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Infrared Spectroscopy of Interphases Between Model Rubber Compounds and Plasma Polymerized Acetylene Films*

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Thin ($\sim 750 \text{ \AA}$) plasma polymerized films of acetylene deposited onto polished steel substrates are promising primers for rubber-to-metal bonding. The as-deposited films contained mono- and di-substituted acetylene groups, aromatic groups, and groups such as carbonyl which apparently resulted from reaction of residual free radicals with oxygen when the films were exposed to the atmosphere. There was some evidence for formation of acetylides in the interphase between the films and the substrates. Reactions occurring in the interphase between the plasma polymerized films and natural rubber were simulated using a model "rubber" consisting of a mixture of squalene, zinc oxide, carbon black, sulfur, stearic acid, diaryl-p-diphenyleneamine, and N, N-dicyclohexyl-benzothiazole sulfenamide (DCBS). It was found that zinc oxide reacted with stearic acid to form zinc stearate in the interphase between squalene and the plasma polymerized acetylene primer. Zinc stearate reacted with DCBS and sulfur to form an accelerator complex and zinc perthiomeraptides. The perthiomeraptides reacted with squalene and the plasma polymer to form pendant groups which eventually reacted to form crosslinks between squalene and the primer. In the absence of cobalt naphthenate, the formation of pendant groups and eventually crosslinks was relatively slow and the length of the sulfur chains in the crosslinks and the pendant groups was relatively long. When cobalt naphthenate was added to the model "rubber," the reactions in the interphase between squalene and the plasma polymerized film occurred much faster and the length of the crosslinks and the pendant groups was much shorter.

KEY WORDS Bonding; rubber-to-metal; primers, plasma polymerized; acetylene, plasma polymerized; infrared spectroscopy; interphases; crosslinking; rubber compounds; model.

I. INTRODUCTION

Although direct adhesion of natural rubber to most metals is very poor, rubber-to-metal adhesion is of considerable practical importance. As a result, metals are

* One of a Collection of papers honoring James P. Wightman, who received the *13th Adhesive and Sealant Council Award* at the ASC's 1993 Fall Convention in St. Louis, Missouri, USA, in October 1993.

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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. The use of a thin brass layer as an "adhesive" for bonding rubber to steel tire cords has led to considerable interest in the fundamental aspects of rubber-brass bond formation. The book by Buchan¹ covered early work on this subject. More recently, van Ooij published extensive reviews about the mechanisms and theories of rubber adhesion to steel tire cords² as well as recent advances in bonding rubber to steel cords.³

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 in the sulfide-rubber interphase and ZnS in the sulfide-metal interphase.² 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".

"Interphases" between actual rubber compounds and brass substrates are difficult to characterize because they are buried and because the reactions which occur within the interphase are very complex. As a result, several investigators have used model rubber compounds in which NR is replaced by a low molecular weight organic compound having a structure similar to that of NR in order to elucidate reactions occurring in the interphase. Van Ooij utilized a model compound consisting of squalene, carbon black, sulfur, accelerator, activator, and antioxidant.⁴⁻⁶ XPS depth profiling was used to determine the structure of the interphase formed by reacting the model compound with brass. The results were compared with those obtained for an actual rubber/brass interphase. Depth profiles for the model/brass interphase were similar to those obtained from the actual rubber/brass interphase. The interphase consisted of rubber, Cu_xS mixed with some ZnS, and a layer of ZnO. No divalent copper was detected. These results suggested that adhesion of natural rubber to brass involved a bond between the crosslinked polymer and copper sulfide.

Ball and co-workers⁷ used XPS and dynamics SIMS to study brass surfaces reacted with model compounds containing squalene. The objective of their study was to determine the correlation between the organic portion (R) of three different adhesion promoters (Co-R) and the composition of a vulcanized brass/squalene "interphase." Depth profiles showed that, starting from the surface of the vulcanized sample, the squalene/brass interphase consisted of an almost completely organic outer layer followed by a mixed organic/sulfide layer, a copper sulfide layer containing some zinc sulfide, and the native zinc oxide layer before the bulk brass substrate was reached. These results were in good agreement with van Ooij's model of NR/brass interphases. In the absence of a cobalt-containing adhesion promoter, only a thin interfacial layer was formed. Clear evidence for mechanical interlocking of the organic layer with copper sulfide dendrites was observed in the depth profiles. When a cobalt mercaptobenzothiazole complex was added to the squalene formulation, the overall thickness of the interfacial layer did not change but the thickness of the interlocked organic/sulfide layer was significantly higher.

Although the technology of rubber-to-metal bonding is well developed, there are still some important problems. Brass plating processes produce chemical wastes which are

expensive 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.

We have recently reported preliminary results concerned with plasma polymerized acetylene films as primers for rubber-to-metal bonding.^{8,9} We found that 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.⁸

We have also reported preliminary results obtained using surface analysis techniques such as XPS, AES, and SIMS to determine the structure of interphases between plasma polymerized acetylene films which were deposited on steel substrates and a model rubber compound in which natural rubber was replaced by squalene. The results showed that sulfur diffused through the primer, forming a layer of sulfide in the primer/substrate interphase. Zinc and cobalt sulfides and perthiomeraptides, which formed in the interphase between squalene and the plasma polymerized acetylene primer, catalyzed the reaction between squalene and the primer. Crosslinks between squalene and the primer were mostly mono-sulfidic although some evidence for di- and tri-sulfidic crosslinks was observed.⁹

The purpose of this paper is to report additional results that we have obtained using reflection-absorption infrared spectroscopy (RAIR) to determine the reactions occurring in the interphase between a plasma polymerized acetylene primer and a model "rubber" compound consisting of a mixture of squalene, zinc oxide, carbon black, sulfur, stearic acid, cobalt naphthenate, N, N-dicyclohexylbenzothiazole sulfenamide, and diaryl-p-diphenyleneamine. The results obtained are consistent with the view that the accelerator breaks down to form a zinc perthiomeraptide which is the species responsible for crosslinking.

II EXPERIMENTAL

1010 cold-rolled steel (CRS) sheets 0.5 mm thick were obtained from The Goodyear Tire and Rubber Company (Akron, Ohio). The as-received steel substrates were mechanically polished to a mirror finish. The polishing sequence began with dry polishing on 600 grit silicon carbide papers to grind the surface. Then the steel coupons were 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.

Plasma polymerization and etching were carried out in a tubular reactor which was inductively coupled to an RF (13.56 MHz) power supply. The main part of the reactor consisted of a Pyrex tube with an internal diameter of 6 inches (15.2 cm). The top portion of the reactor was made of quartz and was surrounded by the RF coil. Samples were supported on a stage which could be moved vertically within the reactor. 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. A detailed description of the reactor has been presented elsewhere.¹⁰ Prior to plasma polymerization, the polished substrates were exposed to an argon plasma for 10 minutes. Plasma polymerized films of acetylene were then deposited on the substrates using argon as the carrier gas.

The thickness of the 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 McCrackin¹¹ was used to calculate the thickness and refractive index of the films from the measured values of the ellipsometric parameters Δ and ψ .

Reflection-absorption infrared (RAIR) spectra were obtained using a Perkin-Elmer 1800 Fourier-transform infrared spectrophotometer equipped with a deuterated triglycine sulfate (DTGS) detector and a reflection accessory from Harrick Scientific Co. The spectrum of a plasma polymerized film was obtained by averaging 100 scans at a resolution of 4 cm^{-1} and then subtracting the spectrum obtained from the polished substrate before deposition of the film. An angle of incidence of 80° was used to obtain the RAIR spectra.

In order to determine the nature of reactions occurring in the "interphase" between rubber and plasma polymerized acetylene films, RAIR was used to examine primed steel substrates after reaction with a "model" rubber system in which natural rubber was replaced by squalene. The model rubber compound consisted of squalene (100 parts per hundred or phr), zinc oxide (10 phr), carbon black (10 phr), sulfur (5 phr), stearic acid (2 phr), N, N-dicyclohexyl-benzothiazole-sulfenamide (DCBS), and diaryl-p-diphenylene-amine (each 1 phr). Polished steel substrates primed with plasma polymerized acetylene films were immersed into a stirred mixture of these materials at a temperature of 150°C to simulate the curing of rubber against a primed steel substrate. In some cases, cobalt naphthenate (1 phr) was added to the mixture. During the reaction, the mixture was continuously purged with nitrogen to reduce oxidation. At appropriate times between 1 and 100 minutes, substrates were removed from the mixture, rinsed with hexane to remove unreacted materials, dried, and examined using RAIR.

III RESULTS AND DISCUSSION

RAIR spectra of as-deposited plasma polymerized acetylene films on polished steel substrates are shown in Figure 1. The thicknesses of these films were 57, 90, 635, and 900 \AA . Detailed band assignments are listed in Table I. Peaks characteristic of hydrocarbons were observed near 2960 (asymmetric CH_3 stretching), 2928 (CH_2 stretching), 2870 (CH_3 symmetric stretching), 1450 (CH_2 bending) and 1375 cm^{-1} (CH_3 bending).

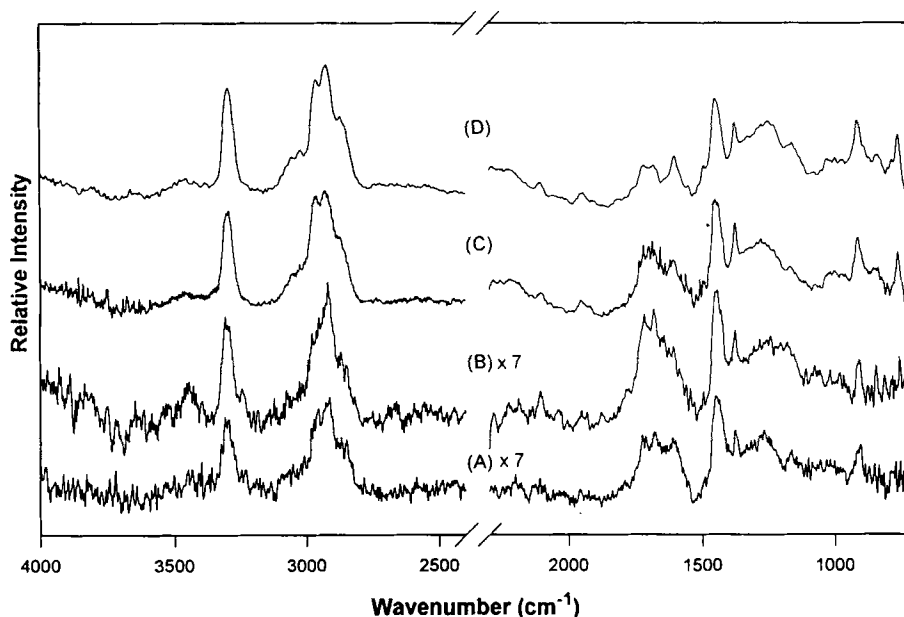


FIGURE 1 RAIR spectra of plasma polymerized acetylene films on polished steel substrates. The thicknesses of these films were (A) – 57, (B) – 90, (C) – 635, and (D) – 900 Å.

The strong, sharp band near 3295 cm^{-1} was assigned to CH stretching in monosubstituted acetylene groups ($\text{R}-\text{C}\equiv\text{C}-\text{H}$).¹² Weak bands related to $-\text{C}\equiv\text{C}-$ stretching in mono- and di-substituted acetylene were observed near 2103 and 2210 cm^{-1} , respectively.¹² A band assigned to $\text{C}=\text{C}$ stretching was observed near 1600 cm^{-1} . The strong, sharp band near 916 cm^{-1} may be related to the CH_2 wagging mode of vinylidene groups.

Several bands related to aromatic groups were also observed. Bands near 758 and 700 cm^{-1} were assigned to CH and CC out-of-plane bending in monosubstituted benzene rings and bands near 3055 and 3027 cm^{-1} were assigned to CH stretching in aromatic groups. Bands near 1595 , 1510 , and 1495 cm^{-1} were assigned to aromatic ring stretching modes. Evidence of oxidation resulting from the reaction of trapped radicals with atmospheric oxygen and moisture was also obtained. Thus, the band near 3455 cm^{-1} was assigned to O-H stretching and bands near 1715 and 1680 cm^{-1} were assigned to $\text{C}=\text{O}$ stretching.

There was not much difference in RAIR spectra of plasma polymerized films as a function of film thickness. The biggest difference concerned the band near 758 cm^{-1} assigned to $\text{C}-\text{H}$ bending mode in mono-substituted benzene rings ($\text{C}_6\text{H}_5-\text{R}$). This band was very strong in thick films (635 and 900 Å), much weaker in the 90 Å film, and undetectable in the 57 Å film. A weak band near 1950 cm^{-1} assigned to $\text{C}=\text{C}=\text{C}$ stretching was also stronger in spectra of thicker films. A very weak band was observed near 3250 cm^{-1} in spectra of the 57 Å and 90 Å films but not in spectra of the thicker films.

TABLE I
Assignment of infrared absorption bands for plasma-polymerized acetylene

Absorption frequency (cm ⁻¹)	Assignment
3455	O-H stretch (bonded)
3295	≡ C-H stretch
3250	H-C stretch in H-C≡C ⁻
3055	C-H stretch (aromatic)
3027	
2960	C-H asym. stretch (CH ₃)
2928	C-H out of phase stretch (CH ₂)
2870	C-H sym. stretch (CH ₃)
2853	C-H in phase stretch (CH ₂)
2200	C≡C stretch (in RC≡CR)
2103	C≡C stretch (in RC≡CH)
1950	C=C stretch (in -C=C=C-)
1715	C=O stretch (in -R-CO-CH ₃)
1680	C=O stretch (in -CH=CH-CO-)
1600	C=C stretch (in cumulated C=C)
1595	C=C stretch (aromatic)
1510	C-H bend (aromatic)
1495	C=C stretch (aromatic)
1450	C-H deformation (CH ₂)
1375	C-H deformation (CH ₃)
1320	C-H wag (CH ₂)
1350-1150	C-H overtone wag (in C≡C)
1240	C-O stretch (in C-C-O)
1160	C-O stretch (in O-CH ₂ -C)
1025	
990	C-H out-of-plane wag (in trans R-CH=CH ₂)
965	
916	CH ₂ out of plane wag (in R-CH=CH ₂)
758	C-H out-of-plane bend (in monosubstituted C ₆ H ₅ -R)
750	
700	C-C out-of-plane bend (in monosubstituted C ₆ H ₅ -R)
675	
660	C-H in-plane wag (in ≡ C-H)
635	C-H out-of-plane wag (in ≡ C-H)

In a study of aromatic acetylenic compounds adsorbed on zinc oxide, Nguyen and co-workers¹³ showed that 3-phenyl-1-propyne (C₆H₅CH₂C≡CH) and 1-phenyl-1-propyne (C₆H₅C≡CCH₃) had a common behavior over zinc oxide in that each gave rise to two types of dissociative chemisorption to yield acetylenic species and propargylic species. The former resulted from dissociation of the acetylenic hydrogen and the later from the removal of a proton attached to a carbon atom in an α -position to the triple bond. The propargylic species were considered to be intermediates in the isomerization reactions, and their two possible structures [(C₆H₅CH-C=CH)⁻ and (C₆H₅-C=C-CH₂)⁻] were characterized by intense infrared absorptions near 1862 cm⁻¹ which were assignable to the ν (C=C) modes. Acetylide species [C₆H₅CH₂C≡C...Zn] were characterized by weak ν (C≡C) bands in the region from 2080 to 2110 cm⁻¹ in both infrared and Raman spectra. Chang and Kokes¹⁴ also concluded that acetylene adsorbs dissociatively on ZnO based on a band near 3550 cm⁻¹ which was assigned to surface OH groups and bands near 3280 and

1975 cm^{-1} which were assigned to CH and C \equiv C stretching in HC \equiv C $^-$. Infrared spectra of methyl acetylene adsorbed onto ZnO were characterized by an absorption band near 3515 cm^{-1} which was assigned to a surface hydroxyl group and by a band 3250 cm^{-1} which was related to acetylenic CH stretching. These results indicated that dissociative chemisorption occurred, that the dissociation involved a methyl hydrogen, and that the acetylenic hydrogen remained intact.¹⁴

Since none of the RAIR spectra obtained from plasma-polymerized acetylene films on CRS substrates showed a band near 1862 cm^{-1} (see Fig. 1), it was concluded that propargylic species were not formed in plasma polymerized films of acetylene on CRS. However, two bands were observed near $2100\text{--}2107$ and 2200 cm^{-1} in all spectra and assigned to C \equiv C stretching in RC \equiv CH and RC \equiv CR, respectively. At this time it is not known whether the band near $2100\text{--}2107\text{ cm}^{-1}$ contained a component due to a surface acetylide. However, the weak band near 3250 cm^{-1} in spectra of the thinnest films may be related to a surface acetylide.

RAIR spectra obtained from plasma polymerized acetylene films which were deposited onto steel substrates and then immersed in the model rubber compound *without* cobalt naphthenate for 0, 15, 30, and 45 minutes are shown in Figure 2. As-deposited films were characterized by bands near $3295, 2960, 2928, 2872, 1708, 1681, 1603, 1460,$ and 1370 cm^{-1} . The assignments of these bands were discussed previously. After reaction of the plasma polymer with the model rubber for 15 minutes, the band near 3295 cm^{-1} decreased in intensity and the band near 1708 cm^{-1} increased in

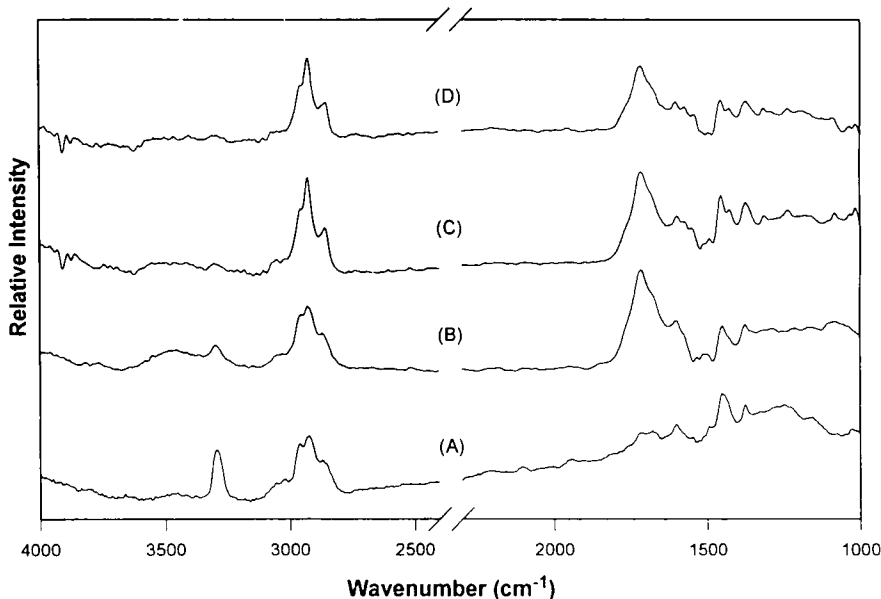


FIGURE 2 RAIR spectra obtained from polished steel substrates that were coated with plasma polymerized acetylene films and then immersed in model "rubber" systems *without* cobalt naphthenate at a temperature of 150°C for (A) – 0, (B) – 15, (C) – 30, and (D) – 45 minutes.

intensity. After reaction for 30 minutes, significant changes were observed in the RAIR spectra. The band near 3295 cm^{-1} disappeared and new bands appeared near 1581 , 1553 , 1429 , 1315 , 1237 , 1083 , 1033 , and 1014 cm^{-1} . After 45 minutes, the spectra were similar but the bands near 1581 and 1553 cm^{-1} disappeared and new bands appeared near 1573 and 1543 cm^{-1} . Weak shoulders also appeared near 1667 and 1649 cm^{-1} .

The decrease in intensity observed for the band near 3295 cm^{-1} during the first 15 minutes of reaction with the model rubber compound was partly related to oxidation and partly to "crosslinking" between the plasma polymerized film and squalene. This band decreases in intensity when plasma polymerized acetylene films are exposed to the atmosphere⁹ because of oxidation reactions. Even though the mixture was purged with nitrogen during the reaction of the model rubber compound with the primer, it is likely that there was sufficient oxygen and water vapor present to cause oxidation of the primer, resulting in some decrease in intensity of the band near 3295 cm^{-1} and an increase in intensity of the broad band near 1710 cm^{-1} . However, as discussed below, crosslinking between the plasma polymerized film and squalene also contributed to the decrease in intensity of the band near 3295 cm^{-1} .

The band which appeared near 1543 cm^{-1} , after 45 minutes reaction, was characteristic of zinc stearate formed by reaction of ZnO with stearic acid in the early stages of the reaction between the model rubber compound and the plasma polymerized film. The infrared spectrum of zinc stearate¹⁵ is characterized by an intense band near 1540 cm^{-1} . Most of the other bands which appeared after reaction times of 30 and 45 minutes, including those near 1429 , 1315 , 1237 , 1083 , 1033 , and 1014 cm^{-1} , were related to the benzothiazole sulfenamide fragment of the DCBS accelerator. Bands were observed near these frequencies in spectra of neat DCBS (see Fig. 3).

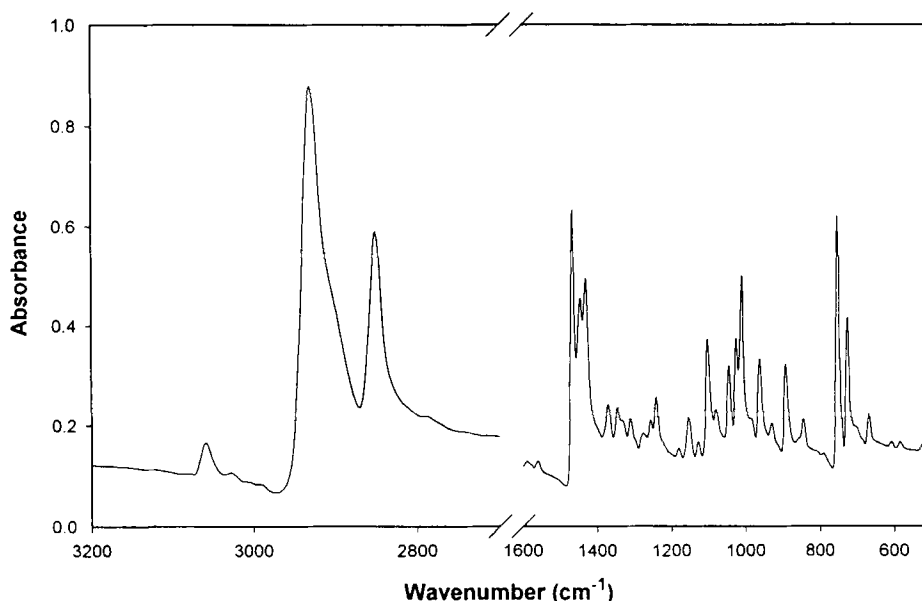
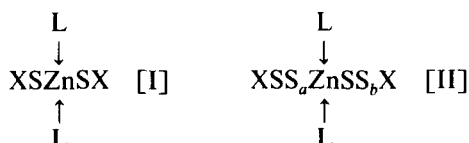


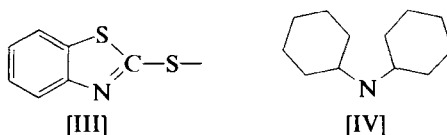
FIGURE 3 Infrared spectrum of N, N-dicyclohexylbenzothiazole sulfenamide (DCBS).

In order to determine the nature of reactions occurring in the interphase, it was important to consider the form in which the benzothiazole sulfenamide fragment of DCBS was present. It was certain that the DCBS fragment was not present as a thiolate. Thioliates¹⁷ are characterized by a very strong band near 1400 cm^{-1} but no band was observed near that frequency.

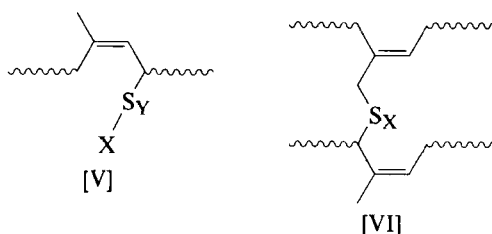
According to Chapman and Porter,¹⁶ the early stages of curing natural rubber with sulfur, an accelerator, and an activator involve formation of zinc stearate and then a zinc accelerator complex or a zinc accelerator perthiomercaptide complex. The zinc accelerator complex has the structure [I] while the zinc accelerator perthiomercaptide has structure [II] where X is an accelerator fragment and L is a ligand:



Since the accelerator used here was N,N-dicyclohexyl-benzothiazole-sulfenamide (DCBS), X has the structure [III] and the ligand L has the structure [IV]:



The zinc accelerator perthiomercaptide reacts with rubber hydrocarbon to form a rubber-bound accelerator perthiomercaptide pendant group such as [V]. Eventually the rubber-bound intermediates react to form crosslinks such as [VI]. Since the DCBS fragment was not present as a thiolate, it was most likely present as the zinc accelerator perthiomercaptide [V] or an accelerator perthiomercaptide pendant group [VI]. This assignment was supported by observation of several bands between 1550 and 1580 cm^{-1} which may be related to the $\text{C}=\text{N}$ stretching mode (see below).



The weak shoulders which appeared near 1667 and 1649 cm^{-1} after 45 minutes were related to $\text{C}=\text{C}$ stretching modes in squalene. The $\text{C}=\text{C}$ stretching vibration is located near 1667 cm^{-1} in infrared spectra of neat squalene. A band was observed near

1649 cm^{-1} in spectra of the model rubber compound after reaction at 155°C for 30 minutes or more.¹⁸ A band has also been observed near 1649 cm^{-1} in spectra of squalene reacted with sulfur and attributed to C = C double bonds with an attached sulfur or to conjugated double bonds.¹⁹ Observation of the bands near 1667 and 1649 cm^{-1} after 45 minutes reaction between the model rubber compound and the plasma polymerized film undoubtedly indicated some “crosslinking” between the plasma polymer and squalene to form structures such as [VI] by the mechanisms described above.

The origin of the bands which appeared near 1581 and 1553 cm^{-1} after reaction for 30 minutes and near 1573 cm^{-1} after 45 minutes is not known for certain and can only be speculated upon at this time. Appearance of these bands correlated with the appearance of bands due to DCBS. A weak band assigned to the C = N stretching mode was observed near 1560 cm^{-1} in spectra of DCBS (see Fig. 3). It is possible that the bands near 1581, 1573, and 1553 cm^{-1} were related to the C = N stretching mode of the sulfenamide fragments of DCBS [III] in structures such as [V] and that the three bands were due to different lengths of the sulfur chains.

As the reaction progressed, there were significant changes in the spectra in the region between 3000 and 2800 cm^{-1} . After about 45 minutes, the band near 2872 cm^{-1} decreased in intensity and a new band appeared near 2860 cm^{-1} . At the same time, the bands related to DCBS fragments, including those near 1571, 1429, 1315, 1237, 1083, 1033, and 1014 cm^{-1} , decreased in intensity. The new band which appeared near 2860 cm^{-1} was related to “crosslinking” between squalene and the plasma polymerized primer. Decrease in intensity by the bands related to DCBS was due to disproportionation of rubber-bound accelerator-perthiomercaptide pendant groups [V] to form crosslinks [VI].

Infrared spectra obtained from plasma polymerized acetylene films on steel substrates after reaction with the model rubber compound *containing* cobalt naphthenate were similar to those described above but with some important exceptions (see Fig. 4). In general, the reaction was much faster in the presence of cobalt. Thus, after only 15 minutes, the intensity of the band near 3295 cm^{-1} decreased greatly. New bands appeared near 1539 and 1512 cm^{-1} while shoulders appeared near 1765 and 1649 cm^{-1} . After 30 minutes reaction time, several additional bands appeared near 1011, 1030, 1085, 1232, 1320, 1430, and 1551 cm^{-1} .

The bands near 1011, 1030, 1085, 1232, 1320, and 1430 cm^{-1} which appeared after 30 minutes were clearly related to the benzothiazole sulfenamide fragment [III] of DCBS while the band near 1539 cm^{-1} was related to zinc or cobalt stearate which both have strong bands near this frequency. As indicated above, the band near 1649 cm^{-1} was related to C=C double bonds with an attached sulfur or to conjugated double bonds.¹⁹ However, the assignments of the bands near 1512 and 1765 cm^{-1} are not known at this time. Finally, after reaction for 45 minutes, the bands due to sulfenamide fragments of DCBS began to disappear.

Once again subtle changes occurred in the region of CH stretching vibrations. After reaction for 15 minutes, the band near 2872 cm^{-1} , which was characteristic of the plasma polymerized film, began to disappear and a shoulder began to appear near 2852 cm^{-1} . After 30 minutes, the band near 2852 cm^{-1} was well resolved and the band near 2872 cm^{-1} was not observable. As discussed previously, these changes are related

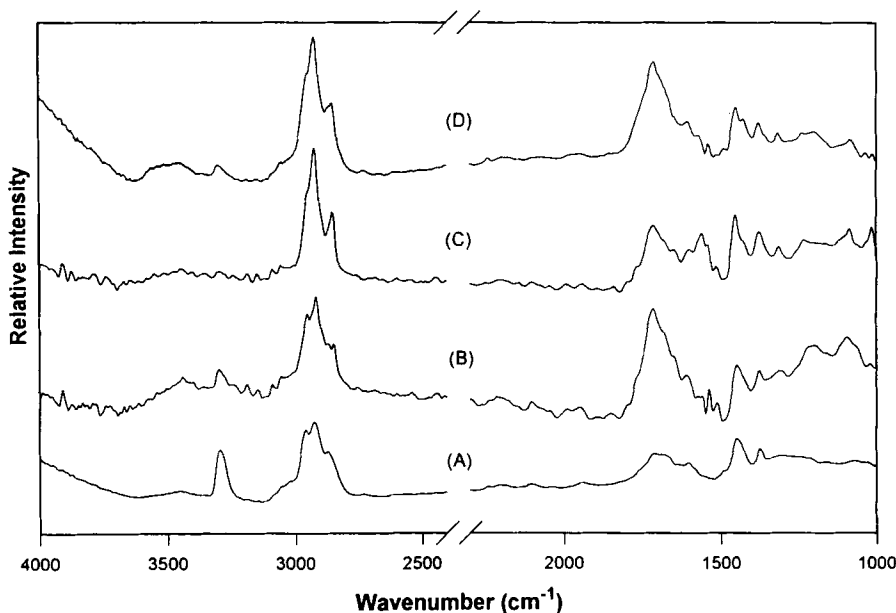


FIGURE 4 RAIR spectra obtained from polished steel substrates that were coated with plasma polymerized acetylene films and then immersed in model "rubber" systems with cobalt naphthenate at a temperature of 150°C for (A) – 0, (B) – 15, (C) – 30, and (D) – 45 minutes.

to "crosslinking" and the addition of squalene to the plasma polymerized acetylene film.

It is interesting to compare the results obtained here with those obtained previously using XPS, AES, and SIMS.⁹ High resolution XPS S(2p) spectra of plasma polymerized acetylene films after 35 minutes reaction in *cobalt-free* squalene mixtures were characterized by peaks near 163.5 eV and 164.3 eV which were assigned to $-S_n-$ present in the form of pendant or crosslinked sulfur. An additional weak peak related to sulfides was observed near 161.9 eV.

Peaks were observed at $-64 (S_2^-)$, $-96 (S_3^-)$, and -128 amu (S_4^-) in the negative SIMS spectra. These peaks were also mostly due to crosslinks or to rubber-bound accelerator-perthiolate pendant groups. Some evidence of the reaction between the plasma polymer film and squalene was provided by the squalene-related peaks ($+55$ and $+69$ amu).¹² The intensities of these peaks seemed to be very similar for 15, 35, and 65 minute reaction times. Also observed in SIMS spectra were traces of the stearic acid activator (-255 and -283 amu) which was adsorbed on the film surface from the reaction mixtures. Peaks characteristic of the accelerator fragment [III] were observed in the negative SIMS spectra at -134 and -166 amu while a peak related to the ligand [IV] was seen at $+182$ amu in the positive spectra.

These results, as well as the RAIR results, are consistent with a process in which ZnO reacted with stearic acid to form zinc stearate which then reacted with DCBS to form the zinc accelerator complex [I]. The complex eventually reacted with squalene and the primer film to form rubber-bound accelerator-perthiomercaptide pendant groups [V]

and crosslinks [VI]. The length of the sulfur sequences in [V] and [VI] was relatively long.

XPS survey spectra showed that plasma polymerized acetylene films reacted in *cobalt-containing* squalene mixtures showed much greater Zn and S concentrations than films reacted in *cobalt-free* squalene mixtures. Although both cobalt and zinc perthiomeraptides were intermediates in the crosslinking of the plasma polymer with squalene, XPS demonstrated clearly that the Zn adsorption was more intense than cobalt adsorption on the surface.

High resolution XPS S(2p) spectra obtained from a plasma polymerized acetylene film after 35 minutes reaction time with *cobalt-containing* squalene mixtures were characterized by a strong component near 161.9 eV which was related to cobalt and zinc sulfides. In addition, relatively weak peaks were observed near 163.5 eV and 164.3 eV which were assigned to $-S_n-$ in the form of pendant and crosslinked sulfur. However, the relative ratio of peaks at 163.5 to 164.3 eV was much larger for the experiments conducted in the *cobalt-containing* mixtures. This indicated that the presence of Co resulted in shorter bridges since it has been found that the more polysulfidic bonds, the higher the S(2p) binding energy.⁴

TOF-SIMS spectra of a plasma polymerized acetylene film before and after immersion in *cobalt-containing* squalene mixtures showed some interesting effects. The intensity of the sulfur peak was much higher in all samples than in the experiment without cobalt salt. The evidence of crosslinking at -64 amu (due to S_2^-) was a little stronger than in the previous experiment, but a similar observation did not apply to ions at -96 (S_3^-) and at -128 amu (S_4^-). They showed very weak intensities. It appeared that the presence of Co resulted in shorter bridges, confirming the results obtained from XPS data.

Peaks related to the accelerator fragment [III] were seen at -134 and -166 amu in all samples and their intensities were higher than in the previous experiment. The ligand [IV] ($+182$ amu) was also strongly adsorbed again. These results seemed to indicate that the cobalt salt promoted deposition of the accelerator at the surface.

The Zn intensities in the experiments *without* cobalt were weak in all samples and showed no trend with time. Experiments with *cobalt-containing* mixtures showed a strong Zn ($+64$) peak and appreciable amounts of Co ($+59$). The intensity of Co on the surface was very high after 15 minutes of reaction and then dropped after this time. On the other hand, the Zn concentration was more intense in 35 minutes reaction than at 15 and 65 minutes reaction. This result was confirmed by XPS analysis. As expected, TOF-SIMS spectra of samples from the previous experiment did not contain any cobalt. In contrast to the previous experiment, the squalene-related peaks (*e.g.* $+55$, $+69$, and $+81$ amu) in the experiment with *cobalt-containing* mixtures showed a much clearer trend with reaction time, increasing in intensity after 35 minutes reaction time.

These results, as well as the RAIR results, are consistent with a process in which ZnO and cobalt naphthenate reacted with stearic acid to form zinc stearate and cobalt stearate which then reacted with DCBS to form the zinc and cobalt accelerator complexes [I]. These complexes reacted with squalene and the primer film to form rubber-bound accelerator-perthiomeraptide pendant groups [V] and crosslinks [VI]. However, the length of the sulfur sequences in [V] and [VI] was relatively short.

IV CONCLUSIONS

Plasma polymerized films of acetylene deposited onto polished steel substrates contained various functional groups, including mono- and di-substituted acetylene, aromatics, methyl, and methylene groups. The films also contained carbonyl groups which apparently resulted from reaction of residual free radicals with oxygen when the films were exposed to the atmosphere. Some acetylides may have formed in the interphase between the films and the steel substrates. When the plasma polymerized films were reacted with a model "rubber" consisting of a mixture of squalene (instead of natural rubber), zinc oxide, carbon black, sulfur, stearic acid, diary-p-diphenyleneamine, and N,N-dicyclohexylbenzothiazole sulfenamide, another interphase was created. The structure of this interphase depended on the presence or absence of cobalt naphthenate in the model rubber. In the absence of cobalt naphthenate, zinc stearate and a zinc complex of benzothiazole sulfenamide formed. Eventually, the zinc complex reacted with sulfur, squalene, and the plasma polymer to form rubber-bound intermediates consisting of pendant perthiomercaptide groups and crosslinks between squalene and the film. The perthiomercaptides disappeared as a function of time, introducing additional crosslinks between the films and squalene. When cobalt naphthenate was added to the model "rubber," the reactions in the interphase between squalene and the plasma polymerized film were much faster. However, the length of the crosslinks and the rubber-bound perthiomercaptide pendant groups was shorter.

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