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Adhesive Bonding of Neoprene to Metals
in Sonar Devices

F. James Boerio
Department of Materials Science
and Engineering
University of Cincinnati
Cincinnati, Ohio 45221-0012

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) The mechanisms responsible for debonding of neoprene/steel adhesive bonds during cathodic delamination or during immersion in aqueous solutions of NaOH to simulate the effects of cathodic delamination have been determined. Delamination of the rubber began at the edges of the bonds and proceeded slowly inward. The centers of the bonds were always intact except for very long times when complete delamination of the rubber was observed. Failure was near the primer/oxide interface but islands of rubber remained on the substrate and islands of oxide remained on the rubber. Two failure mechanisms associated with a proprietary primer applied to the substrate prior to bonding were identified. One mechanism was related to oxidative degradation of a phenolic polymer in the primer. The other was related to large osmotic pressures at the bondline resulting from dissolution of zinc chloride. Zinc chloride was formed by reaction of zinc oxide, a component of the primer, with hydrochloric acid evolved from chlorinated rubber, another component of the primer, during curing of the rubber. Debonding of rubber from polished substrates was much faster, leaving little rubber on the					
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19. substrate failure surfaces and little oxide on the rubber failure surfaces, and indicating that interlocking of the rubber with the substrate has an important effect on the environmental stability of rubber-to-metal bonds. The resistance of the proprietary primer to cathodic delamination was increased by adding γ -aminopropyltriethoxysilane (γ -APS). Primers with improved resistance to cathodic delamination were also prepared from epoxy resins, γ -aminoethylaminopropyltriethoxysilane (γ -AEAPS), and carbon black.
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I. Introduction

The primary objective of this research was to determine the mechanisms responsible for the cathodic delamination of neoprene rubber from steel. An additional objective was to develop new adhesive/primer systems based on silane coupling agents that would provide improved durability of rubber-to-metal bonds subjected to conditions of cathodic delamination.

Rubber-to-metal bonds are important in many applications. However, concern for the durability of sonar transducers was the primary motivation for this research. The acoustical window on wet-end sonar transducers is usually prepared by curing a slab of neoprene in contact with a steel shroud 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 previous investigations concerned with the environmental stability of rubber-to-metal bonds have been reported. The results have shown that most rubber-to-metal bonds are relatively stable except when exposed to conditions of cathodic delamination. 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. Since polymer was also detected on the substrate failure surfaces, it was concluded that cathodic delamination involved degradation of the coatings 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. Delamination was again 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.

In this research, the cathodic delamination of adhesive bonds between neoprene and steel prepared using a proprietary adhesive and primer was investigated. Surface analysis techniques such as x-ray photoelectron spectroscopy (XPS) and reflection-absorption infrared spectroscopy (RAIR) were used to examine the failure surfaces of joints after cathodic delamination and the fracture surfaces of as-prepared joints so as to determine the mechanisms responsible for cathodic delamination. Infrared spectroscopy was also used to characterize the proprietary adhesive and primer and to determine the stability of the polymers in them during exposure to conditions of simulated cathodic delamination. Finally, silane coupling agents were used to develop new primers for rubber-to-metal bonding and to modify the proprietary primer so as to obtain improved resistance to cathodic delamination.

The results obtained have shown that there are two principal failure mechanisms associated with cathodic delamination of rubber-to-metal bonds. One is concerned with oxidation of a phenolic polymer in the primer. The other is concerned with large osmotic pressures in the bondline that result from

dissolution of inorganic salts formed during curing of the rubber. The results of this research have also shown that primers with improved resistance to cathodic delamination can be obtained using silane coupling agents.

II. Experimental

Adhesive joints were prepared by curing neoprene in contact with steel in the strip-blister configuration (see Figure 1). Steel coupons (1 x 6 x 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 solution but that was omitted here. A proprietary 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.

Several non-proprietary adhesives and primers were prepared and evaluated using single strip-blister specimens. The primers were based on epoxy resins, silane coupling agents, and carbon black while the adhesives were based on chlorinated rubber and carbon black. Several different silanes, including γ -aminopropyltriethoxysilane (γ -APS), γ -aminoethylaminopropyltriethoxysilane (γ -AEAPS), and γ -mercaptopropyltrimethoxysilane (γ -MPTMS), were considered in the primers. However, the most effective primers contained an epoxy resin similar to the diglycidyl ether of bisphenol-A (DGEBA) and γ -AEAPS.

In a few cases, double strip-blister specimens were used (see Figure 2). These specimens were similar in appearance to single strip-blister specimens except that neoprene was molded onto both sides of the steel substrates. Also, the substrates for double strip-blister specimens were prepared by vapor degreasing steel coupons with trichloroethane, grit blasting at 275 kpa with 50 grade steel grit, and vapor degreasing again with trichloroethane. The primer and adhesive were brushed onto the substrate and allowed to dry before neoprene was molded against the substrate as described above. In some cases, the primer was modified by addition of 11.7% by weight of γ -APS.

The single and double 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 others, the steel substrates were held at a potential

of -1.0⁵ volts vs SCE in 3.5% NaCl or -1.42 volts vs SCE in 3.5% artificial sea water (ASW). Strip-blister specimens were also immersed in 1N aqueous solutions of NaOH to simulate conditions obtained at the bondline in the other two types of environments.

At intervals, specimens were removed from the test solutions and examined visually. It was 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 decreased when pressure was applied to the faces of the specimens as by the clamps (see Figure 1).

Measurements of delamination were recorded for each sample by using calipers to measure the extent of debonding away from the fluorocarbon rod. In the case of double strip-blister specimens, four separate measurements of delamination were made for each sample and averaged.

At the conclusion of the cathodic delamination experiments, the intact bonds near the centers of the joints were cut with a sharp blade to expose the "rubber" and "substrate" failure surfaces. Samples for surface analysis were cut from both failure surfaces, rinsed in distilled, deionized water, and dried. The rubber samples were usually outgassed at room temperature under vacuum in an oven or a dessicator for a few days before surface analysis.

Fracture surfaces of "as-prepared" neoprene/steel adhesive joints were obtained as follows. Steel substrates were cleaned and etched or polished as explained above. Primer and adhesive were applied to the substrates and dried before neoprene rubber was bonded to the steel by compression molding at 155°C for 45 minutes. The joints were then immersed in liquid nitrogen, causing delamination to occur near the primer/steel interface. The failure surfaces were then analyzed by XPS.

XPS spectra of the failure and fracture surfaces were obtained using a Physical Electronics 5300 X-Ray Photoelectron Spectrometer and Mg K_α radiation at a power of 300 W. 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. 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.

The adhesive and primer consisted of various solids dispersed in a polymer solution. Samples of each were centrifuged for 20 hours at 8,000 RPM to separate the solids from the solutions. The solutions were then decanted so that the solids could be recovered. The solids were rinsed repeatedly with solvent, dried, mixed with KBr, and pressed into thin discs for analysis by infrared spectroscopy.

Films of the polymers separated from the adhesive and primer were prepared by spin-coating the solutions onto steel substrates that were polished using successively finer grits of sand paper and polishing compounds. 0.05 μm γ-alumina was used in the final

polishing step. The films were dried in a hood at room temperature for one hour and then cured in an oven at 155°C for 45 minutes. Reflection-absorption infrared spectroscopy was used to analyze the films before and after curing.

After the films were cured, samples were immersed in 1N 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 1N NaOH solutions, some samples were put in 2.8N NaOH solutions to accelerate the degradation process. When the polymer films delaminated from the substrates, transmission infrared spectroscopy was used to examine the films instead of RAIR. Similar procedures were used to analyze primer films.

A Perkin-Elmer Model 1800 Fourier-transform infrared spectrophotometer was used for the IR analyses. All 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 (10).

III. Results and Discussion

A. Cathodic Delamination of Rubber-to-Metal Bonds

Results from infrared spectroscopy showed that the primer consisted of carbon black, zinc oxide, titanium dioxide, and aluminosilicates dispersed in a solution of phenolic polymer and

chlorinated rubber. The adhesive was mostly carbon black dispersed in a solution of chlorinated rubber (11).

The O(1s), C(1s), Cl(2p), and Pb(4f) spectra observed for the neat primer, adhesive, and rubber are shown in Figure 3 and summarized in Table II (12). The XPS results were consistent with the results obtained from infrared spectroscopy, showing that the primer contained a phenolic polymer and chlorinated rubber and that the adhesive contained mostly chlorinated rubber.

The Cl(2p) spectrum obtained from the adhesive consisted of a 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 (13). The C(1s) spectrum of the primer consisted mostly of bands near 284.6 and 286.2 eV that are typical of hydrocarbons containing hydroxyl groups (13) 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 the inorganic fillers such as TiO_2 , ZnO, and aluminosilicates.

Some interesting features were observed in the spectra of the rubber (12). 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 $\text{Pb}(4f_{7/2})$ and $\text{Pb}(4f_{5/2})$ electrons in PbCl_2 were in fact observed near 138.5 and 143.4 eV. $\text{O}(1s)$ 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 (13). Therefore, the band near 531.6 eV in $\text{O}(1s)$ spectra of the rubber was probably related to the 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 4 and summarized in Table III (12). 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 $\text{O}(1s)$ 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 $\text{C}(1s)$ spectrum of the substrate failure surface consisted of the band near 284.6 eV due to saturated hydrocarbons and additional bands that were shifted upward in binding energy by about 1.6, 3.0, and 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. It was concluded that oxidation of one of the polymers in the primer may have occurred during the debonding reaction.

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, have also been found in the adhesive (14).

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 surface 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. As indicated above, highly oxidized forms of carbon may indicate oxidative degradation of polymers in the primer during debonding.

An interesting result concerned the nature of the chlorine present on the rubber failure surfaces. Two bands assigned to the Cl 2p_{1/2} and 2p_{3/2} electrons of the primer were observed near 199.1 and 200.7 eV, as expected for chlorinated hydrocarbons.

The Cl(2p) spectra obtained from the rubber failure surface contained additional bands near 198.0 and 199.6 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 3).

Several experiments were carried out in order to determine the origin of the lead and the inorganic chlorides found on the rubber and substrate failure surfaces. In one case, strip-blister specimens were prepared as described above except that the steel substrates were mechanically polished before the primer and adhesive were applied (12). 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 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.

When XPS spectra were obtained from the failure surfaces of joints prepared from polished substrates, some interesting results were obtained (see Figure 5 and Table IV). There was very little 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 oxides which are present in the adhesive and primer. However, it was not clear whether dehydrohalogenation occurred during or before cathodic debonding.

In order to determine when the inorganic chlorides were formed, XPS was used to examine the fracture surfaces of "as-prepared" neoprene/steel adhesive joints that were prepared as described above using etched substrates and fractured by being immersed in liquid nitrogen (14). Fracture of these specimens was near the primer/substrate interface. The Cl(2p) XPS spectrum from the "substrate" fracture surface consisted of four bands, near 199.6, 200.9, 201.2 and 202.5 eV (see Figure 6). 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 fracture surfaces of as-prepared strip-blister specimens but other metals such as lead or iron were not, 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" fracture surface consisted of only the two bands related to organic chlorides (see Figure 6). No iron, zinc, or lead was detected on the "rubber" fracture surface. The fact that zinc chlorides are formed near the metal/primer interface, and are present before cathodic delamination, 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 steel substrates (15).

In order to determine the stability of the polymers in the adhesive and primer, reflection-absorption infrared spectroscopy (RAIR) was used to examine thin polymer films spin coated onto steel mirrors from the solutions separated from the adhesive and primer (14). The RAIR spectra of the as-prepared films spun from the adhesive solution were similar to those of chlorinated isoprene (see Figure 7A). When the mirrors were immersed in NaOH for twenty four hours, the films debonded. Thereafter, the detached films were immersed in NaOH solutions and examined periodically using transmission infrared spectroscopy. Even after 216 hours in 1N NaOH and 360 hours in 2.8N NaOH solution, few changes were observed in the spectra, indicating that the chlorinated rubber in the adhesive was stable during exposure to concentrated alkaline solutions (see Figures 7B and 7C).

RAIR spectra of thin films spin-coated onto steel mirrors from polymer solutions separated from the primer are shown in Figure 8 (14). 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 9 (14). 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 (16). At the same time, the intensity of the band near 1482 cm^{-1} , which is related to methylene groups linking 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 (17). 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-disubstituted phenol and 2,6-disubstituted phenol, respectively (17, 18). 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 (19, 20). 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 10 for some characteristic bands in infrared spectra of films cast from solutions of polymers separated from the primer.

Delamination was not observed when strip-blister specimens were exposed to 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 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 dissolution of inorganic chlorides, resulting in large osmotic pressures at the interface.

Degradation of the primer seems to occur by oxidation of the methylene linkages between phenol residues to form carboxylic acids and quinones as previously observed by Conley for high temperature oxidation of phenolic polymers in air (16). As discussed above, carboxylate groups have been detected in XPS spectra obtained from the failure surfaces of strip-blister specimens after actual or simulated cathodic delamination. Oxidation of the phenolic polymer separated from the primer during immersion in alkaline solutions has also been observed.

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 (21) 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 rate of delamination in single strip-blister specimens 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.

B. Silane-Based Primers for Resistance to Cathodic Delamination

One of the objectives of this research was to develop non-proprietary primer systems based on silane coupling agents that would provide improved resistance of rubber-to-metal bonds to cathodic delamination. Primers consisting of an epoxy resin combined with silanes were investigated but the most effective combination was an epoxy, γ -AEAPS, carbon black, and solvents (see Table V). Similarly, the most effective adhesive consisted of chlorinated rubber, carbon black, and solvent (see Table VI).

Single strip-blister specimens were prepared using the proprietary and non-proprietary adhesive systems and immersed in 1N NaOH. The delamination was measured periodically and is shown

in Figure 11. Delamination of the specimens prepared using the proprietary system was considerable but that for the non-proprietary system was small, indicating that improved resistance to cathodic delamination could be obtained using primers based on silane coupling agents.

Work by others showed that the resistance to cathodic delamination of rubber-to-metal bonds prepared using the proprietary primer could also be enhanced by addition of γ -APS to the primer (22). However, no experimental information concerning the mechanisms by which the silane functioned was given. Therefore, neoprene/steel double strip-blister specimens were prepared using the proprietary primer with and without addition of 11.7% γ -APS and their cathodic delamination in 3.5% ASW was investigated while the substrates were held at a potential of -1.42 V vs SCE (23). The extent of cathodic delamination is shown as a function of time in Figure 12. Delamination was extensive for joints prepared with the proprietary primer and adhesive and exceeded 0.6 inches after 28 days. Joints prepared with the proprietary primer modified by addition of 11.7% γ -APS were much more stable and delaminated an average of only 0.04 inches in the same time. Visual examination of the failure surfaces indicated that delamination began at the edges of the specimens and progressed slowly inward and that failure was close to the primer/oxide interface.

Selected multiplex spectra obtained from the substrate and rubber failure surfaces of a specimen prepared with the commercial primer are shown in Figures 13 and 14, respectively

(23). Spectra obtained from the failure surfaces of a specimen prepared with the modified primer are shown in Figures 15 and 16. The atomic concentrations of the elements detected are summarized in Table VII. Considerable amounts of iron were observed on the substrate failure surfaces but much smaller amounts were found on the rubber failure surfaces. Moreover, there was a component near 529.7 eV in the O(1s) spectra obtained from the substrate failure surfaces that was characteristic of metal oxides. In general, that component was weak or not observed in O(1s) spectra from the rubber failure surfaces. Therefore, it was concluded that failure was near the primer/oxide interface for joints prepared using the commercial and modified primers.

Some zinc was observed on the rubber and substrate failure surfaces of joints prepared with the commercial primer but little was observed for joints prepared with the modified primer. By comparison, nitrogen was detected on the failure surfaces of joints prepared with the modified primer but not on the failure surfaces of joints prepared with the commercial primer. Chlorine and lead were detected on all of the failure surfaces.

The Pb(4f) spectra usually consisted of a doublet near 143.2 and 138.3 eV that was assigned to lead chloride. However, additional bands were sometimes observed. Particularly interesting in this regard was a doublet shifted from the chloride bands toward lower binding energies by about 2.5 eV and assigned to lead sulfide. Bands related to lead oxide were also occasionally observed. In general, the Cl(2p) spectra consisted of a doublet at high binding energies that was characteristic of

organic chlorides and a doublet shifted toward lower binding energies by between one and two eV that was related to inorganic chlorides.

Zn(2p_{3/2}) spectra of the substrate and rubber failure surfaces of specimens prepared with the commercial primer consisted of components near 1022.1 and 1024.4 eV that were attributed to zinc chloride and zinc oxide, respectively. As noted above, little zinc was detected on the failure surfaces of specimens prepared from the modified primer. Similarly, no nitrogen was found on the failure surfaces of specimens prepared from the commercial primer. However, two components were observed in the N(1s) spectra obtained from the failure surfaces of the specimen prepared from the modified primer. As discussed below, those components were assigned to free and protonated amino groups.

Selected multiplex spectra obtained from the substrate and rubber fracture surfaces of a specimen prepared with the commercial primer are shown in Figures 17 and 18, respectively. Spectra obtained from the fracture surfaces of a specimen prepared with the modified primer are shown in Figures 19 and 20. Atomic concentrations of the various elements detected are shown in Table VIII. Mostly carbon, oxygen, and chlorine were detected on the fracture surfaces. Little lead or zinc was detected on the fracture surfaces. As previously noted, lead was always detected on the failure surfaces and zinc was usually detected on the failure surfaces of joints prepared from the commercial primer. The amount of chlorine on the fracture surfaces was much

higher than on the failure surfaces. Generally, XPS spectra obtained from the fracture surfaces resembled those of the neat primer, indicating that fracture was mostly cohesive within the primer.

Some interesting observations were made regarding the multiplex spectra of the fracture surfaces. The Cl(2p) spectra usually consisted of an intense doublet assigned to organic chlorides plus a weaker doublet shifted to lower binding energies that was related to inorganic chlorides. The fraction of chlorine in inorganic chlorides was much lower for fracture surfaces than for failure surfaces. No nitrogen was observed for specimens prepared from the commercial primer but a doublet was observed in the N(1s) spectra of the fracture surfaces of specimens prepared with the modified primer.

There were several striking differences in the XPS spectra obtained from the failure and fracture surfaces of specimens prepared with the commercial primer and those prepared with the modified primer. Large amounts of chlorine were detected on the fracture surfaces but much smaller amounts were found on the failure surfaces. Chlorine on the fracture surfaces was mostly organic but a large fraction of the chlorine on the failure surfaces was inorganic. Lead was found on the failure surfaces but not on the fracture surfaces. Zinc was observed on the failure surfaces of specimens prepared with the commercial primer but not on those of the specimens prepared with the modified primer. Similarly, nitrogen was observed for specimens prepared with the modified primer but not for those prepared with the

commercial primer. Moreover, the N(1s) spectra obtained from the failure and fracture surfaces of specimens prepared with the modified primer clearly consisted of components near 399.0 and 401.0 eV. These binding energies were very similar to those observed for γ -APS deposited onto iron substrates from aqueous solutions adjusted to pH 8.0 by addition of HCl (24) and were assigned to free and protonated amino groups, respectively, in the γ -APS used to modify the primer.

It seems likely that amine hydrochlorides are formed by reaction of γ -APS with chlorine evolved from the chlorinated rubber in the primer during curing of the neoprene at elevated temperatures. Amines are HCl acceptors and can be used to stabilize polymers such as polyvinyl chloride and chlorinated rubber against dehydrochlorination but they are rarely used for such purposes because they may release HCl during processing at elevated temperatures (25). As a result, metal oxides such as those of zinc and lead are usually used to stabilize chlorinated polymers. As noted above, zinc chlorides have previously been observed in the bondline of neoprene/steel bonds prepared using the commercial primer and both zinc chlorides and lead chlorides have been observed in the bondline here.

It is interesting to note that zinc oxide and chloride were observed on the failure surfaces of specimens prepared with the commercial primer but not on those of specimens prepared with the modified primer. Similarly, the amount of lead chloride detected on the failure surfaces was greater for specimens prepared from the commercial primer than for those prepared from the modified

primer. Evidently, the presence of large amounts of γ -APS has a significant effect on reactions occurring in the bondline during curing of the neoprene.

The formation of amine hydrochlorides in the modified primer may inhibit cathodic delamination of neoprene from steel by reducing osmotic effects. As indicated earlier, zinc chlorides, which are highly soluble, are formed in the bondline when the unmodified primer is used. As water enters the joint during cathodic delamination, zinc chloride would dissolve to form concentrated solutions. More water would then be drawn into the joint to reduce the concentration gradient but that would result in significant osmotic pressures in the bondline tending to accelerate delamination. Observation of considerable amounts of zinc on the failure surfaces of joints prepared with the commercial primer but not on those of joints prepared with the modified primer is consistent with the proposed failure mechanisms.

Other reactions involving γ -APS may also occur in the bondline. As noted earlier, quinones are formed by oxidation of the phenolic resin in the primer during curing of the rubber. Kaleem, Chertok, and Erhan (26) have described coatings based on the reaction of polyetheramines with p-benzoquinone that resist salt water spray after heat curing. It is possible that in the modified primer, amino groups in γ -APS react with quinones formed by oxidation of the phenolic resin in the primer during curing, contributing to the exceptional resistance of the modified primer

to cathodic delamination. However, no evidence of that reaction has been obtained here.

IV. Conclusions

The results obtained here are consistent with the following conclusions:

1. Neoprene/steel adhesive bonds prepared using a proprietary adhesive and primer system fail near the primer/oxide interface during actual or simulated cathodic debonding.

2. The proprietary primer consists of carbon black, zinc oxide, titanium dioxide, and aluminosilicates dispersed in a solution of chlorinated rubber and phenolic polymer.

3. The proprietary adhesive consists of carbon black dispersed in a solution of chlorinated rubber.

4. Cathodic delamination of neoprene/steel bonds involves two failure mechanisms. One concerns oxidative degradation of the phenolic resin found in the primer. The other is associated with large osmotic pressures at the bondline resulting from dissolution of inorganic chlorides that result from the reaction of zinc oxide in the primer with hydrochloric acid evolved from chlorinated rubber in the primer during curing of the rubber.

5. Either failure mechanism is consistent with the observation that failure of rubber-to-metal bonds during cathodic delamination is not dependent on the nature of the rubber.

6. A primer containing γ -aminoethylaminopropyltriethoxysilane (γ -AEAPS) and an epoxy resin provided improved resistance to cathodic delamination when compared with the proprietary primer.

7. Modification of the proprietary primer by addition of γ -aminopropyltriethoxysilane (γ -APS) also resulted in improved resistance to cathodic delamination.

8. Addition of γ -APS to the proprietary primer resulted in a decrease in the amount of soluble zinc chloride formed near the primer/substrate interface.

9. A decrease in the amount of soluble salts in the bondline may have reduced the contribution of osmotic pressure to the cathodic delamination of rubber-to-metal bonds.

10. γ -APS reacted with HCl evolved from chlorinated rubber in the proprietary primer to form amine hydrochlorides.

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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

Table II. XPS Spectra Observed for Primer, Adhesive, and Neoprene.

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

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	138.2 143.0		284.6 286.2 287.6 288.7	529.7 531.0 531.8 532.9 534.1 535.5
Rubber	138.3 143.2	198.0 199.1 199.6 200.7	284.6 286.1 287.3 288.7	530.1 531.5 533.0

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	

Table V. Non-Proprietary Primer for Bonding Neoprene to Steel.

DGEBA	7.90 grams
Carbon Black	2.25
γ -AEAPS	1.50
Dowanol PM	45.00
Toluene	45.00

Table VI. Adhesive for Bonding Neoprene to Steel.

Carbon Black	10.0 grams
Chlorinated rubber	20.0
Toluene	60.0

Table VII. Atomic Concentrations (%) of Elements Detected on Failure Surfaces of Double Strip-Blister Specimens After Cathodic Delamination in 3.5% ASW at -1.42 V vs SCE.

Element	Commercial Primer		Modified Primer	
	Substrate	Rubber	Substrate	Rubber
C	31.5	79.3	44.3	64.0
O	47.8	12.6	37.6	23.2
Si	8.3	1.5	2.5	2.4
Fe	7.4	0.8	10.8	4.4
Cl	2.2	4.7	3.0	3.1
Zn	1.9	0.5	0.3	0.0
Pb	1.0	0.7	0.2	0.3
N	---	---	1.2	2.6

Table VIII. Atomic Concentrations (%) of Elements Detected on Fracture Surfaces of Neoprene/Steel Adhesive Joints.

Element	Commercial Primer		Modified Primer	
	Substrate	Rubber	Substrate	Rubber
C	72.9	73.6	67.8	72.4
O	6.9	7.7	11.5	9.8
Si	0.4	0.7	2.6	2.5
Fe	0.3	0.0	0.7	0.0
Cl	19.3	17.8	14.9	12.8
Zn	0.2	0.2	0.2	0.2
Pb	0.0	0.0	0.0	0.0
N	---	---	2.4	2.4

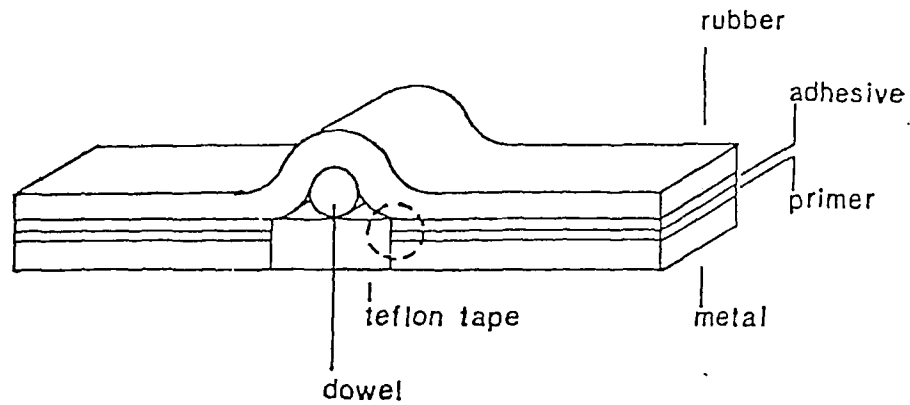


Figure 1. Diagram of the strip-blister specimen.

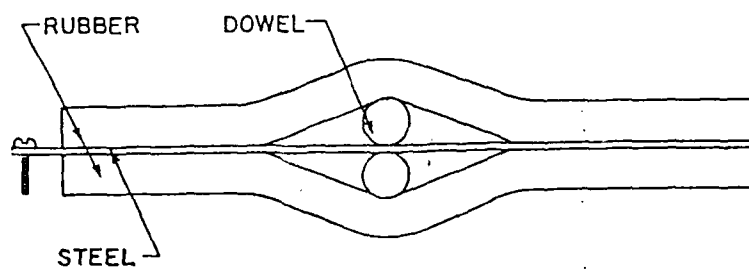


Figure 2. Diagram of the double strip-blister specimen.

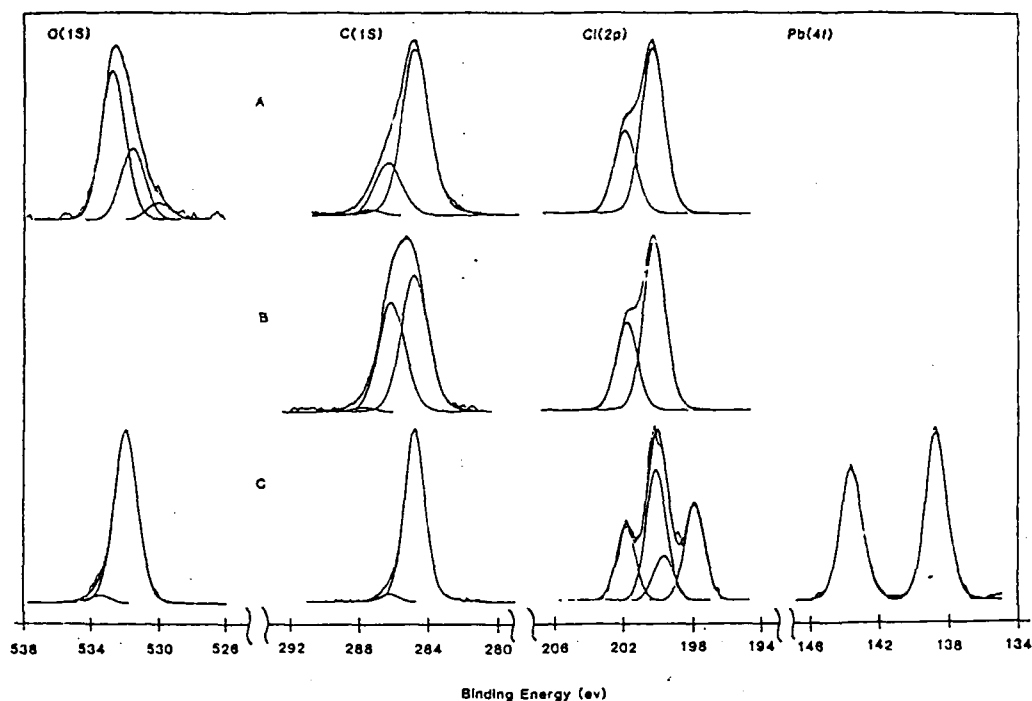


Figure 3. XPS spectra observed for (A)-primer, (B)-adhesive, and (C)-neoprene rubber.

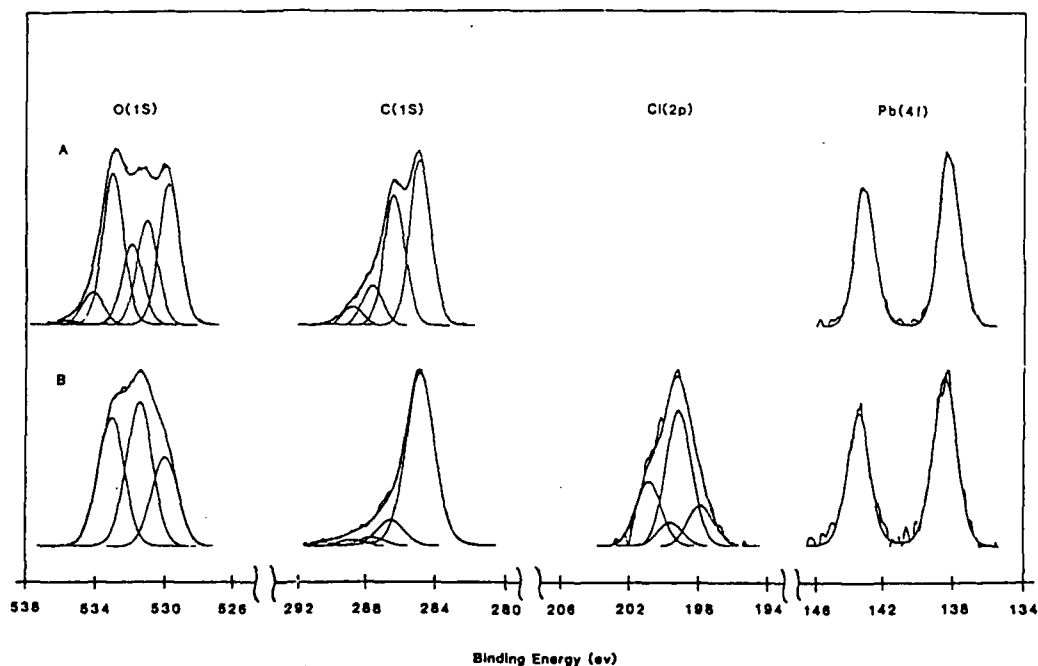


Figure 4. XPS spectra of (A)-substrate and (B)-rubber failure surfaces of strip-blister specimens prepared from etched steel and immersed in 1N NaOH for eight days.

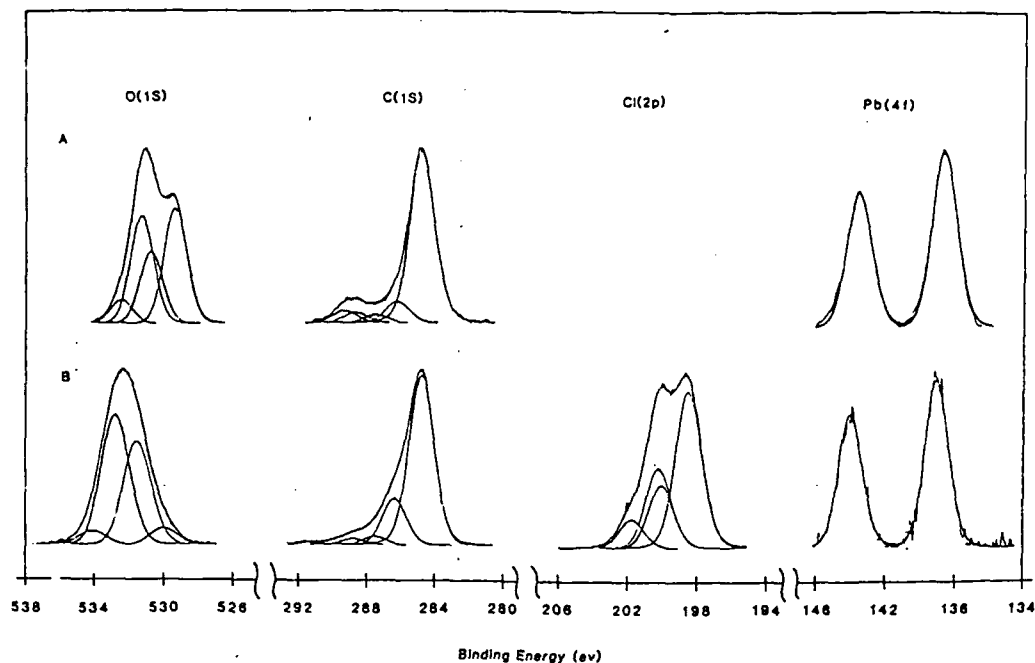


Figure 5. XPS spectra of (A)-substrate and (B)-rubber failure surfaces of strip-blister specimens prepared from polished steel and then immersed in 3.5% NaCl at a potential of -1.05 volts vs SCE.

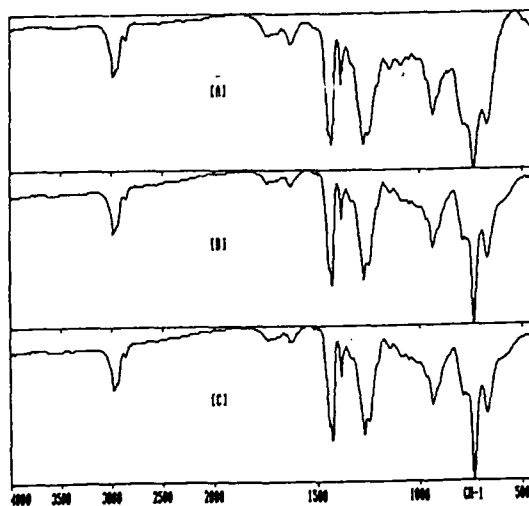


Figure 6. (A)-RAIR spectrum of the film spin-coated onto a steel mirror from the polymer solution separated from the adhesive. When the mirror was immersed in 1N NaOH for 24 hours, the film debonded. The transmission spectra shown in (B) and (C) were obtained after the detached films were immersed in 1N NaOH for 216 hours and in 2.8N NaOH for an additional 360 hours.

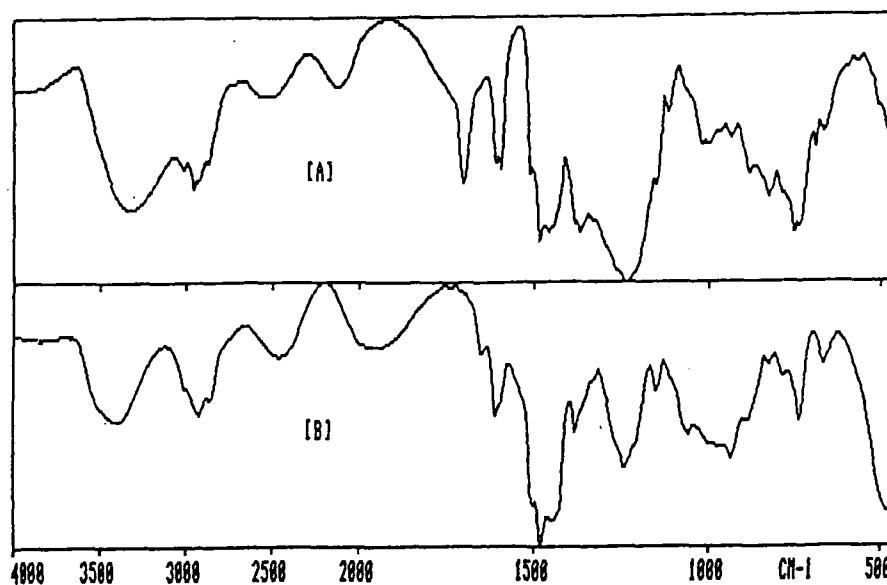


Figure 7. RAIR spectra of thin films spin-coated onto steel mirrors from solutions separated from the primer (A) - before and (B) - after curing for 45 minutes at 155°C.

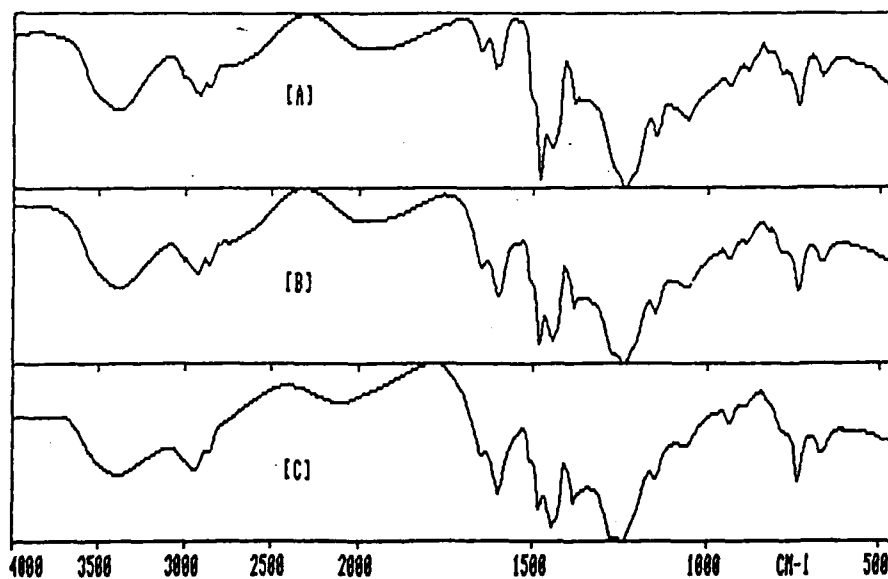
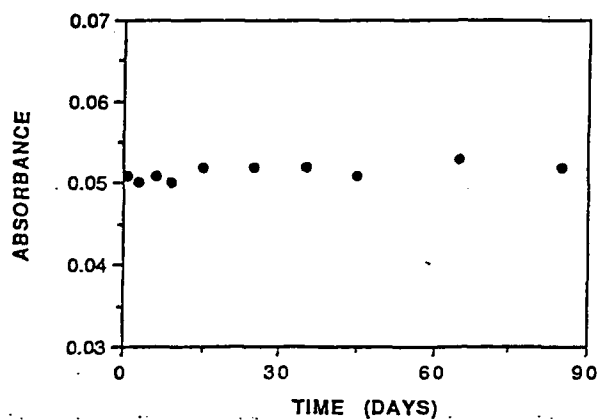
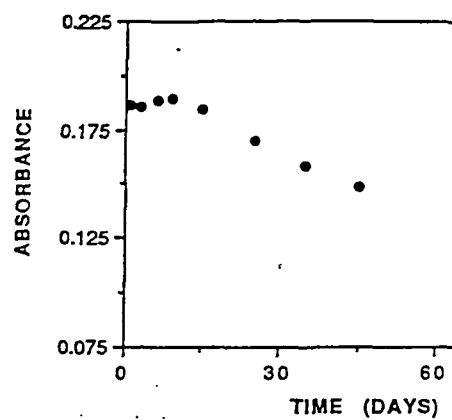


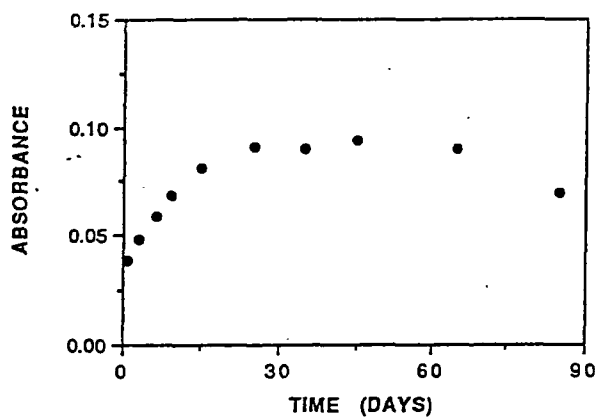
Figure 8. FTIR spectra obtained after polymer films cast from solutions separated from the primer were immersed in 1N NaOH for 216 hours and 2.8N NaOH for an additional (A) - 24 hours, (B) - 600 hours, and (C) - 2040 hours.



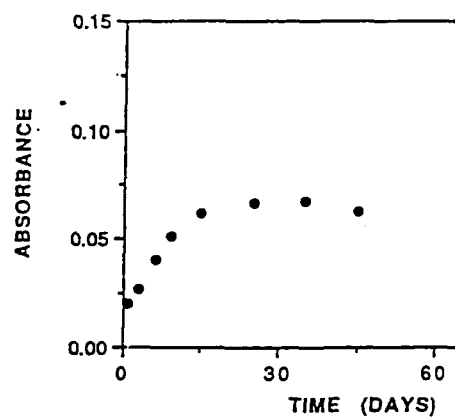
(A)



(B)

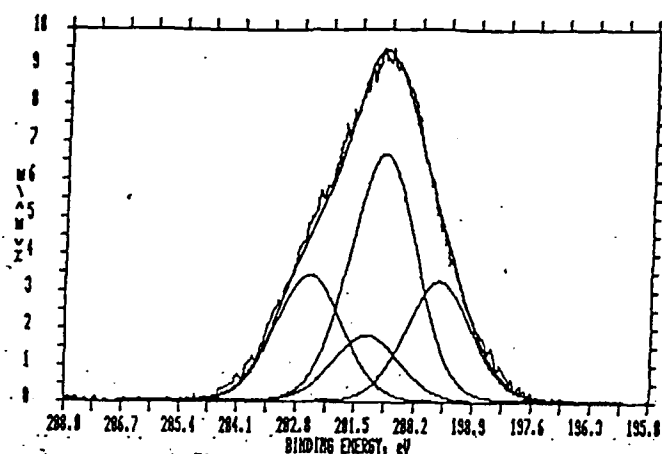


(C)

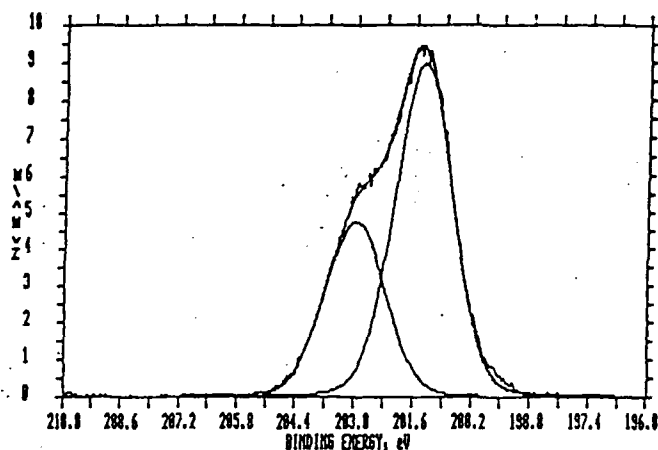


(D)

Figure 9. Absorbance as a function of immersion time in NaOH for bands near (A)-730, (B)-1482, (C)-160 (D)-1650 cm^{-1} in the infrared spectra of the p separated from the primer.



(A)



(B)

Figure 10. Cl(2p) XPS spectra obtained from the (A) - "substrate" and (B) - "rubber" fracture surfaces of an as-prepared strip-blister specimen.

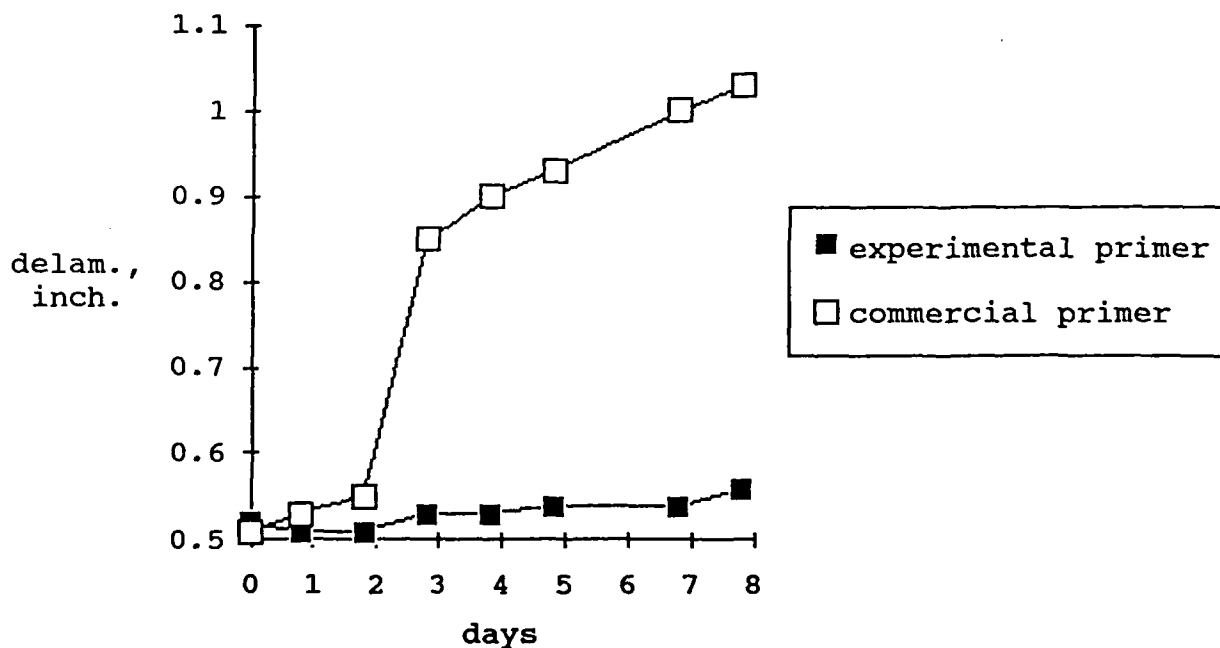


Figure 11. Delamination versus immersion time in 1N NaOH for strip-blister specimens prepared from commercial and experimental primers.

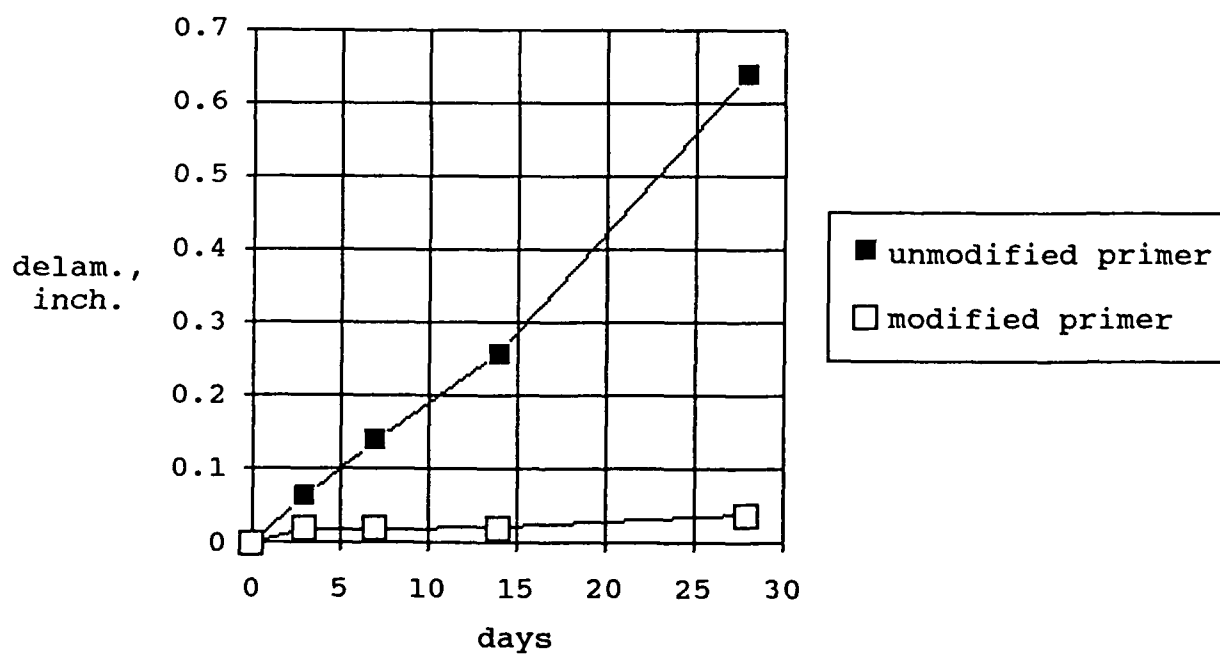


Figure 12. Cathodic delamination as a function of time for double strip-blister specimens immersed in 3.5% artificial sea water at a potential of -1.42 V vs SCE.

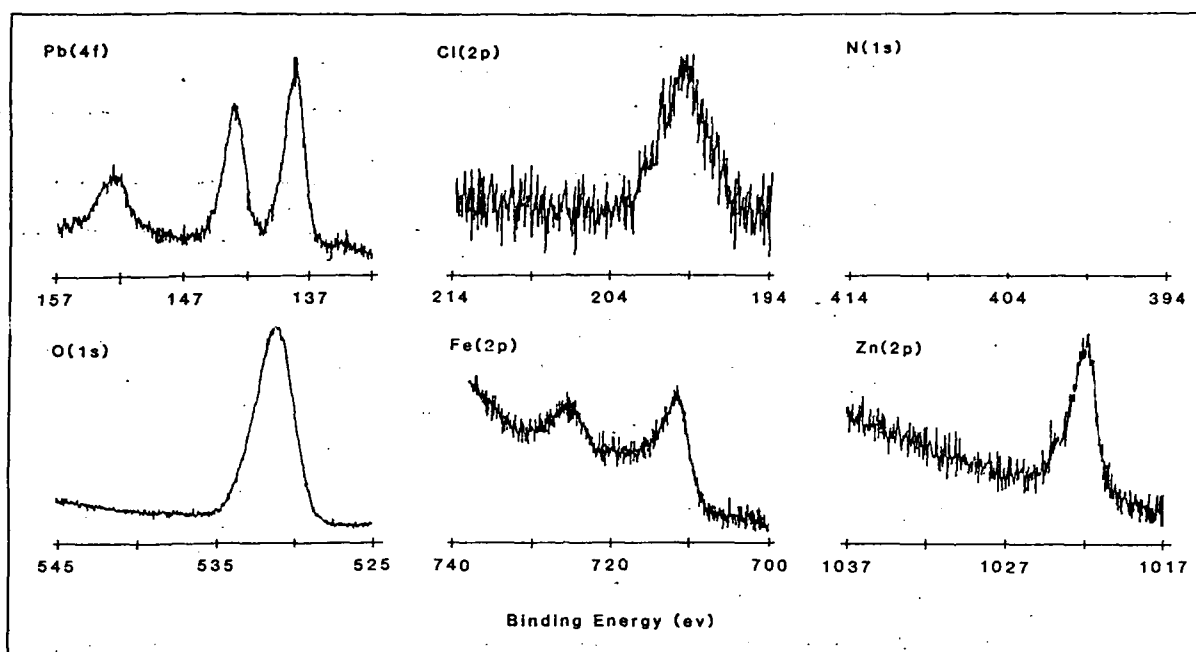


Figure 13. XPS multiplex spectra obtained from the substrate failure surface of a strip-blister specimen prepared using the unmodified primer after cathodic delamination.

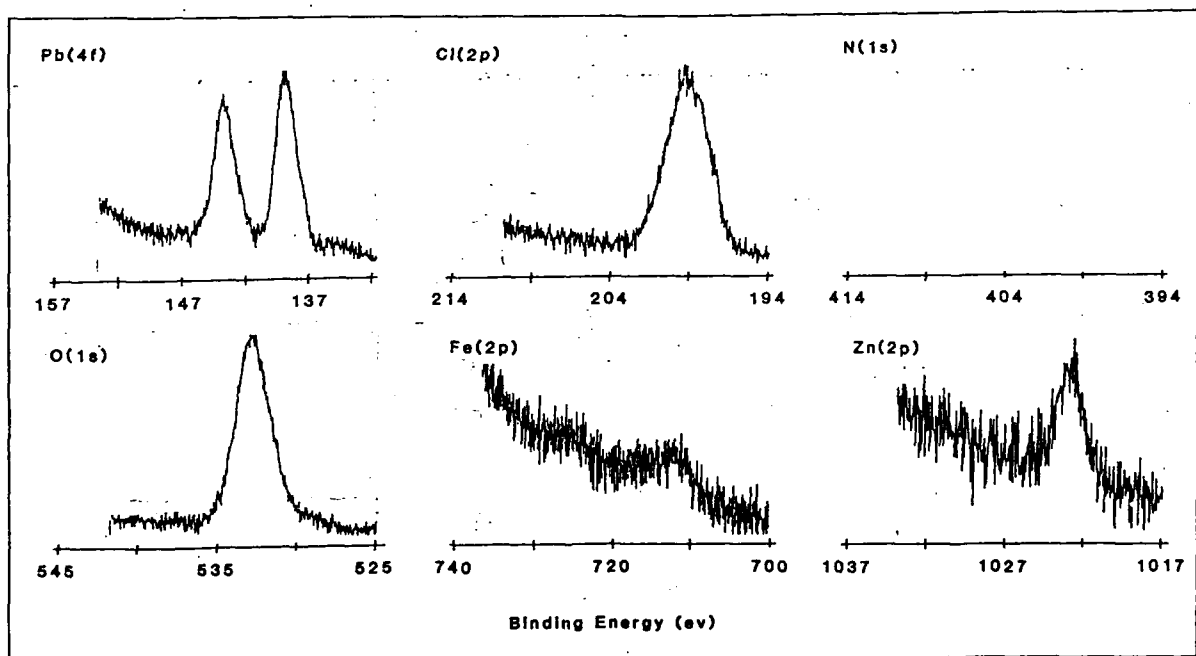


Figure 14. XPS multiplex spectra obtained from the rubber failure surface of a strip-blister specimen prepared using the unmodified primer after cathodic delamination.

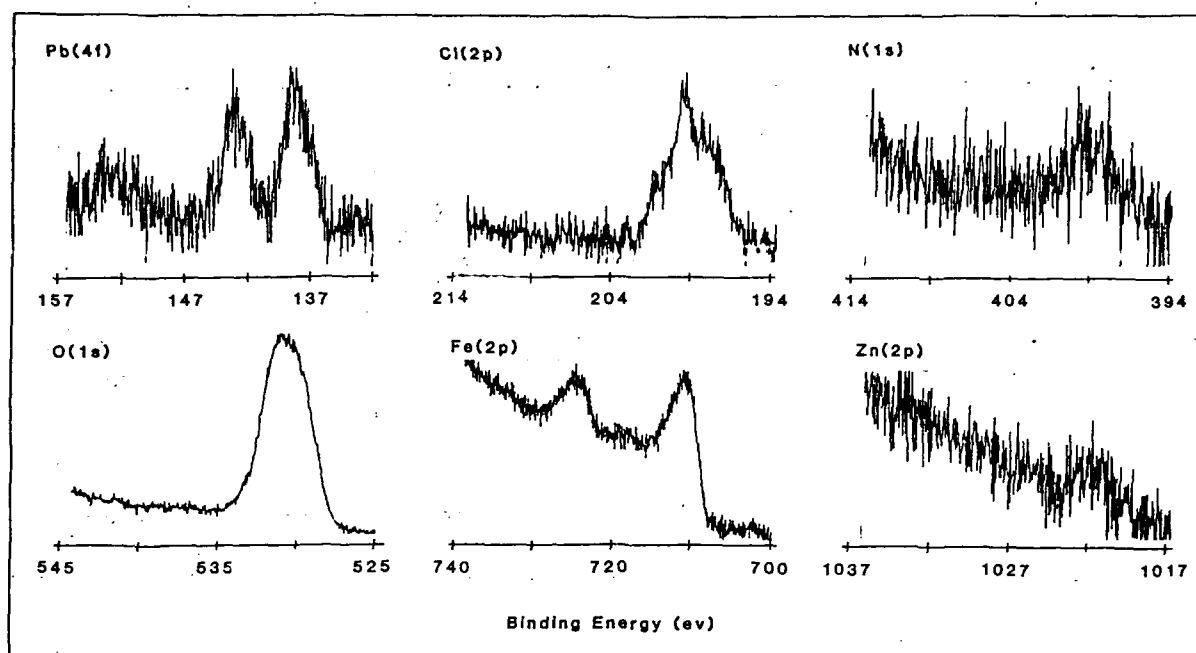


Figure 15. XPS multiplex spectra obtained from the substrate failure surface of a strip-blister specimen prepared using the modified primer after cathodic delamination.

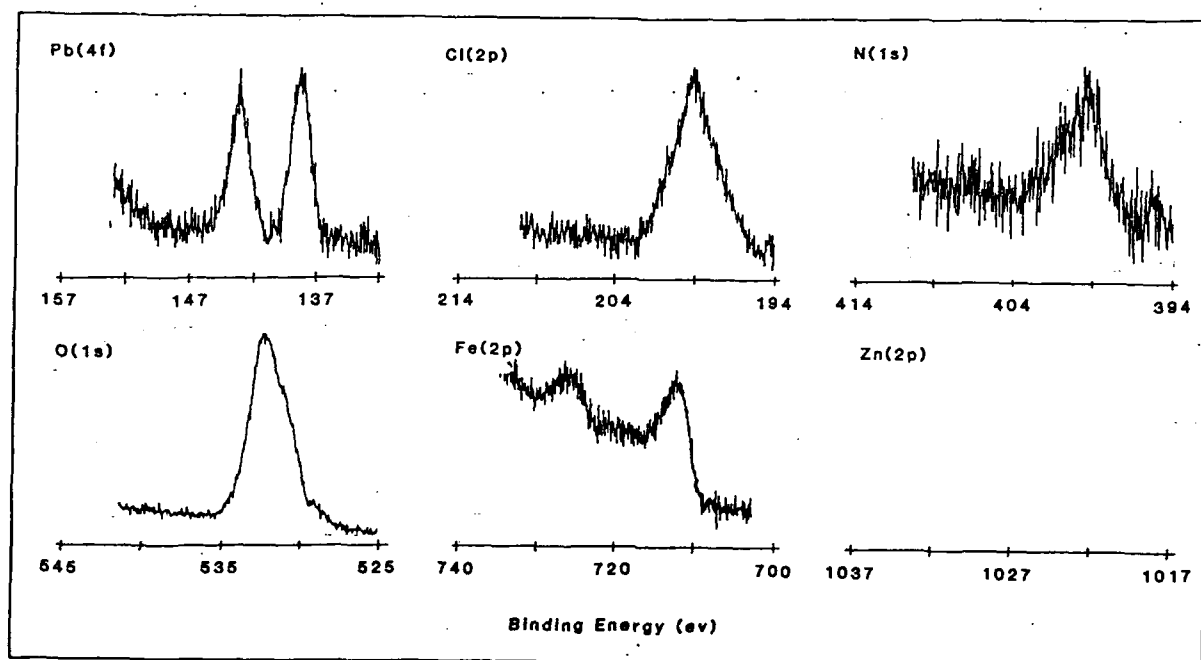


Figure 16. XPS multiplex spectra obtained from the rubber failure surface of a strip-blister specimen prepared using the modified primer after cathodic delamination.

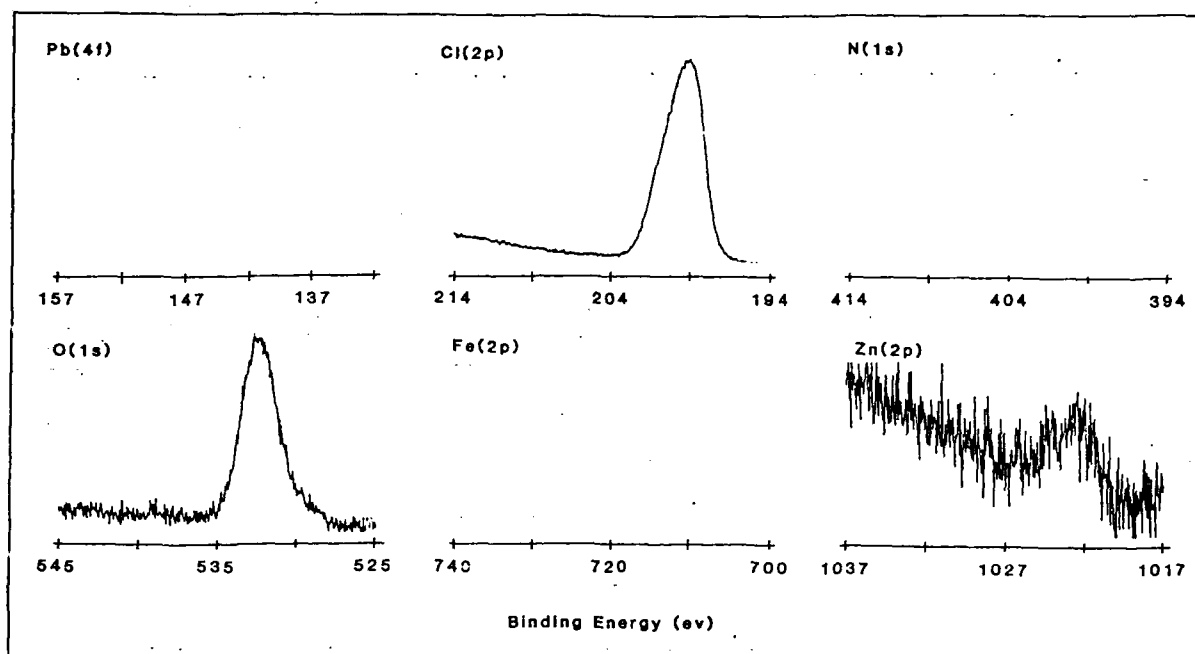


Figure 17. XPS multiplex spectra obtained from the substrate fracture surface of a strip-blister specimen prepared using the unmodified primer.

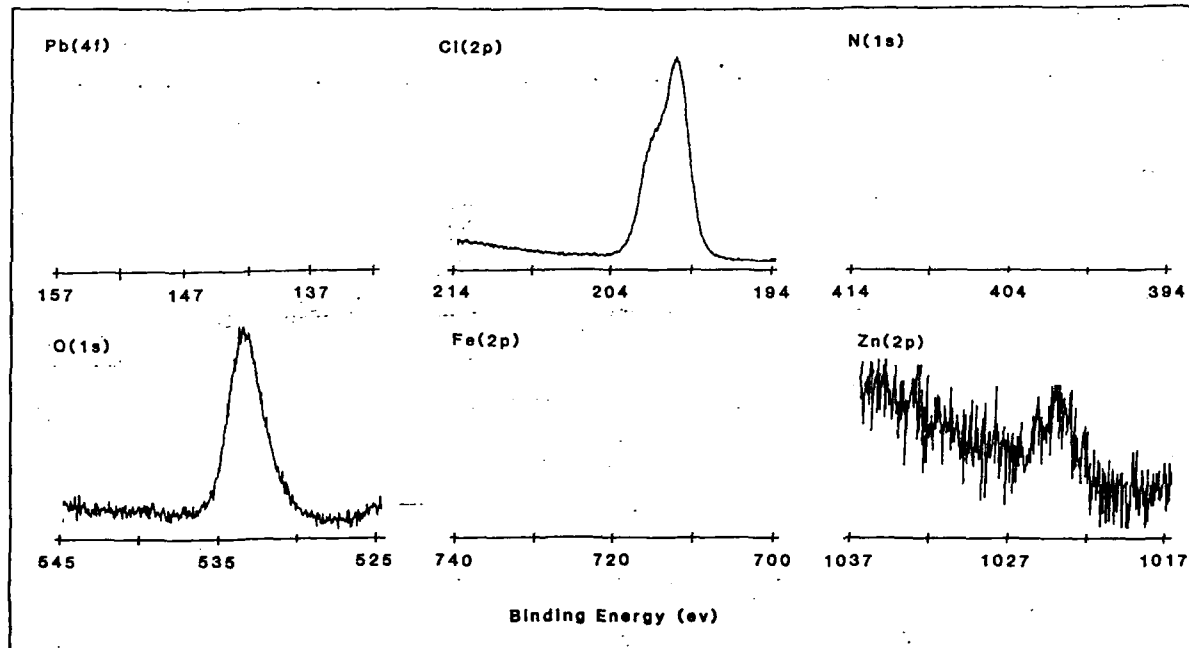


Figure 18. XPS multiplex spectra obtained from the rubber fracture surface of a strip-blister specimen prepared using the unmodified primer.

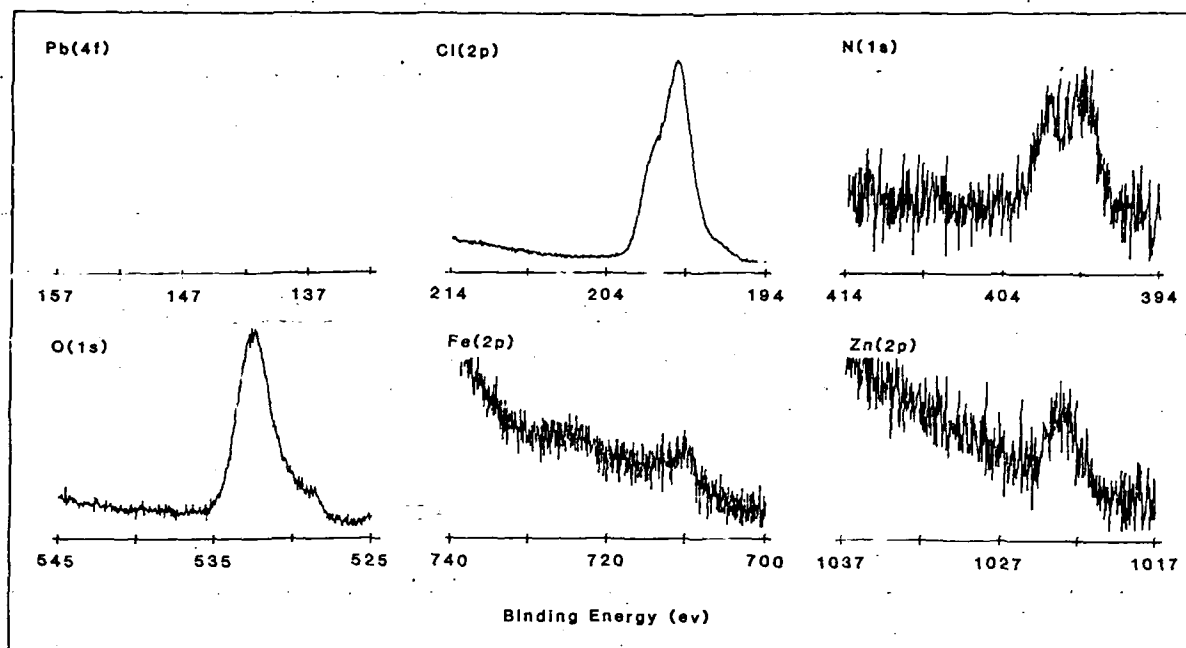


Figure 19. XPS multiplex spectra obtained from the substrate fracture surface of a strip-blister specimen prepared using the modified primer.

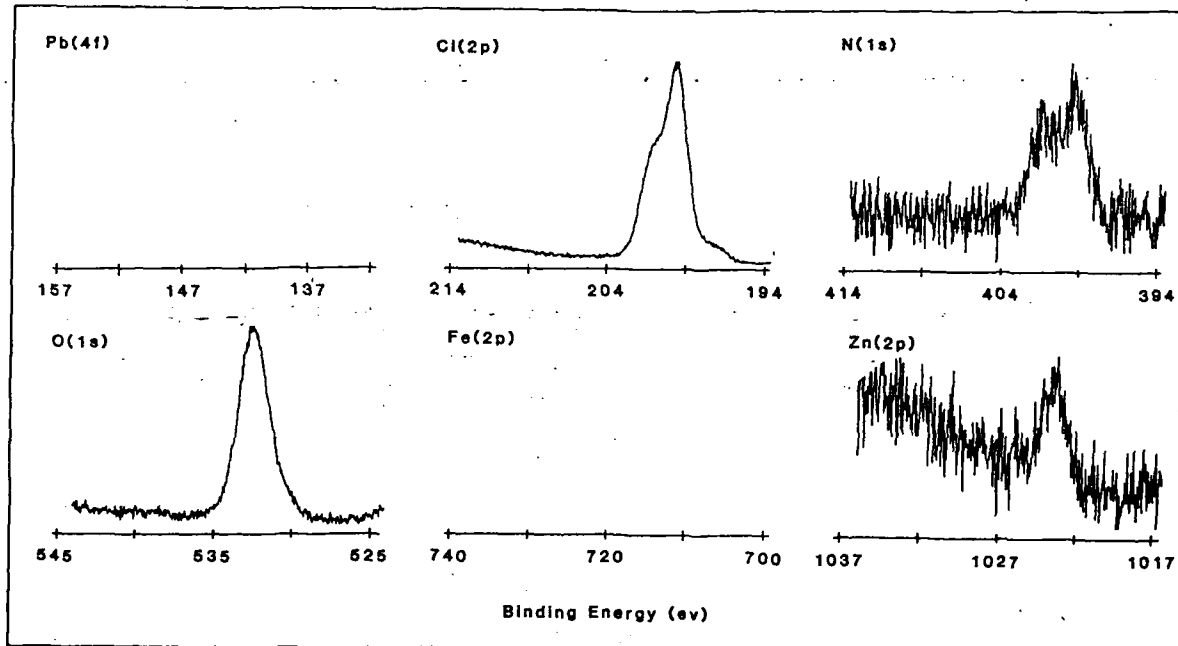


Figure 20. XPS multiplex spectra obtained from the rubber fracture surface of a strip-blister specimen prepared using the modified primer.

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