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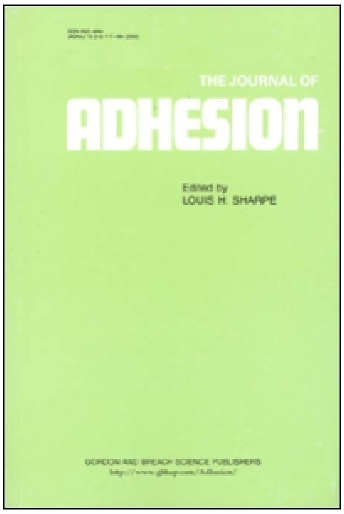

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Adhesion of Natural Rubber Compounds to Plasma-Polymerized Acetylene Films*

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Plasma-polymerized acetylene films were shown to be novel, highly effective primers for rubber-to-steel bonding. However, the performance of the primers depended strongly on processing variables such as the substrate pretreatment and the carrier gas. Miniature lap joints were prepared by using natural rubber as an "adhesive" to bond together pairs of pretreated steel adherends primed with plasma-polymerized acetylene films which were deposited using various carrier gases. The initial strength of joints prepared from substrates which were mechanically polished and then coated with plasma-polymerized acetylene films deposited using an argon or nitrogen carrier gas was 2000 N for a bonded area of 64 mm^2 and failure was 100% cohesive in the rubber. Similar results were obtained for joints prepared from mechanically-polished brass substrates. However, the initial strength of joints prepared from polished substrates which were coated with plasma-polymerized films deposited using oxygen as a carrier gas was lower by a factor of two and there was only 30% rubber coverage on the substrate failure surfaces, demonstrating the importance of the carrier gas.

The initial strength of joints prepared from substrates which were pretreated by alkaline cleaning, acid etching, or mechanical polishing and then coated with plasma polymers using argon as the carrier gas was also approximately 2000 N/64 mm^2 and failure was again 100% cohesive in the rubber. However, the strength of joints prepared from substrates which were pretreated by ultrasonic cleaning in acetone and then coated with plasma polymers using argon as the carrier gas was lower by a factor of almost two, demonstrating the significance of substrate pretreatment.

During exposure to steam at 121°C, the durability of miniature lap joints prepared from polished steel substrates primed with plasma-polymerized acetylene films using argon as a carrier gas was excellent. After exposure for 3 days, the breaking strength of the joints decreased slightly, from 1740 to 1410 N/64 mm^2, but the locus of failure remained cohesive in the rubber, implying that effect of steam was mostly to reduce the

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cohesive strength of the rubber. Similar results were obtained from joints prepared from polished brass substrates. However, the durability of joints prepared from polished brass substrates and from polished steel substrates primed with plasma-polymerized acetylene was poor during exposure to aqueous salt solutions for three days. Although all of the joints decreased significantly in breaking strength, the strength of the joints prepared from brass substrates was about 400 N/64 mm^2 higher than that of joints prepared from steel primed with plasma-polymers. Most of the joints prepared from steel primed with plasma-polymerized acetylene films failed near the interface between the primer and the steel substrate although some specimens had 20–40% rubber coverage on the failure surfaces.

Keywords: Bonding; durability; rubber-to-metal; primers, plasma-polymerized; natural rubber; interphases; crosslinking; X-ray photoelectron spectroscopy

1. INTRODUCTION

Adhesion of rubber to steel is of considerable practical importance in many areas of technology. However, direct adhesion of natural rubber to most metals is very poor. As a result, metals are frequently plated with brass, to which rubber adheres very strongly, or else the metals are coated with proprietary primers and adhesives in order to obtain adhesion of rubber.

Ebonites, natural latex-albumen adhesives (containing sulfur), adhesives made from chlorinated or hydrochlorinated rubber and adhesives based on cyclized rubber all have been used for bonding rubber to metal; the overall strength of rubber-to-metal bond was low. The most widely used method is by means of isocyanates. It is believed that isocyanate groups (—N=C=O) interact with the film of metal oxides always found on the surfaces of metals. As a result, a strong bond is formed between the metal and isocyanate. Isocyanate is bonded with rubber as a result of the diffusion of the adhesive into rubber and subsequent polymerization during the heating required for rubber vulcanization. Upon polymerization, isocyanate forms a three-dimensional network bonding together the metal, adhesive film, and rubber [1, 2].

The use of a thin brass layer as a "pretreatment" for bonding rubber to steel tire cords has resulted in some success in the tire industry; it has also led to considerable interest in the fundamental aspects of rubber-brass bond formation. The book by Buchan [3] covered early work on this subject. More recently, van Ooij has published extensive reviews about the mechanisms and theories of rubber adhesion to steel tire cords [4] as well as recent advances in bonding rubber to steel cords [5].

Adhesion of natural rubber (NR) to brass is believed to involve mechanical interlocking and physical entanglement of the crosslinked NR molecular network in a porous dendritic sulfide film. During vulcanization of NR in contact with a brass surface, the brass is corroded by sulfur, resulting in the formation of a duplex sulfide film on the brass. The film consists of non-stoichiometric Cu_xS at the sulfide-rubber interface and ZnS at the sulfide-metal interface [4]. Bonding of NR to the sulfide layer is the result of a catalytic effect of Cu_xS on the vulcanization rate of NR leading to a higher crosslink density and a higher modulus in the rubber near the "interphase."

However, there are still some problems in the process of bonding rubber to brass-plated steel. For example, chemical wastes from plating processes are difficult to dispose of. Furthermore, brass-plated steel is vulnerable to corrosion because of the galvanic coupling of brass and steel. In a corrosive environment, brass is cathodic, and iron, which is anodic, tends to corrode at an accelerated rate. Once a corrosion cell has been established, the high pH of the environment will also chemically attack the brass coating. Therefore, there is still the need to develop a system for rubber-to-metal bonding with improved corrosion protection and easy or no waste disposal.

Plasma processing has been attracting attention in many areas due to some of its unique features. During the process, the synthesis and deposition of plasma polymers can be accomplished at the same time, making plasma processing a very efficient method for polymer coating. Plasma processing also allows flexible combinations of reactor parameters (*e.g.*, monomer, flow rate, power, and pressure) which would provide a great deal of process control and versatility. Previous experiments [5] revealed the possibility of generating different forms of plasma polymers by changing the reactor conditions. Nearly 1000 Å thick plasma polymer film can be deposited in only a few minutes of reaction. Thus, this is a very efficient method for mass production. Moreover, in plasma processing, there are no solvents involved and there are no solvent-disposal problems.

Despite the advantages that plasma-polymerized films have when compared with conventional metal pretreatment processes, there have been few reports on the use of such films as primers for rubber-to-metal bonding. Recently, we have undertaken a research project to develop novel plasma etching and plasma-polymerization pretreatment processes for metal substrates. Initially, the plasma-polymerized acetylene films were carefully characterized by ellipsometry, reflection-absorption infrared spectroscopy (RAIR), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), secondary ion mass spectrometer (SIMS), and scanning electron spectroscopy (SEM) [6, 7]. FTIR spectra of the as-deposited films were characterized by bands related to mono- and di-substituted acetylene groups and by bands related to methyl and methylene groups. During exposure to the atmosphere, bands related to acetylenic groups decreased in intensity while new bands due to carbonyl groups appeared. When XPS spectra were obtained from films that were exposed to the atmosphere, new components assigned to oxidation products were observed in the C(1s) spectra which were not observed for as-deposited films, verifying that oxidation had occurred. Numerous peaks related to aromatic structures were observed in positive SIMS spectra of as-deposited films. Results obtained from AES showed that the plasma-polymerized films were continuous and that the oxide on the substrate surface was partially reduced during deposition.

The purpose of this paper is to describe the properties of plasma-polymerized acetylene films as primers for rubber-to-metal bonding. Miniature lap joints were prepared by using rubber as an "adhesive" to bond together pairs of steel adherends primed with plasma-polymerized films. The initial strength of the lap joints was determined as a function of the carrier gas used in the film deposition and the substrate surface pretreatment. The results were compared with those obtained from similar joints prepared from brass substrates. Preliminary durability test results are also reported.

2. EXPERIMENTAL

1010 cold-rolled steel (CRS) sheets having a thickness of 0.5 mm and a composition that was mostly Fe (99.0–99.4%), Mn (0.3–0.6%), C (0.008–0.13%), Si (0.1%), S (0.05%), and P (0.04%) [8] were obtained from The Goodyear Tire and Rubber Company (Akron, Ohio). Substrates having the size and shape shown in Figure 1A were cut from the sheets and pretreated in various ways, including acetone rinsing, alkaline cleaning, acid etching, and mechanical polishing. The substrates were then placed into a plasma reactor where they were etched in an argon plasma and then coated with a thin film of plasma-polymerized acetylene. Finally, miniature lap joints were prepared by using natural rubber as an "adhesive" to bond together pairs of substrates as shown in Figure 1B. Ten joints could be prepared simultaneously using a specially-designed mold.

Miniature lap joints were prepared for use as "controls" from brass substrate having a thickness of 0.5 mm. Brass substrates (70% Cu and 30% Zn) having the size and shape shown in Figure 1A were mechanically polished using 0.3 µm diamond paste suspended in lapping oil. Pairs of these substrates were then bonded together to form lap joints as shown in Figure 1B using the specially-designed mold.

Pretreatment of the CRS substrates was carried out as follows. One set of substrates was cleaned by immersion in an acetone bath in an ultrasonic cleaner at room temperature for 30 minutes. Another set was pretreated in an alkaline solution. The solution was prepared by heating 1 liter of deionized water in a beaker to 60°C and then slowly adding 30 grams of Parco cleaner 338 (Parker Chemical Co., Morenci, MI), into the beaker. Steel substrates were immersed into the solution

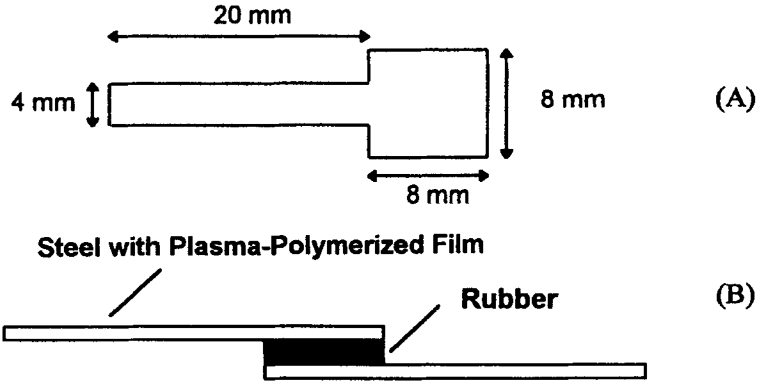

FIGURE 1 Sample arrangement for adhesion measurement of rubber to plasma-polymerized primer films coated steel substrates. (A)-steel sample shape, and (B)-vulcanized arrangement.

for 30 minutes and then cleaned ultrasonically in the same solution for 15 minutes. The substrates were then withdrawn, rinsed in hot water, rinsed in deionized water and blown dry immediately with a stream of nitrogen gas. The entire procedure was then repeated. A third set of substrates was pretreated in an acid cleaning solution made by adding 65 vol.% H_2O, 30 vol.% phosphoric acid, and 5 vol.% nitric acid together at room temperature. Substrates were immersed in the acid solution for 10 minutes, rinsed with deionized water, and dried with nitrogen. The entire procedure was then repeated. Another set of substrates was pretreated by mechanical polishing to a mirror finish. These substrates were first polished dry on 600 grit silicon carbide paper to grind the surface and then wet polished with 14.5, 3.0, and 0.3 μm aluminum oxide abrasive slurries. Finally, the substrates were rinsed in distilled water and acetone and blown dry with nitrogen.

After pretreatment as described above, the substrates were etched immediately in an argon plasma and then coated with a thin film of plasma-polymerized acetylene polymer in a tubular reactor (see Fig. 2) which was inductively coupled to an RF (13.56 MHz) power supply. The main part of the reactor is a Pyrex tube with an internal diameter of 6 inches (15.2 cm). The top portion of the reactor is made of quartz and is surrounded by the RF coil. Carrier gases were introduced at the top of the reactor, just above the coil. Monomers were introduced into the reactor through an inlet tube which was located below the coil. Sample substrates were supported on a stage which could be moved vertically within the reactor. A detailed description of the reactor has been presented elsewhere [9].

Several different carrier gases were considered. They included argon (Matheson ultra high purity, minimum purity 99.999%), nitrogen (Matheson ultra high purity, 99.999% minimum purity), and oxygen (Matheson ultra high purity, 99.98% minimum purity). The monomer was Matheson purified acetylene (99.6% minimum purity).

At the beginning of each set of experiments, the reactor was disassembled and cleaned in water and then methanol. Plasma polymerization products (including oily films and powders) were dissolved off the reactor chamber and accessories. After reassembly, the system was pumped down and etched in an oxygen plasma with 100 sccm (standard cubic centimeters per minute) flow rate at 1 Torr pressure and 200 W power for at least 20 minutes.

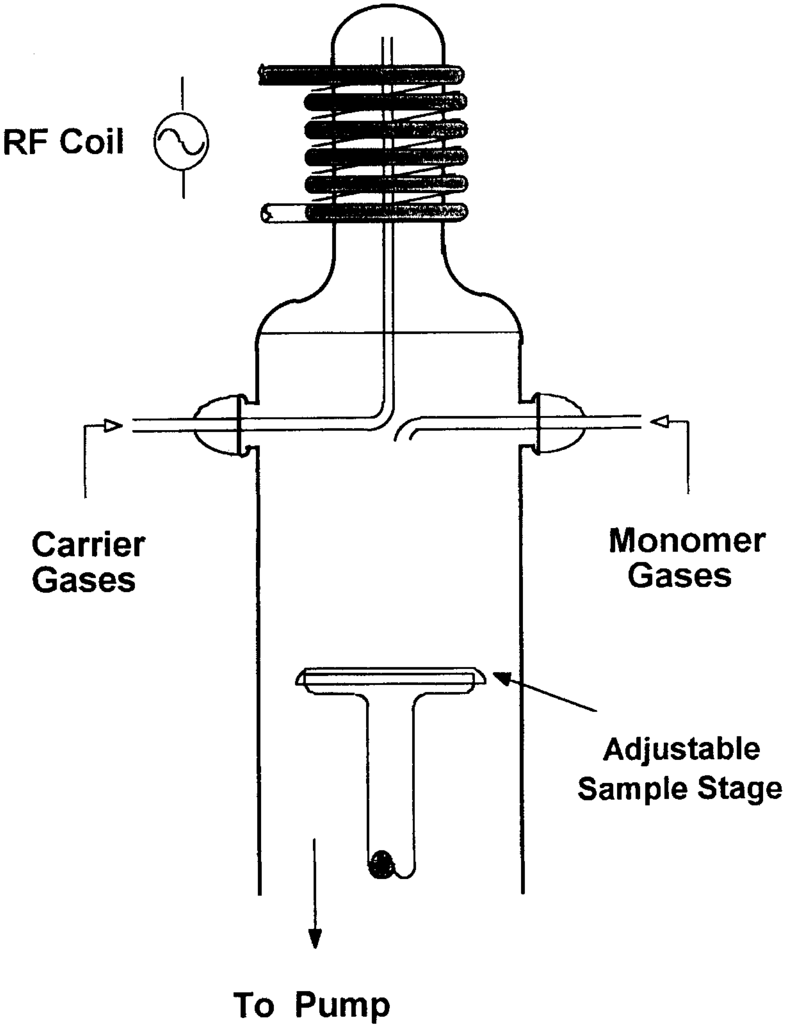

FIGURE 2 Schematic representation of the reactor used for plasma treatment and polymerization.

The substrates were then placed in the reactor, the reactor was pumped down to a pressure of 10 mTorr, and the substrates were exposed to an argon plasma at 1 Torr pressure, 20 sccm flow rate, and power of 20 W for 10 minutes to remove surface contaminants. Plasma-polymerized acetylene films were then deposited onto the substrates immediately after plasma etching. Table I gives the main operating parameters that were used for plasma polymerization. When oxygen or nitrogen was used as the carrier gas, the reactor pressure was lowered and the power was increased. This was done in order to obtain similar film thickness to those films prepared using argon as the carrier gas.

After deposition of the plasma-polymerized films onto the substrates, the substrates were removed from the reactor and miniature lap joints were prepared by bonding pairs of pretreated substrates together using natural rubber as an "adhesive." The rubber compound contained cis-1,4-polyisoprene, carbon black, fatty acids, rosin acids, cobalt carboxylate, phenolic resins, zinc oxide, *p*-phenylenediamine, a sulfenamide accelerator, and sulfur and was cured at a temperature of 155°C and pressure of 133.44 kN for 35 minutes. Upon completion of cure, the joints were removed from the mold and allowed to cool to room temperature and age a minimum of 24 hours before tensile testing.

An Instron tensile tester was operated at room temperature at a strain rate of 20 mm/min and used to determine the strength of the joints (in N/64 mm^2). The maximum force in Newtons required to cause failure of the joints was determined and the rubber coverage of the failure surfaces was qualitatively estimated. The strength of lap joints prepared from steel substrates coated with plasma-polymerized primers was compared with the strength of lap joints prepared from polished brass substrates without plasma-polymerized primers.

In order to determine the effect of atmospheric exposure on the properties of the primers, two sets of substrates coated with plasma-polymerized acetylene films were prepared. One was used to prepare miniature lap joints one day after deposition of the plasma-polymerized primers. The second set was aged in the atmosphere at room

TABLE I Reactor parameters for plasma polymerization of acetylene

Carrier Gas	*Pressure (Torr)*	*Power (Watt)*	*Flow rate (sccm)*
Argon	1.0	55	20(Ar)/25(C_2H_2)
Nitrogen	0.6	60	20(N_2)/25(C_2H_2)
Oxygen	0.6	80	20(O_2)/25(C_2H_2)

temperature for 3 weeks after deposition and then used to prepare miniature lap joints.

Two different methods were used to determine the durability of the rubber-to-steel bonds. In one case, miniature lap joints were aged in steam at 121°C for 3 days and then tested in an Instron at room temperature. In the other case, joints were aged in 5 wt.% aqueous NaCl at 90°C for 3 days and tested in the Instron at room temperature. All of the strengths reported here were actually the average values of five joints. More than three sets of tests were conducted to ensure reproducible results.

Surface composition of the CRS substrates immediately after pretreatment by acetone rinsing, alkaline cleaning, acid etching, or mechanical polishing was determined using X-ray photoelectron spectroscopy. A Perkin-Elmer/Physical Electronics Model 5300 XPS spectrometer with Mg K_α X-rays, operating at 300 W and 15 kV DC, was used to obtain the spectra. Survey spectra were obtained using a pass energy of 44.75 eV and 0.5 eV/step. The resolution was 1.0 eV. High resolution spectra were obtained at a take-off angle of 45° using a pass energy of 17.9 eV and 0.05 eV/step. The resolution was 0.7 eV. An Apollo computer system with Perkin-Elmer/Physical Electronics software was used for data analysis.

The thickness of the plasma-polymerized acetylene films was determined by using a Rudolph Research Model 436 ellipsometer to examine *polished* steel substrates before and after deposition of the films. A computer program developed by McCrackin [10] was used to calculate the thickness and refractive index of the films from the measured values of the ellipsometric parameters Δ and ψ. It was assumed that the film thickness on *unpolished* substrates was similar.

3. RESULTS AND DISCUSSION

A. Thickness of Plasma-Polymerized Films

Results obtained from ellipsometry showed that the thickness of plasma-polymerized acetylene films obtained using argon as the carrier gas and the deposition parameters shown in Table I was about 750 Å. The refractive index of the film was taken as 1.60 and the complex refractive index of the substrate was 2.63 (1-il.32) for the ellipsometry calculations.

B. Effect of Pretreatment on Surface Composition of CRS Substrates

Atomic concentrations obtained from XPS analysis of the surfaces of CRS substrates after various pretreatments are shown in Table II. Large amounts of carbon contaminants (72.7%) but very little iron (0.3%) were observed on the surface of the as-received substrates. After acetone-cleaning, the carbon concentration decreased significantly, from 73% to 54%, and the iron concentration increased from 0.3% to 4.9%. However, the amount of carbon remaining on the substrates after acetone cleaning was considered too great.

As a result, two other methods were used to clean the steel substrates. Hong [11] showed that alkaline cleaning was very effective in removing most foreign contaminants from the surface of steel. Trawinski [12], Hudak [13], and Boerio *et al.* [14], all showed that nitric-phosphoric acid etching produced a clean steel surface with a microrough morphology. Therefore, alkaline cleaning and nitric-phosphoric acid etching were employed to pretreat the surfaces of the steel substrates. From XPS analysis, it was determined that both methods resulted in relatively clean surfaces compared with the as-received. The carbon and iron concentrations on the steel substrates were 20.6 and 9.3%, respectively, after alkaline cleaning and 23.2 and 7.4%, respectively, after acid-etching. Mechanical polishing also resulted in a clean surface with carbon and iron concentrations of 25.9 and 11.6%, respectively.

C. Effect of Substrate Pretreatment on the Breaking Strength of Miniature Lap Joints

Figure 3 shows the effect of substrate pretreatment on the breaking strength of miniature lap joints. In order to determine the effect of substrate pretreatment on the breaking strength of the joints, the same carrier gas (argon) was used in the deposition of the plasma polymer films but the substrate pretreatment was varied. The breaking strength of lap joints prepared from acetone-cleaned substrates primed with

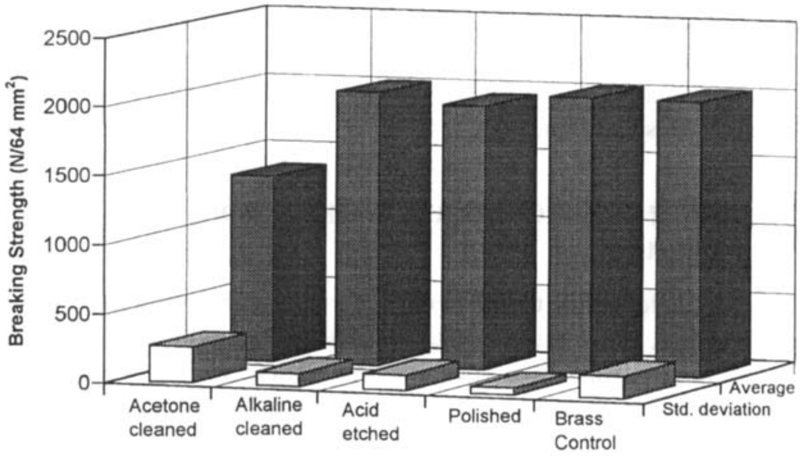

FIGURE 3 Breaking strengths of lap joints prepared from steel substrates primed with plasma polymerized acetylene films as a function of surface pretreatments. Control specimens were prepared from polished brass substrates.

plasma-polymerized acetylene films was 1360 N/64 mm^2 (standard deviation, $\sigma = 260$ N). Rubber coverage on these failure surfaces was about 50–60%. On the other hand, the breaking strength of lap joints prepared from polished substrates primed with plasma-polymerized acetylene films was 2010 N/64 mm^2 ($\sigma = 50$ N) and was comparable with that of joints prepared from polished brass substrates. For joints prepared from polished steel and brass substrates, it was observed that failure had taken place within the rubber rather than at the interface, since 100% rubber coverage was seen on both of the failure surfaces. The poor strength of joints made with acetone-cleaned substrates seemed to indicate inadequate surface pretreatment that resulted in a weak boundary layer. The weak boundary layer most likely consisted of rolling oil residues that were not removed by solvent cleaning.

The breaking strength for joints prepared from alkaline-cleaned substrates primed with plasma-polymerized acetylene films was 2000 N/64 mm^2 ($\sigma = 90$ N/64 mm^2) which was comparable with that of the brass control samples, 2000 N/64 mm^2 ($\sigma = 160$ N). Rubber coverage on the failure surfaces was 100%, indicating that failure occurred in the rubber itself. When the substrates were pretreated with acid, the breaking strength was 1920 N/64 mm^2 ($\sigma = 110$ N) which was similar to that of the control samples. Rubber coverage on these failure samples was also 100%. It was obvious that both alkaline cleaning and acid etching could satisfy the cleaning demand for initial joint strength consideration.

D. Effect of Carrier Gas on the Breaking Strength of Miniature Lap Joints

In order to determine the effect of carrier gas on the breaking strength of the joints, the substrate pretreatment was kept constant (mechanical polishing) but the carrier gas was varied. Figure 4 shows the results that were obtained. The breaking strength of lap joints prepared from polished CRS substrates primed with plasma-polymerized acetylene films which were deposited using argon as a carrier gas was 2010 N/64 mm^2 ($\sigma = 50$ N) and was comparable with that of joints prepared from polished brass substrates (see Fig. 4). More importantly, a remarkably small standard deviation was observed for the breaking

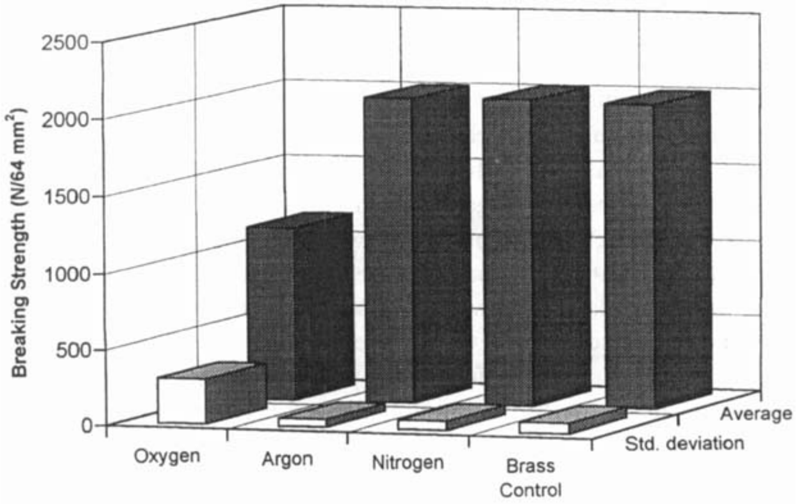

FIGURE 4 Breaking strengths of lap joints prepared from polished steel substrates primed with plasma polymerized acetylene films as a function of carrier gases. Control specimens were prepared from polished brass substrates.

strength when the plasma-polymerized primers were deposited using argon as the carrier gas.

Lap joints prepared from polished steel substrates which were primed with plasma-polymerized acetylene using N_2 as a carrier gas had a breaking strength of 2010 N/64 mm^2 ($\sigma = 60$ N) (see Fig. 4). These strengths again compared well with the breaking strengths of the joints prepared with brass substrates, 2000 N/64 mm^2 ($\sigma = 160$ N). A remarkably small standard deviation was also observed for the breaking strength when the plasma-polymerized primers were deposited using nitrogen as the carrier gas. Rubber coverage on these failure samples was also 100%. It was clear that plasma-polymerized acetylene films prepared using N_2 as a carrier gas were outstanding primers for rubber-to-steel bonding. Apparently, the cohesive failure mechanism indicated that the lap joints prepared from the steel-plasma primer-rubber system was limited by the cohesive strength of the natural rubber compounds.

On the other hand, when oxygen was used as a carrier gas, the breaking strength of the lap joints prepared from steel substrates primed with plasma-polymerized acetylene films was only 1140 N/64 mm^2 ($\sigma = 300$ N), a lower strength by a factor of two.

The relatively high breaking strength that was obtained when argon or nitrogen was used as the carrier gas is believed due to crosslinking between the natural rubber "adhesive" and plasma-polymerized acetylene films and to the excellent adhesion of the primer films to the substrates. It is obviously very difficult to characterize the "interphases" between the plasma-polymerized films and the actual rubber "adhesive" and between the plasma-polymerized films and the CRS substrates. In order to determine the structure of the interphase between rubber and plasma-polymerized acetylene films deposited on steel substrates, we have utilized a model rubber compound in which natural rubber was replaced by squalene. This model consisted of a mixture of squalene, zinc oxide, carbon black, sulfur, stearic acid, diaryl-p-diphenyleneamine, and *N*,*N*-dicyclohexyl-benzothiazole sulfenamide (DCBS). Analytical techniques such as XPS, SIMS, FTIR, and AES have been used to characterize the interphases that were formed when the model compound was reacted with the polymer films [7, 15] It was found that zinc oxide reacted with stearic acid to form zinc stearate at the interface between squalene and the plasma-polymerized acetylene primer. Zinc stearate reacted with DCBS (*N*,*N*-dicyclohexyl-benzothiazole sulfenamide) and sulfur to form an accelerator complex and zinc perthiomercaptides. The perthiomercaptides reacted with squalene and the plasma polymer to form pendant groups which eventually reacted to form crosslinks between squalene and the primer [7, 15]. In the absence of a cobalt-containing "adhesion promoter," the length of the sulfur chains in the crosslinks and the perthiomercaptide intermediates was relatively long.

When cobalt naphthenate was added to the model "rubber," the reactions at the interface between squalene and the plasma-polymerized film were similar except that the length of the crosslinks and the perthiomercaptide intermediates was much shorter. Zinc and cobalt sulfides and perthiomercaptides, which formed at the interface between squalene and the plasma-polymerized acetylene primer catalyzed the reaction between squalene and the primer. Crosslinks between squalene and the primer were mostly monosulfidic although some evidence for di- and tri-sulfidic crosslinks was observed [7].

Less is known regarding the interphase between the plasma-polymerized films and the steel substrates. However, we have recently used surface-enhanced Raman scattering (SERS) to characterize "interphases" between plasma-polymerized acetylene films and silver substrates [16]. Preliminary results indicate that a surface acetylide is formed which has the structure $R{-}C{\equiv}C^{-}\cdots Ag^{+}$.

The low breaking strength of lap joints which were prepared by using oxygen as a carrier gas was attributed to large amounts of oxygen incorporated in the plasma, thus reducing the number of $>C{\equiv}C<$ bonds in the plasma polymers. Hence, when rubber compounds were cured against these plasma polymers, the availability of reactive functional groups was limited. This caused low breaking strengths due to interfacial failure at the rubber-plasma polymer interface and/or cohesive failure of the plasma-polymerized film which was evident from the low rubber coverage (about 30%) on the metal failure surfaces.

As described above, adhesion of natural rubber compounds to brass is believed to involve mechanical interlocking and physical entanglement of the crosslinked natural rubber network in a porous dendritic sulfide film. During vulcanization of natural rubber in contact with a brass surface, the brass is corroded by sulfur, resulting in the formation of a duplex sulfide film on the brass. The film consists of nonstoichiometric Cu_xS at the sulfide-rubber interface and ZnS at the sulfide-metal interface [4] Bonding of natural rubber to the sulfide layer is the result of a catalytic effect of Cu_xS on the vulcanization rate of natural rubber leading to a higher crosslink density and a higher modulus in the rubber near the "interphase." While adhesion of natural rubber to brass is related to the fast development of a thin film of nonstoichiometric copper sulfide at the brass-rubber interface, adhesion of plasma-polymerized acetylene to rubber is due to crosslinking between natural rubber and plasma-polymerized primers.

E. Durability of Miniature Lap Joints

The breaking strengths of miniature lap joints prepared from substrates which were mechanically polished, coated with plasma-polymerized acetylene films using argon as the carrier gas, and then aged in the atmosphere *for one day* after deposition of the films are shown in Figure 5. Similar joints prepared from mechanically-polished solid brass coupons were used as controls. It was evident that the *initial* breaking strengths of joints prepared using steel substrates coated with plasma-polymerized acetylene films were comparable with those of joints prepared from polished brass substrates. Failure in both cases was cohesive in the rubber itself since both failure surfaces were completely covered by rubber.

Exposure to steam for three days resulted in a slight loss of strength for joints prepared from polished brass substrates, from 1730 to 1480 N/64 mm^2. The breaking strength of lap joints prepared from steel substrates coated with plasma-polymerized acetylene primers also declined slightly, from 1740 to 1410 N/64 mm^2. The locus of failure of all of the joints remained cohesive in the rubber after exposure to steam for three days, implying that the effect of steam was mostly to reduce the cohesive strength of rubber.

However, the initial breaking strength for lap joints prepared from polished brass substrates was 1730–1740 N/64 mm^2, about 300 N/64 mm^2 lower than obtained in previous experiments in which the carrier gas and pretreatment effects were studied. This was attributed to the use of different batches of rubber compounds, which were apparently weaker in cohesive strength. Previous experiments have shown that

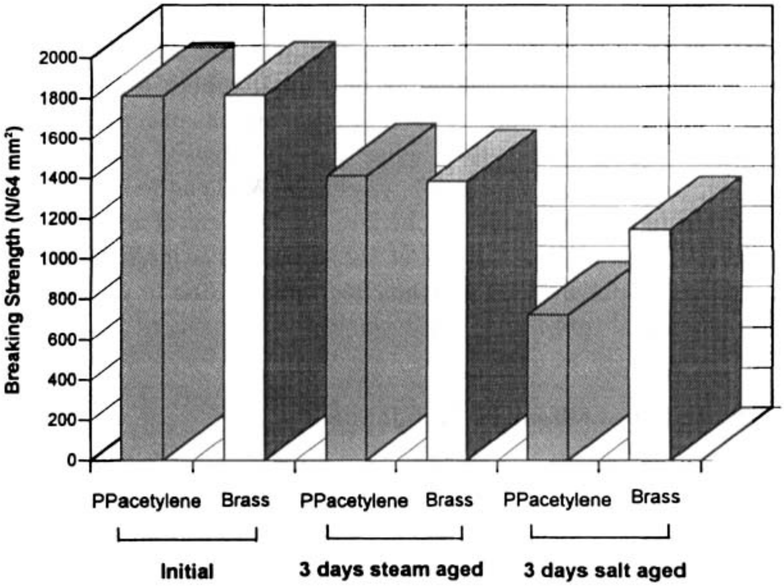

FIGURE 5 Breaking strengths of lap joints as-prepared and after exposure to corrosive environments. Control specimens were prepared from polished brass substrates. The others were prepared from polished steel substrates primed with plasma-polymerized (PP) acetylene films. The joints were prepared one day after deposition of the plasma-polymerized primers.

the breaking strength of lap joints prepared from the rubber-plasma primer-steel system was limited by the cohesive strength of natural rubber compounds. As a result, a lower initial joint strength was observed.

Exposure to aqueous NaCl solutions for three days resulted in significant loss of strength for all of the joints. The breaking strengths of joints prepared from polished steel substrates primed with plasma-polymerized acetylene films and of joints prepared from polished brass substrates all decreased to a few hundred N/64 mm^2. Examination of the failure surfaces showed that the locus of failure shifted from cohesive to adhesive. It was concluded that failure was mostly at the interface between the plasma-polymerized acetylene films and the steel substrates because a large Fe signal was detected by XPS analysis on the failure surfaces which were not covered by any rubber.

Photographs showing the failure surfaces from these joints, which were prepared one day after deposition of the plasma polymer films, are presented in Figures 6 and 7. 100 % rubber coverage was observed on the fracture surfaces of joints prepared from polished steel substrates primed with plasma-polymerized acetylene films and joints prepared from polished brass substrates. Even after 3 days of steam aging, similar results were still obtained. However, there was only 20–40% of rubber coverage on the fracture surfaces for joints aged in aqueous NaCl solutions.

Similar experiments were conducted on lap joints which were prepared after plasma-polymerized primer films were deposited on polished steel substrates using argon as the carrier gas and then aged in the ambient for three weeks. The results are shown in Figure 8. It is interesting to note that the breaking strengths were similar to those observed in previous experiments where lap joints were prepared one day after deposition of the primers. The initial strength of lap joints prepared from steel substrates primed with plasma-polymerized acetylene was 1810 N/64 mm^2. After 3 days exposure to steam, the breaking strength of joints prepared from polished steel substrates primed with plasma-polymerized acetylene films, 1410 N/64 mm^2, was slightly higher than the breaking strength of joints prepared with polished brass, 1380 N/64 mm^2. Failure was completely within the rubber and there was 100% rubber coverage on the fracture surfaces. The variation in breaking strength was likely due to the variation in the rubber compounds themselves.

Previous studies [6, 7] on the characterization of plasma-polymerized acetylene films using RAIR, XPS, SIMS and AES have shown surface structural changes due to the reaction of residual trapped free radicals with oxygen or moisture in the air. However, since similar joint strengths were observed for lap joints prepared from "one-day aged" and "three-week aged" plasma-polymerized primers, the surface structural changes on plasma-polymerized acetylene films did not seem to affect the joint strength significantly.

After exposure to aqueous salt solutions for three days, joints prepared from polished brass substrates and from polished steel substrates primed with plasma-polymerized acetylene all showed low breaking strengths. However, the breaking strength of the control joints was about 400 N/64 mm^2 higher than that of joints prepared from steel

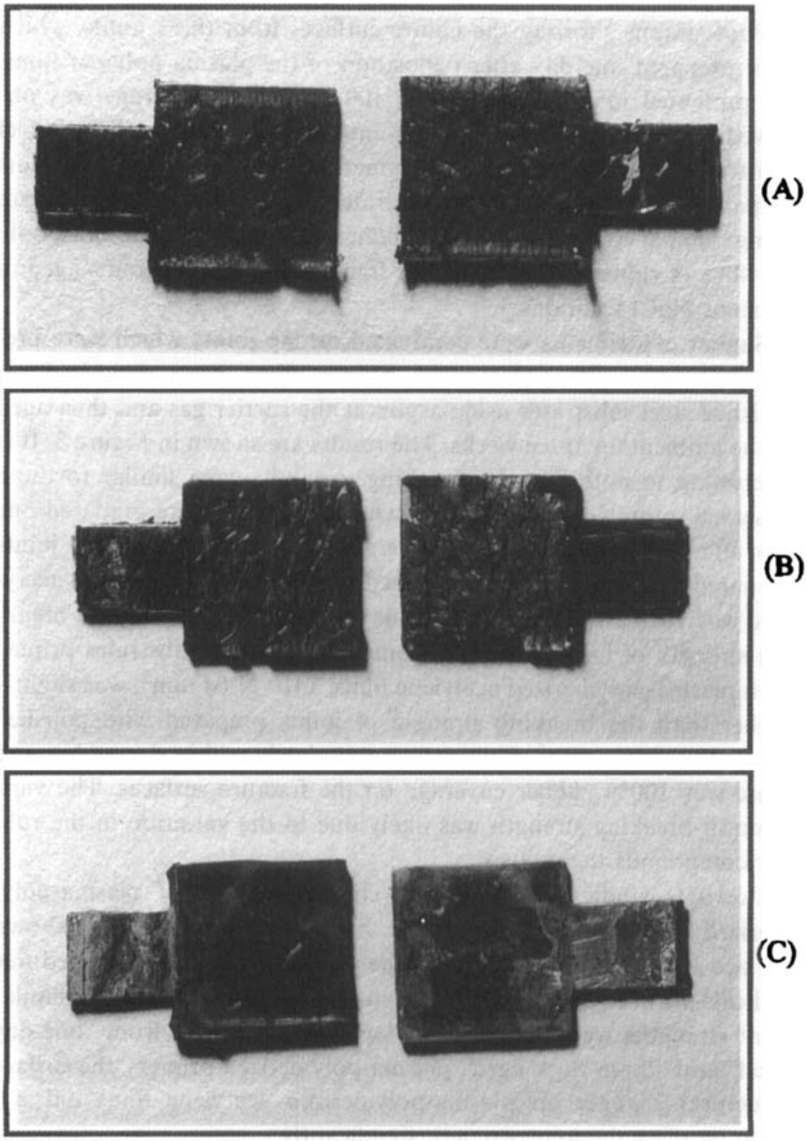

FIGURE 6 Photographs showing fracture surfaces of lap joints prepared from polished steel substrates primed with plasma-polymerized acetylene films. (A)-as prepared, (B)-after exposure to steam for 3 days, and (C)-after exposure to aqueous salt solutions for 3 days. The joints were prepared one day after deposition of the plasma-polymerized primers. (See Color Plate II).

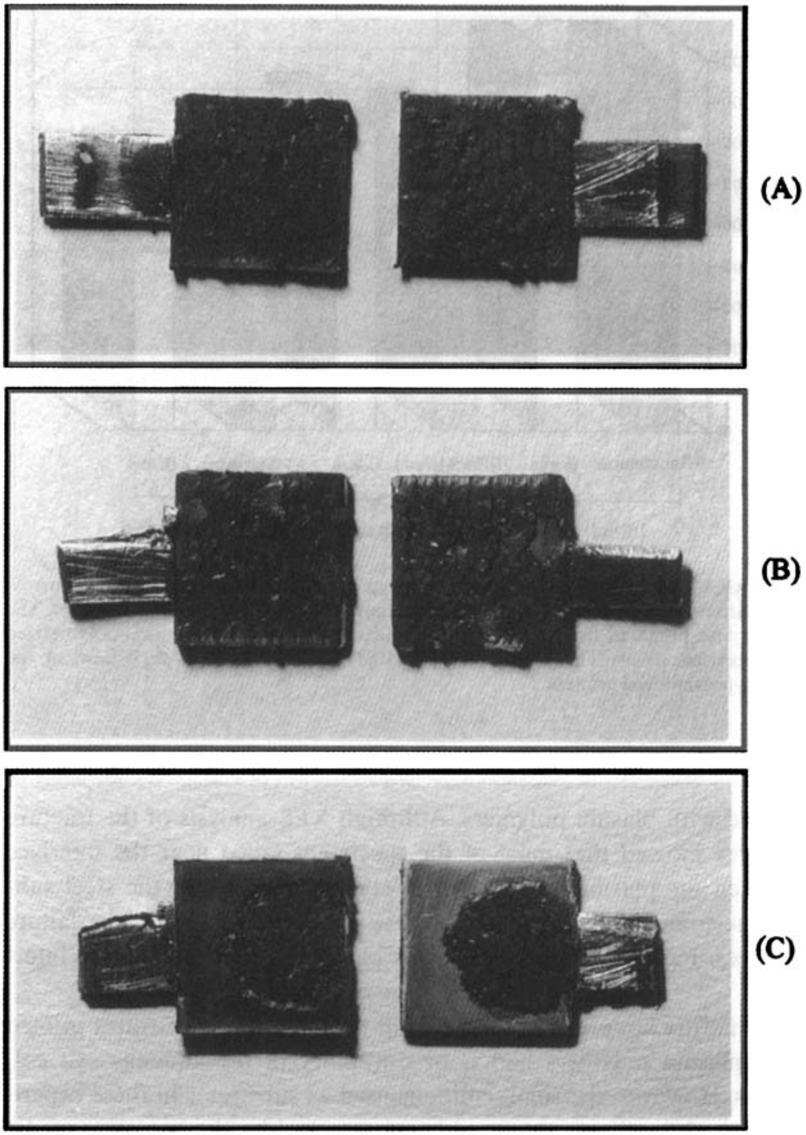

FIGURE 7 Photographs showing fracture surfaces of lap joints prepared from polished brass substrates. (A)-as prepared, (B)-after exposure to steam for 3 days, and (C)-after exposure to aqueous salt solutions for 3 days. (See Color Plate III).

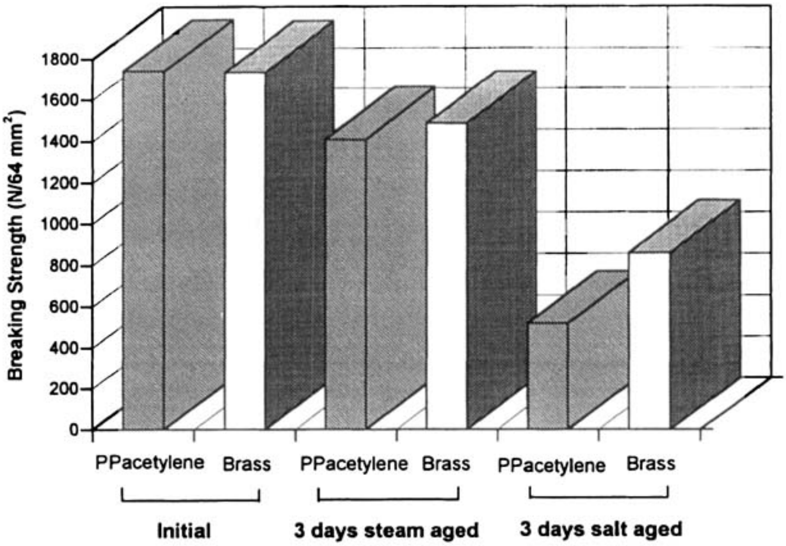

FIGURE 8 Breaking strengths of lap joints as-prepared and after exposure to corrosive environments. Control specimens were prepared from polished brass substrates. The others were prepared from polished steel substrates primed with plasma-polymerized (PP) acetylene films. The joints were prepared three weeks after deposition of the plasma-polymerized primers.

primed with plasma polymers. Although XPS analysis of the fracture surfaces showed that most of the specimens failed near the interface between the plasma-polymerized acetylene primer and the steel substrates, some specimens had 20–40% rubber coverage on the failure surfaces. Failure in those cases was partly cohesive and partly interfacial.

Miniature lap joints prepared from polished steel substrates primed with plasma polymers had poor durability in the aqueous salt solutions. However, the small coupons used as substrates in these experiments had the disadvantage of being attacked by the corrosive media from sides of the coupon between the substrate and plasma polymer. This problem would not be observed in the case of a steel substrate imbedded in a block of rubber. The reason for observing higher breaking strength in the control joints can be attributed to the solid brass used as substrates and to the lack of galvanic coupling.

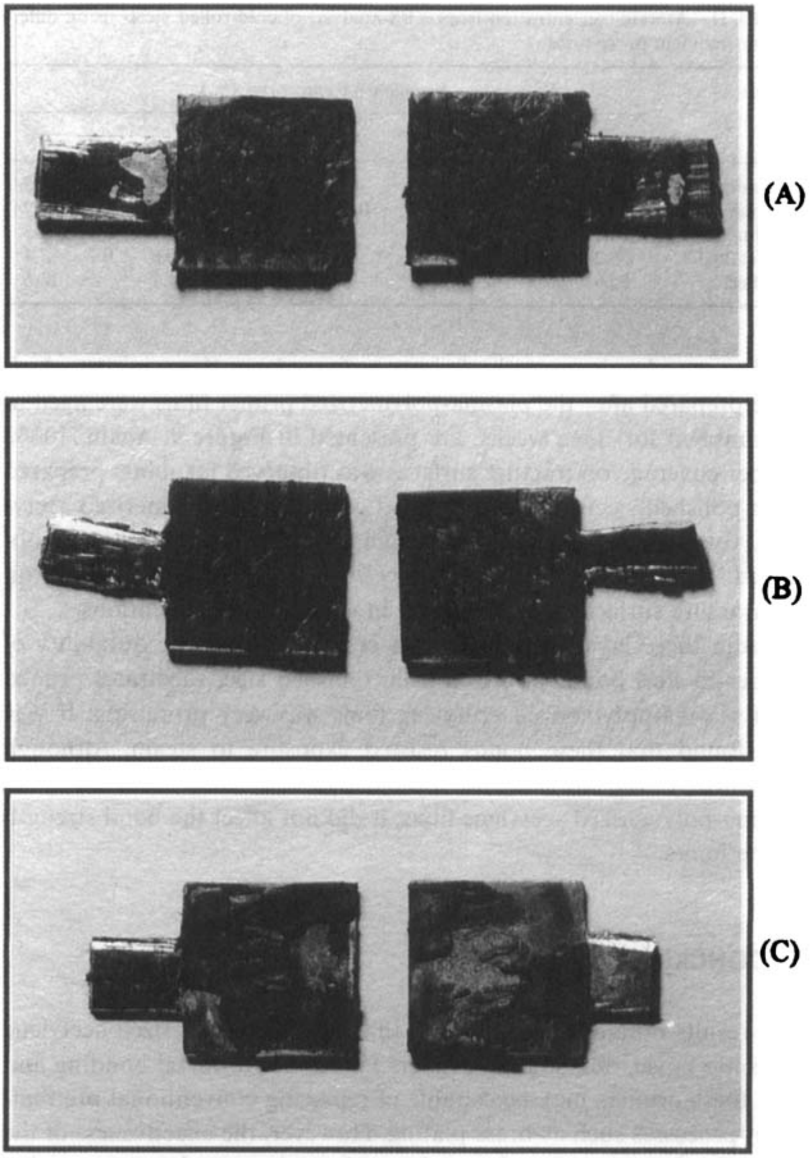

FIGURE 9 Photographs showing fracture surfaces of lap joints prepared from polished steel substrates primed with plasma-polymerized acetylene films. (A)-as prepared, (B)-after exposure to steam for 3 days, and (C)-after exposure to aqueous salt solutions for 3 days. The joints were prepared three weeks after deposition of the plasma polymerized primers. (See Color Plate IV).

TABLE II Atomic concentration from XPS analysis of cold-rolled steels using different pretreatment procedures

Sample	*Atomic Concentrations (%)*									
	C	*O*	*N*	*Si*	*S*	*P*	*Na*	*Ca*	*Cu*	*Fe*
As-received	72.7	18.5	0.2	8.3	–	–	–	–	–	0.3
Acetone cleaned	53.9	39.8	0.7	–	0.7	–	–	–	–	4.9
Alkaline cleaned	20.6	67.0	0.3	–	–	1.5	0.4	0.9	–	9.3
Acid etched	23.2	62.4	0.2	–	–	3.2	–	0.6	0.7	7.4
Polished	25.9	60.5	0.9	–	–	–	–	1.1	–	11.6

Photographs showing the failure surfaces from these joints, which were prepared after the plasma-polymerized primer films were aged in the ambient for three weeks, are presented in Figure 9. Again, 100% rubber coverage on fracture surfaces was observed for joints prepared from polished steel substrates primed with plasma-polymerized acetylene. Even after 3 days of steam aging, similar results were still obtained. However, there was still only 20–40% of rubber coverage on the fracture surfaces for joints aged in aqueous NaCl solutions.

From these investigations, it was concluded that the durability of rubber-to-steel bonds prepared from polished steel substrates primed with plasma-polymerized acetylene films was very promising. It was also found that these bonds resisted exposure to steam. Although exposure to the atmoshpere did change the surface chemistry of plasma-polymerized acetylene films, it did not affect the bond strength of the joints.

4. CONCLUSIONS

The results obtained here indicate that plasma-polymerized acetylene films are novel, outstanding primers for rubber-to-metal bonding and that these primers may be capable of replacing conventional pretreatment processes such as brass plating. However, the effectiveness of the plasma-polymerized acetylene primers depends strongly on processing variables used in their deposition. Thus, the most effective primers were obtained when argon or nitrogen was used as the carrier gas and the steel substrates were pretreated by alkaline cleaning, acid etching, or mechanical polishing. Miniature lap joints which were prepared using rubber as an "adhesive" to bond together pairs of steel adherends which were primed with plasma-polymerized acetylene films deposited using these processing variables had an initial strength of about 2000 N for a bonded area of 64 mm^2 and failure was 100% cohesive in the rubber. Very similar results were obtained for joints prepared using polished brass but no plasma-polymerized primers. The high breaking strength was due to crosslinking between natural rubber and plasma-polymerized acetylene primer films and to the excellent adhesion of the primer films to the substrates. Although exposure to the atmosphere resulted in changes in the surface chemistry of plasma-polymerized acetylene films, it did not affect the bond strength of the joints.

When oxygen was used as a carrier gas or the substrates were simply cleaned in acetone before deposition of the primer films, the breaking strength of the lap joints was lowered by a factor of two. This low breaking strength was attributed to large amounts of oxygen incorporated in the plasma polymers, thus reducing the numbers of $>C{=}C<$ bonds in the plasma polymers or to inadequate surface pretreatment that resulted in a weak boundary layer. The weak boundary layer most likely consisted of rolling oil residues that could not be removed by solvent cleaning.

The durability of rubber-to-steel bonds prepared from polished steel substrates primed with plasma-polymerized acetylene films using argon as the carrier gas was outstanding during exposure to steam. However, the durability of similar bonds during exposure to aqueous salt solutions was less promising. Before plasma-polymerized films can be used to prepare rubber-to-metal bonds for use in highly corrosive environments, some improvement in the corrosion resistance of the films may be required.

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