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Plasma Processing for Enhanced Adhesion of Steel and Polymer Fibers to Rubber

Final Report

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Plasma Processing for Enhanced Adhesion of Steel and Polymer Fibers to Rubber

FINAL REPORT

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Abstract

Plasma treatment of zinc-coated steel, polyimide sheet, polyaramid fibers, and polyester sheet and fibers increased the adhesion of these materials to a rubber compound formulation that is similar to that used in automotive tires. For galvanized steel, a two-step plasma, hydrogen followed by CS_2 deposition, gave excellent adhesion. Other plasma treatments, including plasma cleaning, were much less effective. Plasma grafting onto polyimide and polyester, in which initial treatment with an inert gas plasma was followed by exposure to a reactive monomer, resulted in good adhesion to rubber.

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SUMMARY

The Goodyear Tire & Rubber Co. and Sandia National Laboratories conducted a five-year program to investigate the potential for plasma treatment of several materials to improve compatibility with tire rubber. The program had two major subdivisions, promoting adhesion of steel cord to rubber while retaining corrosion resistance, and enhancing compatibility of polymer fibers to the rubber.

In addressing the steel cord adhesion, efforts were directed toward galvanized steel, which has corrosion resistance but does not adhere to rubber. A variety of plasma approaches were explored including plasma cleaning, oxide removal, plasma grafting and plasma polymerization. The most successful treatment is a pretreatment with hydrogen plasma to remove the native zinc oxide, followed immediately by plasma deposition of a carbon disulfide film. Pull and peel tests of Zn/steel with this plasma treatment indicated excellent adhesion to rubber, with cohesive failure in the rubber. A plasma model for CS_2 was developed and tested.

Reinforcement of tire rubber could be improved by use of various polymer fibers if certain material incompatibilities could be resolved. Polyaramid and polyester fibers have poor wettability, hence, dispersability and do not adhere to the rubber. Several plasma approaches to improving these properties were explored. Direct plasma polymerization of thin films on polyimide and polyester sheets proved ineffective at promoting adhesion. Grafting of monomers onto the polymer surface after argon plasma treatment was difficult to observe and quantify, but gave good adhesion properties in the case of diallyl disulfide. There are manufacturability questions related to diallyl disulfide arising from its stench. A second plasma grafting candidate, isoprene, gave good adhesion on test samples of polyimide and polyester.

An apparatus for tumbling fiber pulp during plasma treatment was designed and tested. Exposure of polyaramid pulp to an argon plasma for a few seconds, greatly increases its wettability.

INTRODUCTION

Incorporation of steel into tires requires several processing steps to achieve corrosion resistance and adhesion. One approach to solving the corrosion problem is zinc plating of the steel wire. Unfortunately, zinc does not adhere well to the tire rubber formulated for brass adhesion. The purpose of part of this program was to investigate plasma treatment as an alternative to brass coating for promoting adhesion of zinc to rubber. For some systems, plasma cleaning by brief exposure to argon or oxygen plasma to remove surface contaminants is very effective at improving adhesive joints. The mechanisms involved in this effect have been widely discussed and include simple cleaning of contaminants, physical or morphological changes in the surface, and chemical activation[1]. The effectiveness of plasma cleaning must still be determined empirically for any specific surface/adhesive system.

Other approaches to improving interfaces using plasmas include plasma grafting and plasma polymerization[2]. In grafting, an inert gas plasma treatment is followed by exposure to a monomer. If the surface becomes activated and has unpaired electrons existing as attached surface radicals, there is the potential to bond monomer chemically and initiate chain polymerization. The exposure of a plasma-treated surface might be to monomer vapor or to liquid phase chemical although the latter requires intermediate air exposure, which could potentially cap surface radicals. In plasma polymerization[3] the monomer is introduced directly into the plasma. By one of several mechanisms, a film of polymer can grow on surfaces exposed to the plasma. Whether plasma polymerization leads to enhanced adhesion will depend on details of the interaction at the surface of the gas-phase species that initiate the deposition. Additionally, for both plasma grafting and polymerization, the resulting thin film should interact well with the rubber adhesive, perhaps possessing chemical functionality that promotes bonding.

One approach to bonding of zinc/steel to rubber is to functionalize the zinc with a chemical group that can bond to some component of the rubber formulation. Adhesion of brass to rubber is known to be excellent because the copper makes strong bonds with the sulfur that is present from the vulcanization. Chemically, zinc should also make strong sulfur bonds but it is possible that the native zinc oxide prevents direct zinc-sulfur bonds. Among the ideas explored in this program were plasma cleaning using argon or oxygen, plasma grafting and polymerization of compounds with sulfur functionality and also plasma incorporation of olefinic functionality.

Polymer fiber can be added to rubber to improve mechanical properties. In order to achieve optimum performance, the fibers must be dispersed and wetted by the rubber and adhere well after rubber cure. Two fibers that have promising physical characteristics are a polyaramid pulp (Kevlar®[4]) and a polyester fiber bundle. The approach is similar to that of the zinc/rubber system. By some combination of plasma cleaning/grafting/polymerization, one tries to alter the surface properties to promote compatibility and bonding with the rubber formulation.

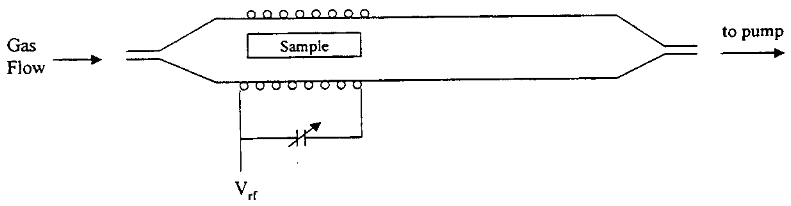
For both systems, there are issues associated with making a plasma treatment manufacturable. The steel cable would need a quasi-continuous plasma treatment that could process realistic lengths. The fiber pulp must be uniformly plasma exposed, perhaps with physical agitation.

This final report describes all of the varied activities associated with this five-year program. Included are some metalography studies on steel cord, plasma treatments of zinc/steel coupons and wire, and plasma treatments of polymer sheets and fiber. X-ray photoelectron spectroscopy (XPS), Fourier Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy, Scanning Electron Microscopy (SEM), water contact angle measurements and pull and peel tests were used to characterize the plasma treated surfaces.

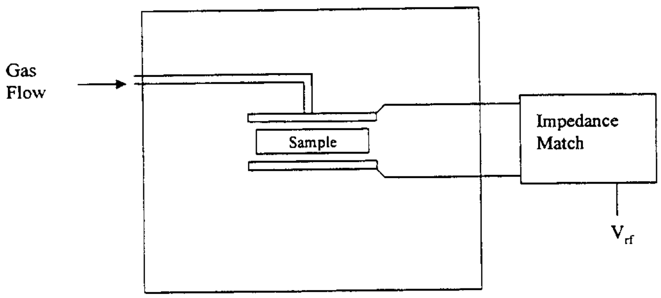
EXPERIMENTAL

For the plasma treatment of samples, two basic configurations are used, capacitive and inductively coupled. The inductively coupled chamber, shown schematically in Fig 1 consists of a horizontal 5 cm diameter glass tube, 30 cm long, with the gases flowing in one end and being pumped from the other end by a mechanical pump trapped with liquid nitrogen. Rf power (13.56 MHz) is coupled to the chamber by an 8-turn external coil, the ends of which are attached to an adjustable capacitor forming a tank circuit resonant at the driving frequency. Typically the plasma is most intense directly beneath the coil, with some weaker glow extending throughout the volume. Gases are regulated by either a flow controller or a leak valve, depending on the vapor pressure. For a typical grafting experiment, a sheet of polyester, 2.5 cm by 15 cm is mounted on a fixture and inserted in the tube, centered beneath the coil. At the end of an argon plasma exposure, the plasma is extinguished and the chamber is flooded with the monomer vapor. After an appropriate exposure time, the sample is removed, and, for some experiments, immersed in the monomer fluid.

The capacitively coupled chamber, shown schematically in Fig 1 is an aluminum box, 45 cm on a side with parallel plate electrodes in the center. The electrodes are 15 cm diameter and spaced 4 cm apart. The gas is delivered through the upper, grounded electrode in showerhead configuration. Rf power is coupled through a π impedance matching network.



Inductively Coupled Plasma



Capacitively Coupled Plasma

Figure 1. Schematic of the plasma apparatus.

In experiments involving the vapor of liquid monomers, the procedure is as follows. The liquid is placed in a glass flask with stopcock and connected to the plasma apparatus. The air in the flask is pumped out through the apparatus, and the liquid is chilled to freezing with liquid nitrogen to reduce its vapor pressure and allow all remnant air to be eliminated. These freeze-pump-thaw cycles are repeated twice. The flask is then returned to room temperature, immersed in a constant temperature bath, and the flow of monomer adjusted with a variable leak valve.

Contact angles are determined by water drop and simple optical goniometer measurements. FTIR spectra are measured on a Perkin Elmer 1700. Samples are sent out for XPS and Raman analysis.

Adhesion measurements are made using several testing protocols. Rapid screening uses a scotch-tape test, in which tape is carefully applied and rapidly removed. Butt tensile tests performed at Sandia (ASTM D2095) use steel disks (1 square inch cross section), roughened on one side with sand blasting and hot-dip galvanized on the side to be tested. The tests are run on an Instron Series IX System with a crosshead speed of 0.05 in/min. Lap shear tests are performed at Goodyear using galvanized steel samples cut to a specific shape accommodated by their fixturing. The paddle-shaped samples are 27 mm long, with the contact surface area being an 8 mm square. Finally, peel tests are performed at both Sandia and Goodyear. Typically, a strip of rubber compound is applied to a flat sample, 2.5 cm by 15 cm. Alternatively, the sample to be tested is masked with polyester (Mylar®, polyethylene terephthalate, PET) film in which a window has been cut. The rubber compound is applied over the window and cured at 160°C for 30 minutes in a preheated press at 3.3 English tons. At Sandia, the pressure is monitored and periodically adjusted. At Goodyear the pressure is applied by gas regulator and is constant.

RESULTS AND DISCUSSION

STEEL TREATMENT

The initial discussions between Sandia and Goodyear identified a set of potential monomers that might lead to useful functionality in a thin film. Winnowed from the list were any compounds which were difficult to acquire, or for which the vapor pressure at room temperature was insufficient (less than 2 Torr) to deliver chemical to the plasma. The list of attractive monomers was reduced to seven: thiophene, allyl methyl sulfide, allyl mercaptan, diallyl disulfide, 2-methyl 1-buten 3-yne, 1,3-butadiene and carbon disulfide.

Butt tensile tests were used to evaluate the effectiveness of various plasma treatments. Shown in Fig 2 are the results of butt tensile tests on Zn/steel samples exposed to various surface preparation treatments. Each graph is the average result from five pull-test measurements, the typical experimental standard deviation is about 5% of the value. The first graph, labeled control, is a test of as-received galvanized steel with a solvent preclean, sonication in methanol for 5 minutes. All plasma treatments are inductively coupled.

Argon plasma and hydrogen plasma treatments result in a modest increase in adhesive strength, presumably from cleaning effects. Plasma deposition of CS_2 film gives a further improvement in adhesion, but the films delaminate at the Zn/film interface.

We postulated that the native zinc oxide was interfering with the zinc-sulfur bonding that should lead to good adhesion. Hydrogen plasmas can remove the oxide from some metals, most notably copper. We tested the idea of pretreating the zinc with hydrogen plasma to remove the oxide and immediately following this with the CS_2 deposition without exposure to air. Hydrogen plasma exposure was for 3 minutes in a 35 Watt plasma. The CS_2 film thickness was approximately 5000Å. Fig. 2 shows the results for CS_2 deposition alone, compared with argon and hydrogen plasma pretreatments. Both pretreatments result in significantly improved adhesion, and the hydrogen plasma treatment leads to cohesive failure in the rubber. The final two graphs are sets of five plasma treatments in which failure was cohesive in 60% vs. 100% of

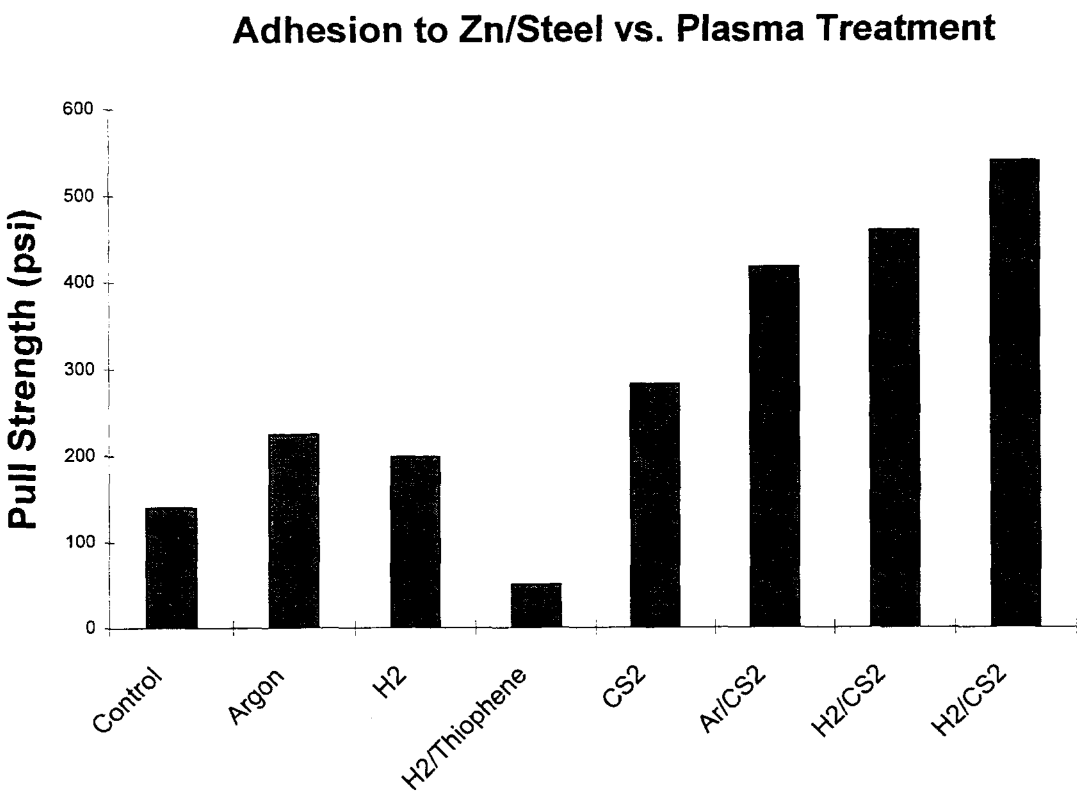


Figure 2. Butt tensile tests on galvanized steel with various surface preparation treatments.

the samples. Similar experiments were performed using thiophene plasmas and poor adhesion results as is seen in Fig. 2, graph 4. It appears that the thiophene plasma does not lead to adhesion between the film and the zinc. As a result of the excellent results for the hydrogen/CS_2 plasma treatment, all further work on steel/rubber adhesion was concentrated on this plasma system.

XPS surface analysis of the steel was used to verify that the concept of oxide removal was valid. Samples of hot-dip galvanized steel were prepared with three treatments, acetone clean, acetone/HNO_3/acetone/H_2 plasma, and the same with a CS_2 plasma deposition. Surfaces were compared, and the plasma polymerized sample was Ar ion milled to the interface. The results are shown in Table 1. The solvent cleaned, and hydrogen plasma treated samples have ZnO on the surface and are contaminated with carbon. The CS_2 deposit has some adsorbed carbon and oxygen containing species as well. Milling to the interface demonstrated that the oxygen has been almost completely removed. The hydrogen plasma appears effective at removing oxygen, but unsurprisingly, an oxide is reformed on exposure to air. Immediate deposition of plasma polymerized CS_2 without exposure to atmosphere preserves the oxide-free surface and leads to zinc-sulfur bonding and apparently good adhesion.

Table I. XPS results for galvanized steel samples.

Elements	Solvent clean	H2 plasma	CS_2 deposit	Ion Mill
C	39	42	66	39
O	42	26	8	0.4
Zn	14	9	0	41
S	5	13	26	17

The pressure behavior of a CS_2 plasma is quite different from the usual plasma polymerization system. In a plasma, the molecules experience collisions with electrons which lead to ionization, fragmentation and excitation. Some of the daughter molecules react at surfaces and are incorporated into the growing film. Others are unreactive and are either further pressure depends on the balance of fragmentation into reactive, depositing species, vs. unreactive molecules. For some gases such as methane, more volumes of hydrogen are formed than molecules lost to the walls, and the system pressure rises. For others such as C_2F_4, some CF_4 is generated, but more CF_n is lost to the walls, and the system pressure falls slightly when the plasma is started. Fig. 3 shows the pressure dependence of a CS_2 plasma for different plasma powers, and different initial pre-plasma CS_2 pressures. The initial pressure is achieved by varying the flow rate of gas (1 sccm gives 40 mTorr CS_2) into the system while maintaining a constant pumping speed. It is clear that for sufficient power, the pressure plummets to essentially zero. To achieve complete conversion of the CS_2 gas to film, approximately 4 Watts/sccm of rf power is necessary.

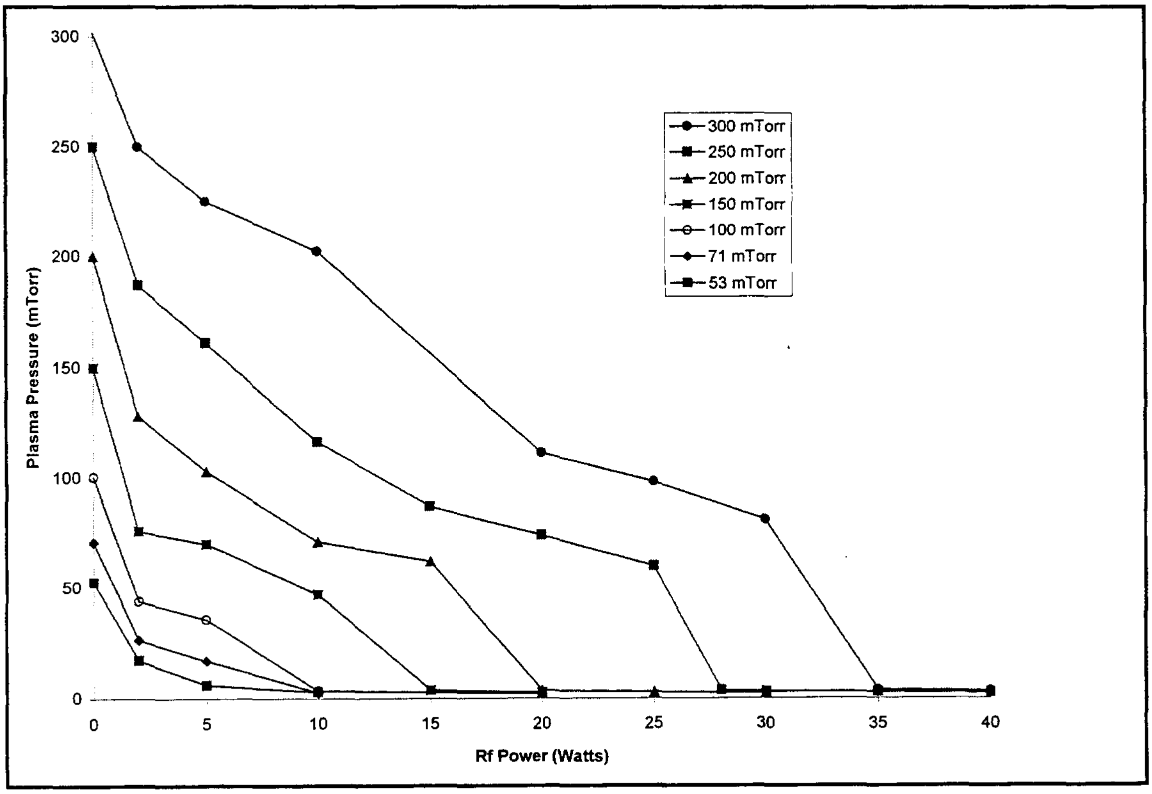


Figure 3. The pressure behavior of the CS_2 plasma as a function of rf power for different initial system pressures.

There is a negative consequence to this pressure behavior. In all cases, on igniting the plasma, the system pressure falls and the impedance matching changes. For high power to pressure ratios, the system becomes unstable as the pressure goes below what is needed to sustain a stable plasma. A flickering phenomenon occurs as the plasma attempts to extinguish and re-ignite with pressure fluctuations.

Another important observation for the CS_2 plasma system is the formation of particles. For higher pressures, greater than 200 mTorr, powder is observed to accumulate in the region downstream from the coil. A loose plug of glass wool placed in the tube leading to the pump, collects powder. SEM analysis shows the powder to consist of sub-micron polydisperse spheres. It is probable that at sufficiently high pressures, gas phase nucleation occurs from radical-radical collisions. This powder formation in plasmas is an area of intense investigation[5].

The deposition rate within the apparatus is not uniform, but varies with distance down the reactor length. Fig 4 shows this deposition rate change with axial distance by graphing film thickness for 180 seconds deposition from a 20 Watt plasma at 180 mTorr pressure. It can be seen that the deposition rate reaches a maximum at about 7 cm into the reactor, which is close to

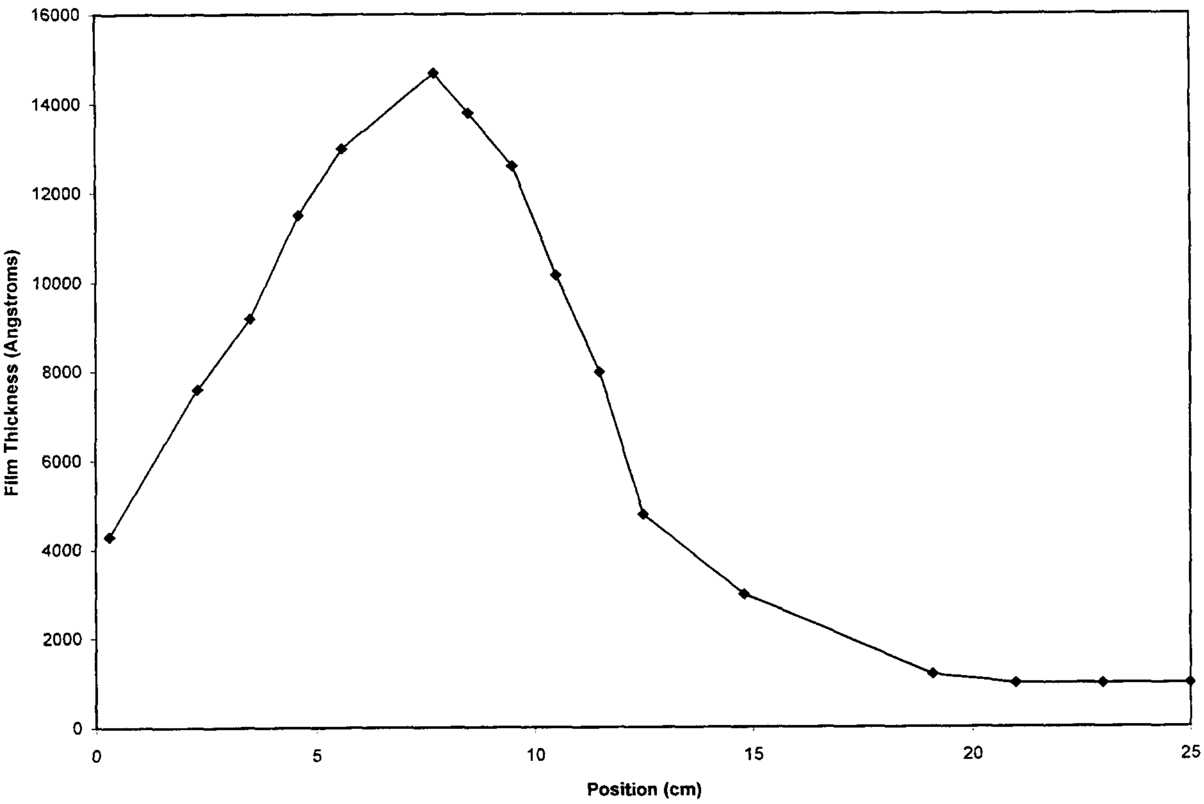


Figure 4. The film thickness as a function of axial distance down the plasma tube.

the center of the coil. Tests were run to determine the maximum rate of CS_2 deposition obtainable. For 330 mTorr (pre-plasma pressure) and 55 Watts, 348 Å/sec was measured.

Mass spectrometry of the CS_2 plasma was used to determine more about the chemistry of the deposition process. In order to sample the plasma gases, a molecular beam is generated through an orifice (0.3 cm diameter) connecting the inductive plasma to a vacuum chamber (1E-7 Torr base pressure). The molecular beam generated in this way is essentially effusive and collisionless between the orifice and the ionizer (located 10 cm away). The electron bombardment ionizer allows measurement of the neutral plasma species that typically are several orders of magnitude greater in concentration than the ions.

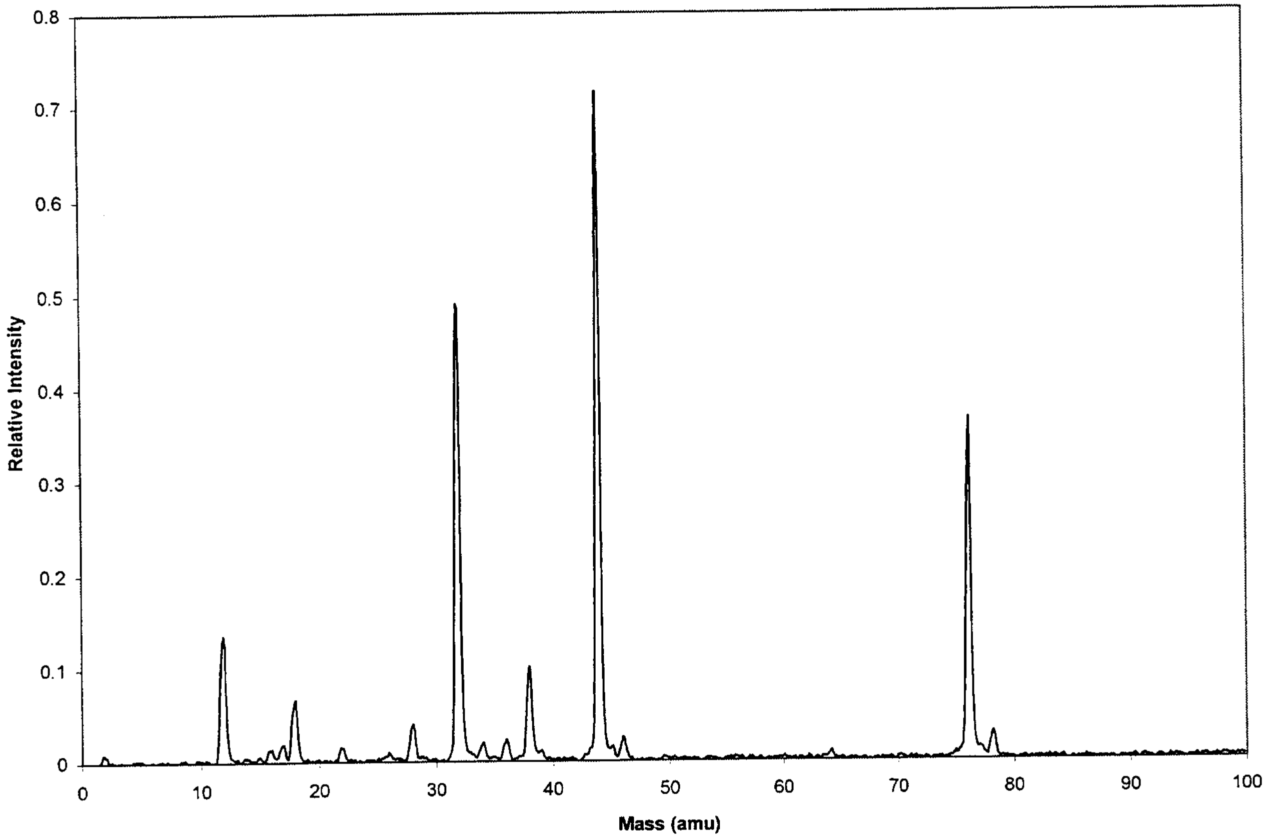


Figure 5. Mass spectrum of CS_2 molecular beam, with no plasma.

Figure 5 shows the mass spectrum of CS_2 before lighting the plasma. All peaks can be assigned to fragmentation during ionization. Principle species include CS_2^+ (76), CS^+ (44), S^+ (32) and C^+ (12). There is also a small amount of H_2O, H_2 and CO from background in the chamber.

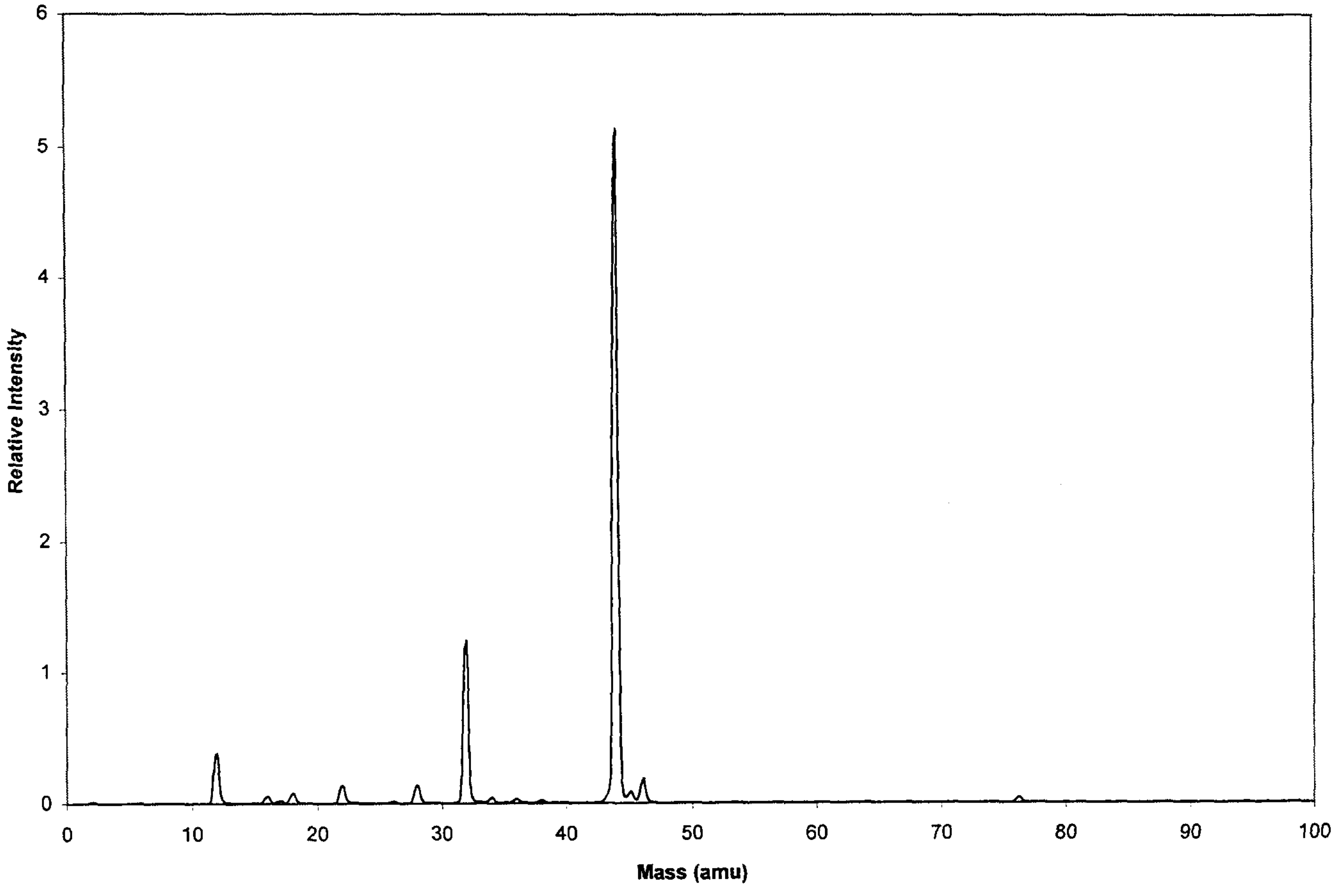


Figure 6. Mass spectrum of CS_2 plasma (4.8 mTorr, 10 Watt) from a molecular beam probe.

Fig. 6 shows the mass spectrum obtained when a 10 Watt plasma of CS_2 is present. Under these conditions, about half of the source gas is being deposited as film. The parent CS_2^+ ion is almost completely missing from the spectrum. The CS^+ ion has become the dominant feature. No higher mass species $C_nS_m^+$ are observed. If the mass 44 peak is assumed to have only two components, cracking of CS_2 and direct ionization of CS, then the power and pressure dependence of the mass spectra can be analyzed as a conversion of CS_2 into CS. Fig. 7 shows the pressure dependence of the CS_2 plasma (circles with heavy line) vs. power along with the pressure of CS (squares with light line). For a weak plasma, only a fraction of the CS_2 is decomposed to CS, but at higher power, almost all remaining gas in the system is composed of CS. It is apparent from these mass spectrometry measurements that the CS molecule is not particularly reactive at the film surface during deposition. Highly reactive species are removed from the plasma through wall collisions. The ratio of wall area to orifice area is a factor of about 2000, thus any species reacting at the wall is reduced to undetectable concentrations.

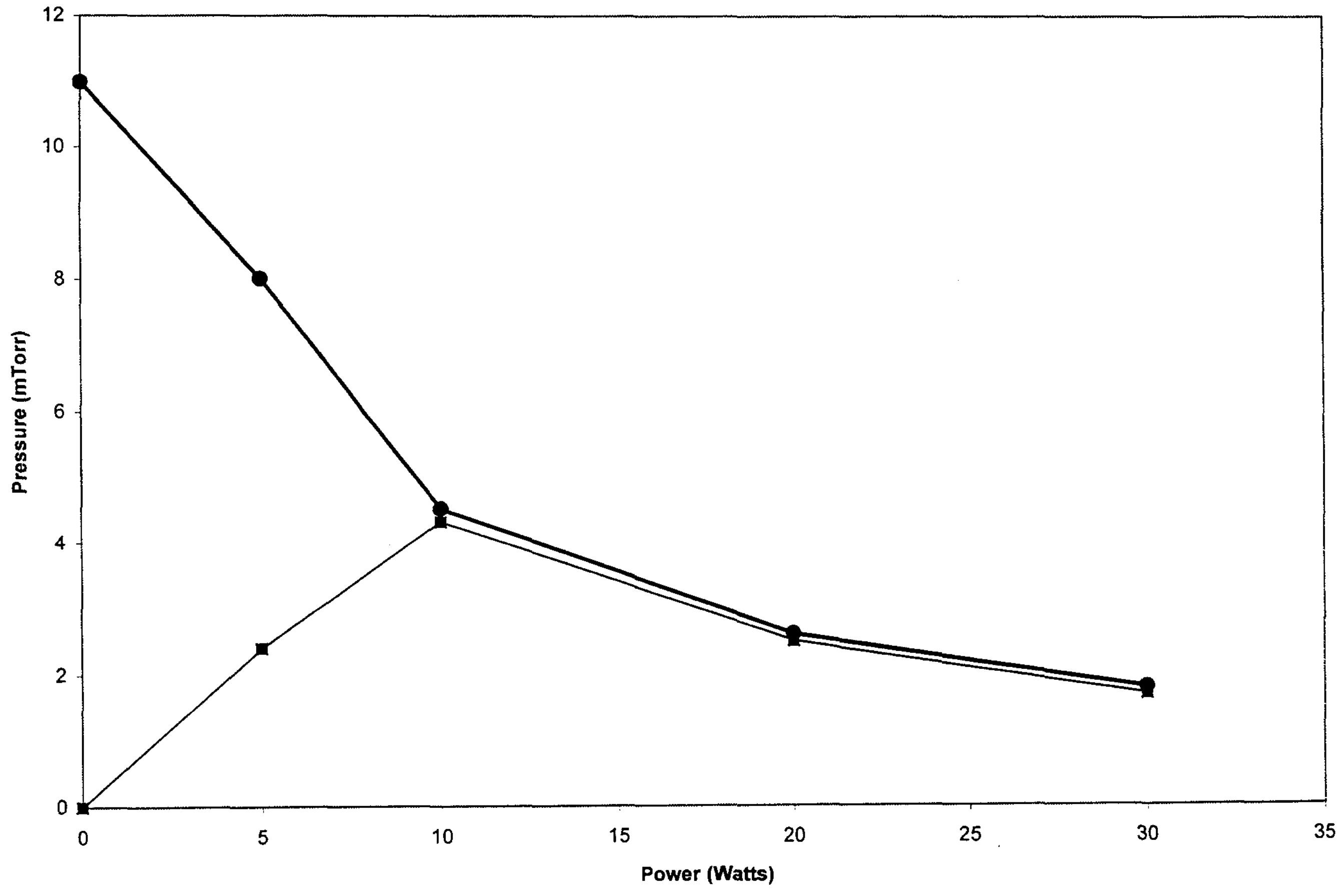


Figure 7. The pressure dependence of an inductive plasma of CS_2 vs. power. Total pressure (thick line, filled circles) and CS partial pressure (thin line, filled squares).

The CS molecule has been reported in a number of chemical systems including laser photodecomposition[7] of CS_2 and in rf discharges[8].

A reasonable model for the CS_2 plasma deposition process would be as follows. Through electron-molecule collisions, the CS_2 is fragmented into CS, C, S, S_2 etc. The C, S, and S_2 react readily at the walls depositing a film. The CS is either pumped from the system or further fragmented to atomic species, which deposit.

The deposited material was analyzed using a variety of techniques. Combustion analysis of a sample deposited from the higher power plasma regime (40 Watt, 200 mTorr) verified that the film composition was stoichiometrically CS_2. This is, of course, a necessity from mass balance considerations. FTIR analysis of the film shows almost complete transparency in the infrared. Only a weak absorption at 1670 cm^{-1} corresponding to the C=C stretch, and a very weak and broad feature around 700 cm^{-1} which might be the CS stretch, and an even weaker absorption around 500 cm^{-1} which may be the CSSC disulfide stretch. Raman spectroscopy

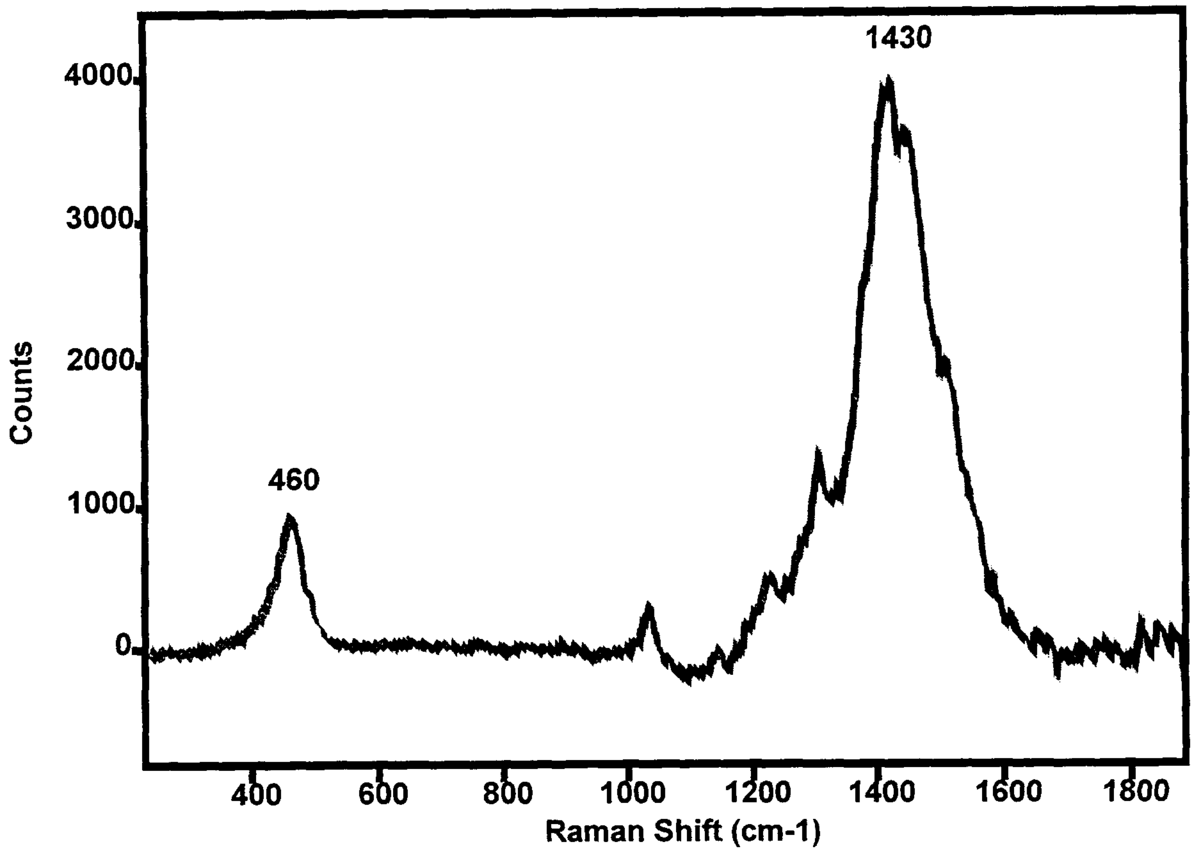


Figure 8. Raman spectrum of plasma deposited CS_2 film.

revealed more information about the film composition. Spectra were obtained using 458 nm excitation. As seen in Fig. 8, a broad feature at 460 cm^{-1} is the SS stretch as in sulfanes, RS_nH (n=2,4). The largest feature at 1430 cm^{-1} is assigned as a C-C stretch, with SP^2-like carbon as in amorphous silicon carbide.

A previous Raman study[9] of sulfur-carbon materials showed no similarity to the Raman on these plasma deposited materials, but those samples were generated by reacting charcoal with SO_2 gas at high temperature. None of their samples exceeded 25 atomic percent sulfur.

It is interesting to note that the composition of plasma polymerized CS_2 could be isoelectronic with SiO_2. Using covalent radii, it is apparent that the geometry of SiO_2 and CS_2 could be quite similar with the oxygen (0.74Å) being substituted by carbon (0.77Å) and the silicon (1.17Å) being replaced by sulfur (1.04Å). SiO_2 exists in many amorphous and crystalline phases and there is the potential for the plasma polymerized CS_2 structure to be quite complex. The IR and Raman spectroscopies reveal that the structure is very different from SiO_2. Rather than being predominantly C-S bonds in a tetrahedral arrangement, the material appears to consist of C-C and S-S bonding with relatively minor contribution from C-S. The IR and Raman spectroscopies are not quantitative when comparing between lines of unknown absorption coefficient and thus, it is impossible to specify the material chemical structure at this stage.

Several other observations were made on the plasma polymerized CS_2. The material density was determined, both by depositing thick films, 10 micrometers, and weighing, and by immersion of film pieces in fluids of various densities. The film density is 2.0 g/cc. Film was deposited on steel wire provided by Goodyear (4 filament, 0.22mm diameter wire). Fig. 9 shows SEM photographs of the film after bending the single filament wire substrate.

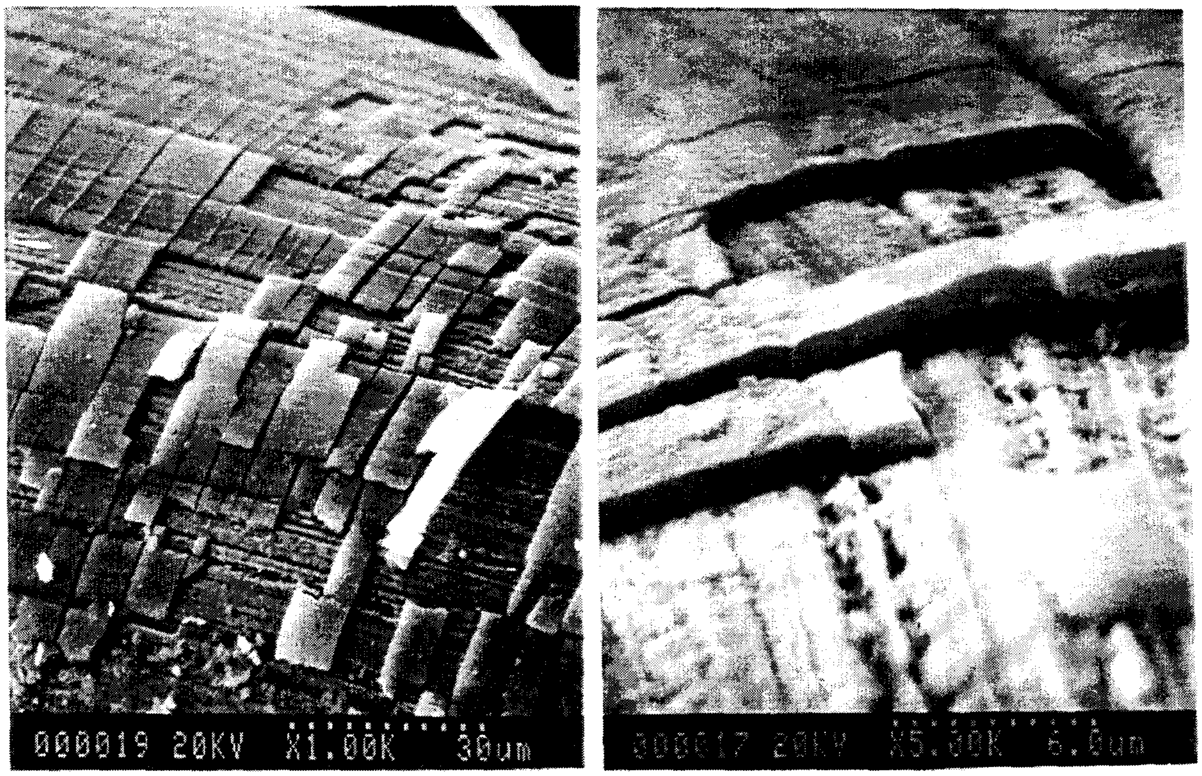


Figure 9. SEM photo of CS_2 deposit on wire (steel with electrolytic Zn).

It is clear from the image that the film is brittle and can delaminate from the galvanized steel. Extensive testing was performed to evaluate the adhesion properties of the plasma deposited CS_2 films on test coupons and on wires.

ADHESION TESTING

In testing the adhesion of the plasma deposited CS_2 a variety of approaches was taken and the results were not always easily interpreted. The initial screening measurements using butt tensile tests on steel disks described above and shown in Fig. 2, gave excellent adhesion with cohesive failure in the rubber. Lap shear samples were prepared from both commercial, hot-dip, galvanized steel, and electrolytically grown zinc from Goodyear. Excellent adhesion was obtained for some sets of plasma-treated samples, but occasional anomalously poor results occurred. Exhaustive repetition and investigation of cleaning techniques and surface analysis resulted in many theories but no definite answers. Cleaning procedures included solvent (acetone, methanol, isopropanol, methylene chloride) and acid (HCl or HNO_3). Much speculation concerning initial unknown contamination remained unconfirmed, and finally, a simple methanol sonication followed by plasma treatment was identified as effective.

Samples of wire, electrolytic zinc coated, were prepared with different thicknesses of CS_2 films, 200 Å, 400 Å, 800 Å and 1600 Å. Adhesion was measured at Goodyear by imbedding the coated ends in rubber compound and pulling the wires out. The adhesion improved with thickness (390N, 520N, 600N, 650N respectively) and reached a maximum. However, the best adhesion was only about half of the brass control (1200N), suggesting that the adhesion is not as good as had been observed for other samples.

Corrosion testing of plasma treated coupons was carried out at Goodyear. Samples were prepared with the H_2/CS_2 treatment. Adhesion testing on these gave results equal to the brass controls. When subjected to steam aging, the adhesion remained equal or better than the controls. Salt water aging resulted in rapid degradation of the zinc, suggesting that the film does not produce a hermetic seal for the metal.

PLASMA COUPLING MODES

When plasma deposition is applied to treatment of long lengths of steel cord, some engineering issues arise. The small research reactor used in these studies could be modified, with difficulty, so that the cord could enter and leave the vacuum. An alternative approach is to modify the plasma apparatus to accommodate large spools of steel cord. The larger, capacitively coupled plasma is ideal for testing this concept.

The plasma characteristics of the capacitively coupled plasma were studied. When plasma power density, and gas flow rates were adjusted to match that of the inductively coupled system, the deposition rate, and pressure characteristics were reproduced. Lap shear and peel tests on galvanized steel with H_2/CS_2 plasma depositions in the capacitive mode gave cohesive failure in the rubber. Experiments on electrolytic zinc coated steel wire were also successful. A reel to reel transfer of a 10 meter length of steel cord through a CS_2 plasma resulted in apparent uniform coating of the wire. At a linear rate of 10 cm/sec, and a deposition rate of 100 Å/sec, the coating was estimated to be 150 Å thick. No hydrogen pretreatment was attempted, and adhesion measurements on short lengths of this cord gave poor results, consistent with the earlier tests. Further studies are needed to determine whether a two plasma-chamber approach, or a two pass treatment (H_2 followed by CS_2) would give satisfactory adhesion.

MODELING

In recent years, plasma modeling has made major advances as computation speed has increased. Modeling and simulation, together with experimentation, can provide necessary information about the competing processes in a plasma reactor and allow better control of the process performance. Sandia has developed a suite of computer codes that can model plasma systems from 0-D to 3-D spatially, and with various levels of chemistry sophistication. AURORA[10] is a code which incorporates a detailed description of the chemistry (using the chemistry encoding formalism of CHEMKIN and SURFACE CHEMKIN[11]) including electron-molecule, ion-molecule and neutral reactions and performs a 0-D calculation of plasma etch or deposition rates, temperatures and species concentrations. In trying to understand the CS_2 plasma, we developed a mechanism for the plasma deposition and used AURORA to test the model. In Appendix A is a table of the reaction kinetics used in the calculation. Fig 10 shows a fit of the observed deposition rate to the model calculations as a function of power. The agreement is fair and it is clear that the model will need refining.

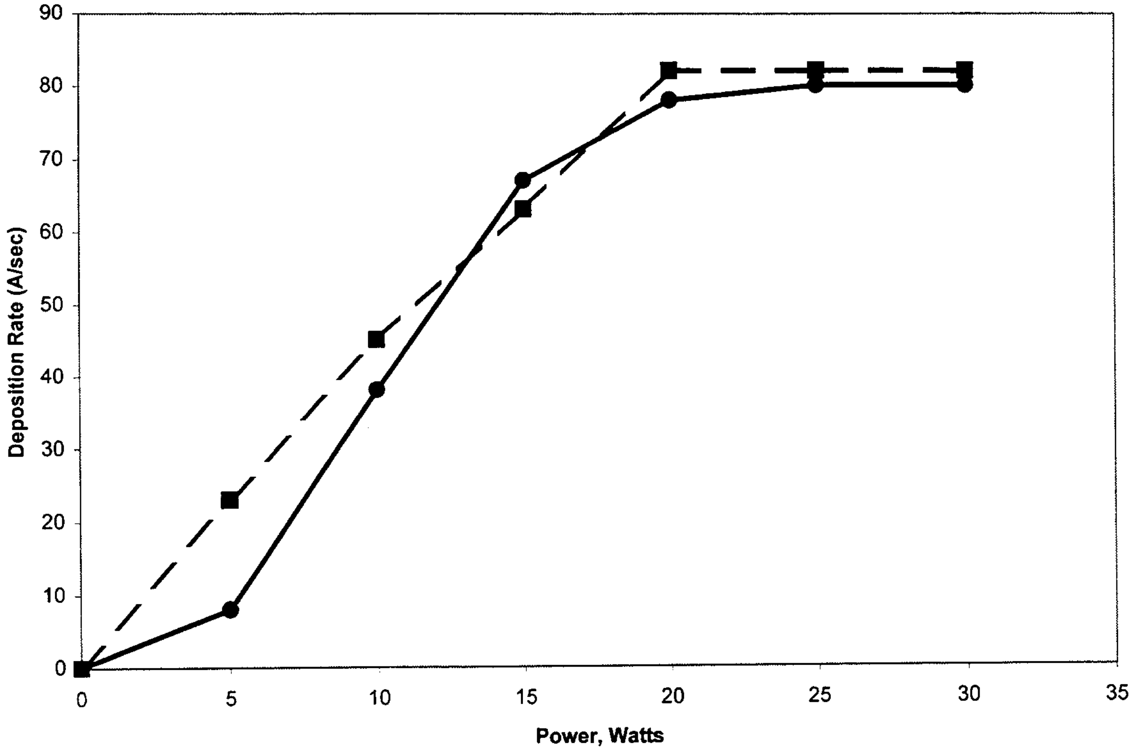


Figure 10: Deposition rate in CS_2 plasma. Comparison of experiment (solid line) with calculation (dashed line).

Fiber Treatment

Earlier work at Goodyear had identified that various plasma treatments of polyaramid pulp show promise for improving the compatibility with rubber although no treatment had been reported which is a significant improvement over existing non-plasma treatments. Our initial approach to exploring alternative plasma treatments was the identification of monomers that might introduce chemical functionality that would interact strongly with the tire rubber. The two most promising ideas were introducing sulfur functionalities such as mercapto or sulfide groups, and functionalizing with olefinic structures. Many variations of plasma treatments have promise for developing an adhesive interface.

Plasma polymerization of a monomer onto the polymer surface will alter the surface characteristics, but little or no work has been done with the selected monomers. In order to survey this approach, each of the monomers was plasma deposited onto sheets of polyester (PET). The film was measured for water contact angle and was subjected to a scotch tape test. The results are shown in Table II. All plasmas were 100 to 200 mTorr of gas pressure and 30 Watts of rf power. The plasma deposited films exhibited relatively high contact angles. However, all excepting CS_2 failed the scotch tape tests, with failure occurring at the polyester interface. Only the CS_2 film passed the scotch tape test, consistent with early work at Goodyear. Also shown in the table are the integrated absorbances measured on the plasma deposited films (deposited on KBr windows) at the two regions νCH (3000 cm^{-1}) and νC=C (1650 cm^{-1}) for each film. Absorbances were normalized to film thickness.

Table II

	Deposition Rate Å/sec	Water Contact Angle	Scotch Tape Test	FTIR νCH	FTIR νC=C
2-Methyl-1-Buten-3-yne	43.7	92°	Fail	32	1.5
1,3-Butadiene	25.0	95°	Fail	24	3.4
Allyl Disulfide	9.9	83°	Fail	14	8.7
Allyl Methyl Sulfide	30.0	80°	Fail	12	1.0
Carbon Disulfide	350	68°	Pass	0	2.5

There is no indication that the amount of olefinic carbon is related to the adhesion characteristics to the polyester. Although the relative amount of olefinic carbon differs in the plasma-deposited films, there is little hope for overall good adhesion to rubber unless the interface between the polyester and the plasma film is improved.

Further screening experiments were conducted using varied approaches including pretreatment of the polyester with oxygen or argon plasma followed by deposition and post-deposition exposure to oxygen plasma to reduce the contact angle. Table III summarizes these results. The untreated polyester has a low surface energy, which is significantly raised by exposure to argon or oxygen plasmas. Plasma deposition of diallyl disulfide, allyl mercaptan, or carbon disulfide, raises the water contact angle to 65-80°. After plasma deposition of diallyl

Table III.

Plasma pretreatment	Deposit	Post-plasma	Graft	H20 contact angle	Tape test
none	none		none	66	
Argon				20	
Oxygen				5	
	DiAllyldisulfide			84	fail
	DiAllyldisulfide	Oxygen		12	fail
Oxygen	DiAllyldisulfide	Oxygen		13	pass
Oxygen	DiAllyldisulfide			80	pass
Oxygen	DiAllyldisulfide			77	pass
Oxygen	DiAllyldisulfide			81	pass
Argon	DiAllyldisulfide			80	pass
Oxygen			DiAllyldisulfide	18	
O2/Ar			DiAllyldisulfide	37	
Argon			DiAllyldisulfide	54	
	CS2			68	pass
Oxygen	CS2			68	pass
Oxygen	Allylmercaptan			67	pass
O2/Ar	Allylmercaptan			68	pass
O2/Ar			Allylmercaptan	24	
Argon			Allylmercaptan	23	

disulfide, the water contact angle can be reduced by a 3 second exposure to an oxygen plasma. Results are ambiguous for the plasma grafting experiments in which the initial plasma treatment is oxygen or argon, and the apparatus is then flooded with at least 3 Torr of monomer vapor and no plasma. Contact angles are not reproducible, and the values do not help to identify whether grafting has actually occurred.

Samples were prepared for peel tests at Goodyear. PET sheet was mounted under the coil region, vertical and centered so that both sides are exposed to the plasma. At low plasma power (below 7 Watts), a more diffuse plasma fills the plasma chamber region under the coil. Around 7 to 10 Watts, the plasma becomes unstable with respect to a second mode in which the plasma is localized on one side or the other of the polyester sheet. In this mode, the power density of the plasma should be about twice that of the diffuse plasma. After several seconds in this localized mode, the polyester sheet develops permanent structural changes as if it were partially melting. For preparing samples for adhesion testing, plasmas were maintained in the diffuse mode, by lowering the power to 7 Watts. Results of peel tests were often erratic, with major variation between samples and occasionally preferential adhesion on one side or the other of the polyester. It is possible that unobserved, brief excursions of the plasma into the localized mode could account for some of this variation. Were a larger diameter plasma tube to be used, the modal instability would probably be eliminated. The polyester sheet, 2.5 cm width, split the plasma tube into two relatively separated regions, which would not have been the case in a larger tube.

Plasma modification of polymer surfaces to enhance adhesion has been investigated for years[2]. Inagaki[10] has reported surface functionalization of Kapton® H[11] using reactive plasmas. The concept of plasma grafting has been investigated and reported over the years. Mermilliod and coworkers[12] modified the surface of polypropylene, both by reactive plasma, and by grafting. Poncin-Epaillard et al[13] grafted acrylic acid onto the aramid poly(p-phenylene terephthalamide). The principle involves the chemical reaction of an olefin at a radical site created by the plasma on a surface. The barrier to radical-olefin reactions is typically 3 to 8 kcal/mole for gas phase reactions. Calculating the collision frequency for monomer vapor at a radical site, and accounting for an 8 kcal/mole barrier, reaction of the monomer at 1 Torr pressure should occur in about 2 seconds. Thus chain growth from the vapor would be expected to grow a relatively thick film in a few minutes. Convincing demonstration of plasma grafting has been reported using FTIR to examine the grafted polymer film[14]. In this program we explored the use of transmission as well as attenuated total reflection (ATR) FTIR to identify a grafted film. In order to be successful, it is important that the grafted film have a strong absorption that does not overlap an absorption of the base material. The C-S or S-S stretching modes of the various sulfur-containing species are weak in the IR. In order to test the FTIR approach, we investigated plasma grafting of acrylic acid, methyl methacrylate, allyl amine, and vinyl chloride onto polyester, polyethylene, and polyimide. In no case did we observe any evidence from IR spectroscopy that any grafting had occurred. Even a close reproduction of the plasma treatment reported in ref 14, grafting acrylic acid onto polyethylene, resulted in failure. There is no satisfactory explanation for this at the present time.

XPS was also used to study the plasma-grafting phenomenon. Samples of PET were prepared with argon plasma followed by allyl mercaptan or diallyl disulfide. The analysis reflected a clean PET surface with negligible sulfur present. A second set of 4 PET samples was prepared as follows: 1. a blank sample placed in the apparatus and evacuated, but without exposure to any plasma, 2. argon plasma only, 3. argon plasma followed by exposure to methyl allyl sulfide gas, 4. exposure to a methyl allyl sulfide plasma. The XPS of the blank was in excellent agreement with theoretical PET, 73% C and 24% O. The blank had not picked up sulfur by being in the plasma apparatus. The argon plasma treated sample gave a slight increase in oxygen content of the surface which might arise either by preferential sputtering of carbon-rich moieties, or by post-plasma attachment of oxygen to radicals created by the argon plasma treatment. The plasma grafted sample #4, had 3% S, 32% O and 55% C. If we assume that this corresponds to PET (S/O/C=0/0.25/0.75) with an overlayer of grafted methyl allyl sulfide (S/O/C=0.26/0/0.71) and a sampling depth for the XPS of 50Å, then the 3% sulfur would correspond to about 6Å of grafted overlayer, that is about one monolayer. The plasma polymerized sample #5 showed S/O/C=0.26/0.03/0.71, nearly stoichiometric methyl allyl sulfide. Thus, the XPS tends to confirm that the process of plasma grafting can occur, although, in this case, attenuating after the growth of a single monolayer. Theoretically, the plasma grafting would lead to radical chain growth of the monomer on the plasma-induced active sites and could lead to very thick films. The FTIR technique, as used above, would not be sensitive to the presence of a single monolayer of grafted material.

Plasma grafting of diallyl disulfide was examined in a similar way. Sheets of PET and polyimide were exposed to an argon plasma and subsequently immersed in liquid diallyl disulfide. XPS showed that for both PET and polyimide, the surface concentration of sulfur was 8-9%. Ion milling an estimated 10Å from the surface removed the sulfur. The 9% sulfur also corresponds to approximately 10Å of grafted film by an analysis similar to the above for methyl allyl sulfide.

In order to test the interface of the PET/rubber, another set of two PET samples were prepared. Each was argon plasma treated, and one sample was immersed in liquid diallyl disulfide. Both samples were cured in rubber compound and the PET sheet was peeled off. The surface of the PET was then examined for sulfur. Negligible sulfur was found for either sample. The absence of sulfur suggests that either the plasma grafting was unsuccessful, or a weak boundary layer at the PET surface resulted in all sulfur moieties being pulled off with the rubber compound.

After extensive testing of the diallyl disulfide graft to PET involving argon plasma followed by liquid immersion, an evaluation of the process was made from a manufacturing perspective. Diallyl disulfide has a very intense stench, not wholly unpleasant, being similar to garlic. However, it might be difficult to implement this treatment to bulk pulp in a factory environment without taking extraordinary measures to contain the odor. Rather than testing the diallyl disulfide treatment on pulp, we explored another potential grafting monomer, isoprene.

Isoprene, 2-methyl 1,3-butadiene, has the potential to graft onto the surface while functionalizing with olefinic groups which would promote adhesion to rubber. Plasma grafting was explored using inductive and capacitive plasmas, and with variations in the plasma treatment. A typical treatment was 5 minutes of argon plasma at 5 sccm flow rate, 170 mTorr pressure and 5 Watts rf power. The plasma was either turned off or quenched by flooding the chamber with isoprene. While the argon plasma is on, a steady state of surface radical concentration should develop, and it is unknown what the post-plasma decay kinetics for these radicals is. Thus, the quench with isoprene has the potential to cap more of the radicals before they react with other background species such as O_2 or H_2O. Even though the system is nominally leak free, these gases are always present in trace amounts. Post-plasma, the samples were exposed to either isoprene vapor only, or vapor followed by immersion in a chilled (0° C) bath of isoprene liquid. The vapor pressure of isoprene at room temperature is too high to make a convenient immersion bath. After extensive peel testing at Sandia and Goodyear, it was concluded that isoprene grafting can lead to good adhesion with cohesive failure in the rubber, however no treatment gave consistently superior results. The best results for PET occurred for the inductively coupled plasma, with best adhesion in the center of the PET sample where the plasma was most intense. It was impossible to explore higher power densities for the plasma, because the heat deposition in the sample leads to melting.

Similar treatment of polyimide sheets in the inductively coupled plasma followed by isoprene liquid immersion resulted in excellent adhesion to rubber compound. The polyimide (Kapton®) has a higher melting point than the PET and therefore the plasma power was increased to 20 Watts without sample degradation. The plasma grafting of isoprene to polyimide looks very promising for adhesion enhancement to rubber.

FTIR of the isoprene-grafted PET gave no detectable evidence for a grafted layer. Deposition of 3000 Å of plasma-polymerized isoprene on silicon for transmission FTIR demonstrated that the deposit was pure amorphous hydrogenated carbon with no retention of the isoprene characteristic absorptions. This same film thickness on PET was invisible in the IR due to absorption overlap. Thus again, FTIR did not prove to be a useful technique for testing plasma grafting.

Table IV illustrates the effectiveness of the plasma grafting procedure on Mylar and Kapton film when cured in rubber as a two-ply laminate. The test piece or 'sandwich' is built, cured and the force required to separate the outer rubber layers from the treated film by 180^0 peeling is measured. For all the tests reported here, various degrees of rubber tearing, i.e. cohesive failure, were observed with the larger peel-force values corresponding to complete rubber failure. Note that the adhesion to Kapton is generally greater than to Mylar under similar conditions and that the conditions of rubber cure can impact the degree of adhesion.

Table IV

Adhesion Testing of Treated Mylar in Rubber Compound

2-Ply Reinforced Laminate Peel Test

Ar Plasma	Isoprene Vapor	Isoprene Liquid	Adhesion (N/cm)
None			~1
8 min	5 Torr	Standard	22
8 min	5 Torr	Inhibitor Removed	66
8 min (inductive)		Standard	46

Substrate	Cure	Adhesion ((N/cm)
Mylar	15'@360	10
Kapton	15'@360	73
Mylar	20'@360	10
Kapton	20'@360	48
Kapton	20'@340	114
Kapton	20'@350	60
Kapton	15'@360	72

TREATMENT OF PULP

Goodyear supplied a sample of polyaramid (Kevlar®) pulp for testing plasma approaches to improving dispersability and adhesion in rubber. SEM examination of this pulp shows that the individual fibers are split and curled giving a very "fluffy" texture to the material. A simple wetting experiment is to place a piece of pulp (about 10 mm^3) on the surface of de-ionized water. The wetting is negligible, and the pulp floats with little water contact. When the pulp is placed in an argon plasma (inductive, 5 Watts, 2 minutes), it wets instantly and completely, sinking into the water. Intermediate behavior can be observed in which the pulp slowly settles into the liquid. We observed that the plasma chamber might become contaminated with oil from the mechanical pump, whereupon an argon plasma does not lead to wetting of the pulp. An oxygen plasma clean of the chamber before pulp treatment is necessary to get reproducible results. An oxygen plasma treatment of the pulp is too aggressive, and results in combustion of the pulp with light emission. An argon plasma treatment of the pulp was conducted with a sheet of polyimide (Kapton®) in the chamber. The water contact angle of the polyimide sheet changed from 71° to 33°, while the pulp went from completely hydrophobic to instantly wetting.

Wettability of the pulp is desirable to increase its dispersion in the rubber, however this is not sufficient to yield good adhesion. In order to study the treatment of bulk fiber, a modification of the plasma apparatus was made to allow tumbling of the pulp during plasma treatment. A cylindrical metal chamber, 25 cm long and 15 cm diameter with closed ends was attached to a motor which could rotate the canister at 1 RPM. Three metal wings were installed internally to promote tumbling. A cylindrical metal shaft was inserted through a hole in one end plate and electrically isolated from the canister. The rf power was applied to the central shaft and generated a fairly uniform plasma inside the canister (as seen through a transparent viewport in the side of the canister). Argon plasma treatment of 5 g of pulp gave good wettability.

One sample of pulp was tumbled in a CS_2 plasma and inspected for coating uniformity. The dark brown color of the plasma-polymerized film allows direct visual inspection of the coated pulp. It is clear that only the outermost fibers in the bundles acquire a visible coating. This is consistent with the plasma deposition mechanism developed here, in which very reactive atomic species, C and S, react at surfaces with unit sticking probability. In order to get internal coating of the pulp, it would be necessary to have the depositing species undergo many wall collisions as it diffuses deep into the bulk. Other plasma treatments might be more effective at achieving uniformity.

Samples were prepared with argon plasma treatment followed by isoprene vapor and liquid immersion. Goodyear analyzed these for rubber compatibility.

CONCLUSIONS

A two-step plasma treatment of galvanized steel shows potential for replacing brass as the adhesion promoter. A number of technical questions remain, including the reliability and robustness of the coating technique, and the feasibility of continuous plasma treatment of steel wire with two plasmas.

Plasma grafting of an adhesion-promoting monomer to the surface of polyimide and polyester shows promise for both diallyl disulfide and isoprene. The best adhesion is observed for plasma treatment of Kapton® sheet with higher plasma density than is feasible for the polyester (which melts). More experiments with Kevlar® pulp will be necessary to prove the technique.

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APPENDIX

```
Model For CS2 Plasma
AURORA with CHEMKIN and SURFACE CHEMKIN)
Species:    E C- C2- S- S2- CS2+ CS+ C+ C2+ S+ S2+ C C2 S S2 CS CS2

Gas Phase Reactions
Parameters are Arrhenius form A*T^B*exp(-E/kT)

                                     A              B              E
 E + CS2 => E    + CS2          2.6194E-06   -4.1458E-01    2.8562E+03
 E + CS2 => E    + CS2          7.4047E-06   -4.9942E-01    1.3186E+05
 E + CS2 => E    + CS2          8.0901E-16    1.5389E+00    1.3078E+05
 E + CS2 => E    + CS2          1.2776E-13    1.1228E+00    1.8056E+05
 E + CS2 => C-   + S2           6.0070E-03   -1.4959E+00    5.6600E+04
 E + CS2 => S-   + CS           7.0956E-06   -1.3390E+00    2.7000E+04
 E + CS2 => S2-  + C            1.4668E-03   -1.4328E+00    6.40007E+04
 E + CS2 => 2E   + CS2+         2.6700E-14    1.2376E+00    1.16978E+05
 E + CS2 => CS+  + S   + 2E     4.4191E-17    1.5379E+00    1.86E+05
 E + CS2 => S+   + CS  + 2E     1.1744E-13    1.0286E+00    1.718E+05
 E + CS2 => C+   + S2  + 2E     3.3087E-16    1.4033E+00    2.3210E+05
 E + CS2 => S2+  + C   + 2E     9.8862E-15    1.1754E+00    1.729E+05
 E + CS2 => CS   + S   + E      1.7935E-12    7.1941E-01    5.17E+04
 E + CS2 => C    + S2  + E      7.9482E-13    8.3138E-01    8.74E+04
 E + CS2 => C    + 2S  + E      2.0291E-13    7.0781E-01    1.392E+05
 E + CS  => CS   + E            2.1086E-03   -1.4457E+00    9.9549E+03
 E + CS  => C-   + S            2.5060E-03   -1.4165E+00    7.22E+04
 E + CS  => CS+  + 2E           2.3373E-12    7.8282E-01    1.352E+05
 E + CS  => C+   + S +   2E     2.3373E-12    7.8282E-01    2.173E+05
 E + CS  => S+   + C +   2E     2.3373E-12    7.8282E-01    2.07E+05
 E + C   => C+   + 2E           7.4892E-13    8.5951E-01    1.307E+05
 E + S   => S+   + 2E           7.4892E-13    8.5951E-01    1.202E+05
 E + C   => E    + C            1.5323E-09    1.8345E-01    1.1328E+05
 E + S   => E    + S            1.0673E-08    7.5412E-02    1.3428E+05
Electron detachment
 E + C-  => C  + 2E             1.7361E-10    5.8335E-01    1.471E+04
 E + C2- => C2 + 2E             2.1451E-10    5.7525E-01    4.062E+04
 E + S-  => S  + 2E             1.3242E-10    5.6177E-01    2.403E+04
 E + S2- => 2S + 2E             1.8164E-10    5.1233E-01    2.323E+04
Reactions compiled from the NIST database
 C   + C   + M = C2  + M         5.46E-31   -1.6         0.0
 S   + S   + M = S2  + M         1.18E-29    0.0         0.0
 C   + S   + M = CS  + M         2.00E-30    0.0         0.0
 CS  + S   + M = CS2 + M         1.00E-29    0.0         0.0
 S2  + C       = CS  + S         2.10E-11    0.0         0.0
 C2  + S       = CS  + C         1.09E-11    0.0         0.0
 C   + CS2     = CS  + CS        2.81E-11    0.0         0.0
Ion chemistry
 S-    + C2 => C2- + S           5.2E-10    0.0     0.0
 S2-   + C2 => C2- + S2          8.1E-11    0.0     0.0
 C-    + S  => S-  + C           8.7E-11    0.0     0.0
 C-    + S2 => S2- + C           4.2E-10    0.0     0.0
 C-    + C2 => C2- + C           7.6E-10    0.0     0.0
 S2-   + S  => S-  + S2          1.2E-10    0.0     0.0
 S2+   + CS => CS+ + S2          3.e-11     0.0     0.0
 S2+   + C  => C+  + S2          6.e-11     0.0     0.0
 S2+   + C2 => C2+ + S2          2.e-11     0.0     0.0
 S2+   + S  => S+  + S2          3.e-11     0.0     0.0
 S2+   + CS2 => CS2+ + S2        8.e-11     0.0     0.0
 CS2+ + C2 => C2+ + CS2          5.e-11     0.0     0.0
 CS2+ + CS => CS+ + CS2          4.e-13     0.0     0.0
```

```
 CS2+ + C  => C+  + CS2        5.e-11    0.0     0.0
 CS2+ + S  => S+  + CS2        1.e-10    0.0     0.0
 S+   + C2 => C2+ + S          4.e-11    0.0     0.0
 S+   + CS => CS+ + S          1.e-10    0.0     0.0
 S+   + C  => C+  + S          7.e-11    0.0     0.0
 C+   + C2 => C2+ + C          5.e-11    0.0     0.0
 C+   + CS => CS+ + C          3.e-13    0.0     0.0
 CS+  + C2 => C2+ + CS         6.e-11    0.0     0.0
 S-  + CS => CS2 + E           1.3E-9    0.0     0.0
 C-  + S2 => CS2 + E           1.7E-9    0.0     0.0
 C-  + C  => C2  + E           2.6E-9    0.0     0.0
 S2- + C  => CS2 + E           1.0E-9    0.0     0.0
Ion mutual neutralization: Smirnov formula p. 131
 C2- + CS2+ => C2 + C + S + S   2.8E-7  -0.5    0.0
 C2- + CS+  => C2 + C + S       2.4E-7  -0.5    0.0
 C2- + S2+  => C2 + S + S       3.1E-7  -0.5    0.0
 C2- + C2+  => C2 + C + C       1.5E-7  -0.5    0.0
 C-  + CS2+ => C  + C + S + S   2.7E-7  -0.5    0.0
 C-  + CS+  => C  + C + S       2.3E-7  -0.5    0.0
 C-  + S2+  => C  + S + S       3.0E-7  -0.5    0.0
 C-  + C2+  => C  + C + C       1.4E-7  -0.5    0.0
 S2- + CS2+ => S2 + C + S + S   4.3E-7  -0.5    0.0
 S2- + CS+  => S2 + C + S       3.3E-7  -0.5    0.0
 S2- + S2+  => S2 + S + S       3.6E-7  -0.5    0.0
 S2- + C2+  => S2 + C + C       3.1E-7  -0.5    0.0
 S-  + CS2+ => S  + C + S + S   2.9E-7  -0.5    0.0
 S-  + CS+  => S  + C + S       2.7E-7  -0.5    0.0
 S-  + S2+  => S  + S + S       3.1E-7  -0.5    0.0
 S-  + C2+  => S  + C + C       2.3E-7  -0.5    0.0
Surface mechanism for CS2 plasma. "A" is a sticking probability.
   CS+ +  E + C(S) => CS  + C(S)                  .5  0.0  0.0
   C+  +  E + C(S) => C   + C(S)                 1.0  0.0  0.0
   C2+ +  E + C(S) => C2  + C(S)                 1.0  0.0  0.0
   S2+ +  E + C(S) => S2  + C(S)                 1.0  0.0  0.0
   S+  +  E + C(S) => S   + C(S)                 1.0  0.0  0.0
   CS+ +  E + S(S) => CS  + S(S)                  .5  0.0  0.0
   C+  +  E + S(S) => C   + S(S)                 1.0  0.0  0.0
   C2+ +  E + S(S) => C2  + S(S)                 1.0  0.0  0.0
   S2+ +  E + S(S) => S2  + S(S)                 1.0  0.0  0.0
   S+  +  E + S(S) => S   + S(S)                 1.0  0.0  0.0
  C  + S(S) => C(S) + S(D)                       1.0  0.0  0.0
  C2 + S(S) => C(S) + C(D) + S(D)                1.0  0.0  0.0
  C  + C(S) => C(S) + C(D)                       1.0  0.0  0.0
  C2 + C(S) => C(S) + C(D) + C(D)                1.0  0.0  0.0
  S  + S(S) => S(S) + S(D)                       1.0  0.0  0.0
  S  + C(S) => S(S) + C(D)                       1.0  0.0  0.0
  S2 + S(S) => S(S) + 2S(D)                      1.0  0.0  0.0
  S2 + C(S) => S(S) + C(D) + S(D)                1.0  0.0  0.0
```

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