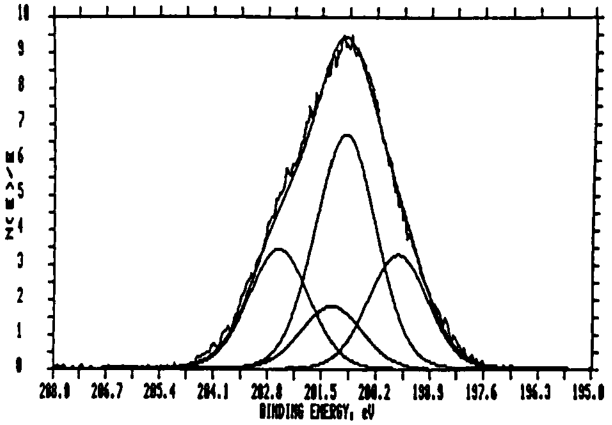

FIGURE 7 Cl(2p) XPS spectra obtained from the "substrate" failure surface of an as-prepared strip-blister specimen.

it was concluded that the inorganic chlorides were salts of zinc formed by dehydrohalogenation of chlorinated rubber in the primer during curing of the neoprene.

The Cl(2p) XPS spectrum from the "rubber" failure surface was similar to those shown in Figure 6 and consisted of only the two bands related to organic chlorides. No iron, zinc, or lead was detected on the "rubber" failure surface. This result is consistent with the previous results indicating that no inorganic chlorides were formed in the bulk region of the primer. The fact that the zinc chlorides are formed near the metal/primer interface, and are present before cathodic delamination, may be an important factor in determining the bond durability.

It is interesting to note that the concentration of chlorine on both rubber and substrate failure surfaces of as-prepared strip-blister specimens was greater than in the bulk primer. When the take-off angle was 15°, the concentration of chlorine on the rubber and substrate failure surfaces was 23.1 and 29.2%, respectively. When the take-off angle was increased to 45°, the chlorine content of the rubber and substrate surfaces decreased to 17.3 and 22.0%, respectively. The chlorine content of the bulk primer was 18.3%. These results indicate there may have been some phase separation of the chlorinated rubber and phenolic resin in the primer near the substrate surface. Failure in the as-prepared joints occurred in a region containing a relatively high concentration of chlorinated rubber. Presence of inorganic chlorides in the primer near the substrate but not in the bulk primer may indicate that the substrate influenced dehydrohalogenation of the chlorinated rubber in the primer. Smelt has in fact observed substrate-induced degradation of chlorinated rubber lacquers applied to abraded mild steel substrates.[21]

Phase separation of the polymers in the primer may account for some of the difference between the adhesive and primer in resistance to cathodic delamination even though both contain chlorinated rubber. The primer closest to the steel surface may contain more phenolic resin than the bulk primer. As noted above, the adhesive delaminated from polished steel surfaces after being immersed for only 24 hours in 1 N NaOH solution, but the primer delaminated only after nearly 216 hours under similar test conditions.

The experiment described above was repeated except that the fillers were removed from the primer before the primer was applied to the substrate. Cl(2p) XPS spectra from the "substrate" failure surface were similar to those shown in Figure 7 and consisted of four bands, near 198.3, 200.0, 200.6 and 202.3 eV, each with a FWMH equal to 1.7 eV. The bands near 200.6 and 202.3 eV were related to Cl $2p_{3/2}$ and Cl $2p_{1/2}$ spectra of organic chlorides while those near 198.3 and 200.0 eV were related to inorganic chlorides. The binding energies of the Cl 2p spectra in these inorganic chlorides were 2.3 eV lower than those of organic chlorine. Since there was no zinc present on the "substrate" failure surface and the binding energies of the Cl 2p spectra of $ZnCl_2$ are only 1.3 eV lower than those of organic chlorides, it was concluded that the inorganic chlorides formed on the "substrate" failure surfaces in this case were due to lead chlorides.

This result was confirmed by observation of the lead 4f multiplex spectra. As shown in Figure 8, the lead 4f spectra consisted of two bands due to $Pb(4f_{7/2})$ and $Pb(4f_{5/2})$ electrons. Each band contained three components with a full width at half maximum equal to 1.23 eV. In each band, the component at lowest binding energy was assigned to PbS. The components in the middle and at the highest binding energies were assigned to Pb_3O_4 and $PbCl_2$, respectively. PbS was apparently formed during the curing reaction of the rubber, which was actually a copolymer of sulfur and neoprene. Metal sulfides are known to form during the cure of neoprene/sulfur copolymers with metal oxides.[22]

$PbCl_2$ was also detected on the "rubber" failure surface. Results obtained from angle-resolved XPS showed that fracture occurred near the adhesive/primer interface. The low Cl-to-C ratio in this region (2.9% to 84.1% on the "substrate" side, and 3.9% to 83.7% on the "rubber" side) seems to be an indication of layers rich in phenolic resins formed in this interface area. These results may be

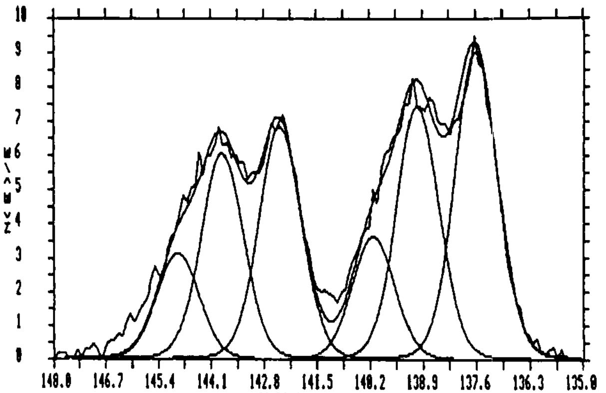

FIGURE 8 Pb(4f) multiplex spectra from the "substrate" failure surface of a strip-blister specimen that was prepared with the fillers removed from the primer.

expalined by the assumption that uncured phenolic resins with short chains have greater mobility and diffuse to the upper surface of the primer during drying and form a phenolic rich layer.

It may be concluded that during the curing process $ZnCl_2$ is generated in the primer near the primer/substrate interface and $PbCl_2$ is generated near the primer/adhesive interface. $PbCl_2$ is also formed in the rubber during curing.[23] The solubilities of ZnO and $PbCl_2$ in water are very low but that of $ZnCl_2$ is very high. The high solubility of the $ZnCl_2$ can contribute to debonding through osmotic effects.

D X-ray photoelectron spectroscopy of failure surfaces of strip-blister specimens after simulated cathodic delamination

When neoprene was delaminated from steel after immersion in 1 N NaOH. solutions for 10 days, the "rubber" failure surface was black whereas the primer was gray. The composition of this surface was 78.5% C, 17.0% O, 2.4% Cl, 0.1% Ti, 0.2% Pb, 0.4% Si and 1.5% Al but no zinc was detected by XPS. $ZnCl_2$ and ZnO apparently dissolved in the NaOH solution, making the color of the "rubber" failure surface change from gray to black. The low concentration of chlorine on the "rubber" failure surface (2.4%) was consistent with this conclusion.

The "substrate" failure surface contained 9.9% Fe, 55.7% C, 33.9% O and 0.5% Pb. Small amounts of lead were attributed to reprecipitation of dissolved $PbCl_2$ or lead stabilizers. Even though zinc chloride was formed in the bondline during cure by dehydrohalogenation of chlorinated rubber in the primer, none was detected on either the "rubber" or "substrate" failure surface after immersion in NaOH. This is additional evidence for dissolution of inorganic chlorides in the bondline during immersion in NaOH or during cathodic delamination.

The results described above indicate that oxidation of the phenolic resin in the primer is an important mechanism for cathodic delamination of neoprene from steel. In strong alkaline solutions, methylene groups linking phenol moieties in the phenolic resin were first attacked by oxygen to form benzophenone groups. Other investigators have shown that the oxidation of hindered phenols is catalyzed by hydroxyl ions.[24] As the reaction proceeds, bonds between phenol moieties are broken, resulting in formation of carboxylate and quinone groups, and in the gradual degration of the primer and loss of adhesion.

In the final stage of degradation, bonds between phenyl groups were broken, resulting in formation of phenolic compounds with different substitution patterns. This is one reason for the increase in intensity of the $1598 cm^{-1}$ band, which is related to substituted benzene ring deformation and aromatic C—H in-plane bending.[25] The conjugation of carbonyl groups with phenyl groups may also contribute to the intensity of this band.[17] When enough methylene groups have been attacked and broken, compounds with low molecular weight are formed which dissolve in NaOH solution. The fact that the bands near 887, 823, and

782 cm^{-1}, which are due to different substituted phenyl groups, decreased in intensity was a clear indication of such changes. Because these three absorption bands are related to crosslinks in the phenolic resins, chain-scission processes happening in the these compounds could cause the crosslinking density to decrease and result in a product with inferior physical and chemical properties compared to the original resins. The bands near 1609 and 1598 cm^{-1} decreased in intensity in the later period of test, also showing that some phenolic material was lost during the latter stages of the degradation process. Another clear indication of loss of phenolic material in the primer film is shown by the disappearence of the band near 3010 cm^{-1}, which is related to aromatic C—H stretching in the phenolic resins.

Alkaline degradation of the chlorinated rubber in the primer and adhesive does not contribute significantly to cathodic delamination of neoprene from steel. Chlorinated rubber is stable during exposure to aqueous solutions at high pH values and the inorganic chlorides that are observed on the failure surfaces of neoprene/steel joints after cathodic delamination are related to dehydrohalogenation of the chlorinated rubber during curing and reaction of the evolved chlorine with ZnO.

Nevertheless, inorganic chlorides may still contribute to delamination. During cathodic delamination, zinc chlorides may pass into solution. This may lead to additional water being absorbed by the rubber, resulting in large stresses at the bondline.

The conclusions reached here regarding cathodic delamination of neoprene from steel are thus similar to those reached by Hammond and co-workers[5] and by Watts and Castle[6] for a number of polymer systems undergoing cathodic delamination from steel. Transformations involving the oxide are not considered important in the present case.

A new primer that is expected to be more resistant to cathodic delamination has been prepared by blending a novolak-epoxy with chlorinated rubber, titanium dioxide, and zinc oxide.[26] Preliminary results indicate that thin films of the new primer, which is cured using a polyamine such as methylene dianiline (MDA), are extremely resistant to oxidation during immersion in concentrated NaOH solutions. More extensive tests of the cathodic delamination of strip blister specimens prepared using the new primer are in progress and will be reported elsewhere.[27]

Improvements in the resistance of neoprene-to-steel adhesive bonds to cathodic delamination can also be obtained by blending a silane coupling agent such as γ-aminopropytrilethoxysilane (γ-APS) with the currently-used primer.[26] Small amounts of silanes are frequently blended with adhesives to enhance their durability during exposure to aggressive environments. However, in the case of rubber-to-metal bonds, it has been found that the rate of cathodic delamination can be decreased by an order of magnitude when more than 10% of the silane is blended with the primer,[25] perhaps indicating that most of the silane is adsorbed onto the acidic carbon black.

Finally, improvements in the durability of neoprene-to-steel adhesive bonds might also be obtained by using lead compounds to react with chlorides produced by dehyrohalogenation of chlorinated rubber in the primer during cure. As noted above, lead chlorides have low solubility and would reduce any osmotic effects in the bondline that might arise from dissolution of zinc chlorides.

IV CONCLUSIONS

During cure of neoprene against steel, chlorinated rubber in the adhesive and primer undergoes dehydrohalogenation. Chlorine evolved reacts with ZnO in the primer to form $ZnCl_2$ at the bondline. At the same time, chlorine reacts with lead stabilizers to form $PbCl_2$ near the adhesive/primer interface. The chlorinated rubber in the adhesive and primer is stable during cathodic delamination of neoprene from steel or during immersion of neoprene/steel adhesive joints in NaOH to simulate conditions obtained at the bondline during cathodic delamination. However, methylene groups linking phenol moieties in the phenolic resins in the primer are rapidly attacked by OH^- ions, resulting in failure of the bonds. The solubility of lead chlorides in water is very low. However, zinc chlorides are very soluble in water and may contribute to delamination through osmotic effects.

Acknowledgements

This research was supported in part by a grant from the office of Naval Research. The assistance of Kristen A. Boerio in preparing the figures is acknowledged.

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