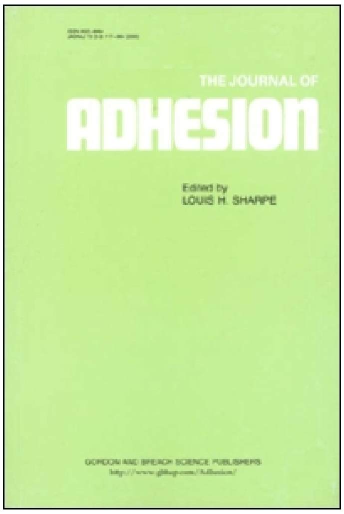

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R. Fountain[a][b]; J. L. Kardos[a]
[a] Materials Research Laboratory and Department of Chemical Engineering, Washington University, St. Louis, Missouri, U.S.A. [b] Bell Aerospace Company, Buffalo, New York

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Prevention of Hydrosilation Cure Inhibition in a Polysiloxane Adhesive by Surface Oxidation

R. FOUNTAIN† and J. L. KARDOS

Materials Research Laboratory and Department of Chemical Engineering, Washington University, St. Louis, Missouri 63130, U.S.A.

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For a variety of reasons epichlorohydrin-ethylene oxide (ECO)-based compounds, in the form of rain erosion boots or sleeves, are bonded to aircraft radomes using a hydrosilation-cured RTV polysiloxane adhesive. Unfortunately, cure of the adhesive can be completely inhibited by unreacted vulcanizing agent and/or ECO cure by-products. We have earlier shown that this inhibition can be prevented by treating the ECO surface with hydrogen peroxide to oxidize the hydrosilation catalyst poisons to a harmless state. In this study we have used spectroscopic techniques to monitor the hydrosilation reaction kinetics and in turn to identify the poison, define the poisoning level and monitor the poison removal by hydrogen peroxide treatment. The degree of poison removal is also correlated with adhesive bond strength using a 180° peel test. The critical poison in the system was excess ECO vulcanizing agent which can be completely removed from the surface using a 30 vol. % H_2O_2 treatment for 30 minutes as long as the initial vulcanizing agent concentration is 1 p.p.h. or less.

INTRODUCTION

High speed aircraft, after exposure to rainfall, hail or sand, suffer erosion at leading edges and other exposed areas such as the radome. For many reasons a solid precured elastomer bonded to these areas gives the best combined protection against the high temperature extremes and erosion forces which produce a high shear stress on the contact surface. The elastomer reduces the impact pressure and consequently the flow velocity and shear stress resulting from an impinging particle.[1]

Silicone elastomers, due to their poor mechanical properties (e.g., tear

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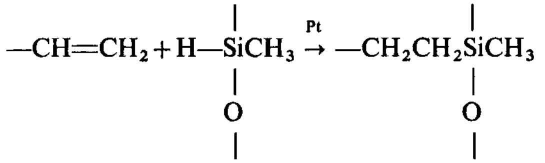
† Present address: Bell Aerospace Company, P.O. Box 1, Buffalo, New York 14240.

and abrasion resistance) relative to other synthetic elastomers, are not very erosion resistant. However, due to their high temperature capabilities and resilient nature they are desirable as adhesives for bonding high temperature (10 minutes at 400°F) erosion-resistant elastomers to erosion-prone areas. The silicone adhesive should provide a bond maintainable after extreme temperature exposure (e.g., $-100°F$ to $+400°F$), whereas other elastomeric adhesives and precured erosion-resistant elastomers would have been detrimentally aged. Other normally equivalent adhesives such as modified epoxies tend to become brittle after high temperature exposure and suffer impact adhesion bond failure during erosion. Future aircraft will require erosion resistance after up to 600°F exposure. The use of high strength RTV silicones as adhesives will ensure that the elastomer only erodes after elevated temperature exposure, rather than blistering and subsequently tearing due to an initial bond failure.

Commercially available, room temperature vulcanizing (RTV), vinyl-terminated polysiloxanes cure by a hydrosilation addition reaction in the presence of a platinum catalyst and a silane component. Network crosslinking takes place when the silane-containing polysiloxane components possess in-chain silane hydrogens.



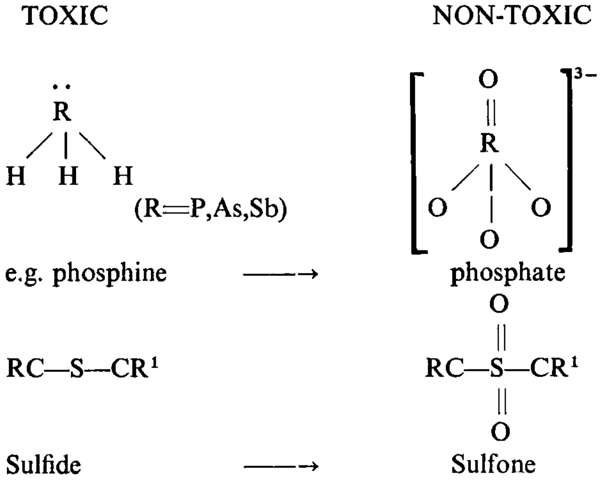
$$-CH{=}CH_2 + H-\underset{\substack{|\\ O\\ |}}{\overset{|}{Si}}CH_3 \xrightarrow{Pt} -CH_2CH_2\underset{\substack{|\\ O\\ |}}{\overset{|}{Si}}CH_3 \qquad (1)$$

If materials are present in the RTV system that can form more stable compounds with the organometallic catalyst than with the reactants for polymer cure, inhibition of the cure process will result. It may be partial or total depending upon the concentration of the poison relative to that of the catalyst.

Erosion resistant elastomeric compounds based upon polymers such as polychloroprene, ethylene propylene terpolymer (EPDM) and epichlorohydrin ethylene oxide copolymer (ECO) cause inhibition of the RTV hydrosilation cure throughout the adhesive thickness and at the elastomer-adhesive interface even when the vendor-recommended primer is used with the RTV adhesive. Using a barrier coating prior to the cure prevents the cure inhibition but acts as a mold release agent causing no bond. Acid etching treatments including H_2SO_4, HCl_4, and HNO_3/HCl all result in rubber degradation and no RTV cure.

In the RTV system, cure inhibition can be caused by the poisoning of the platinum catalyst, thus preventing hydrosilation. Maxted[2] discusses the poisoning of metallic catalysts, which he defines as a preferential absorption effect dependent on the formation of abnormally strong absorptive bonds between a catalyst and certain types of foreign absorbed species. The strong absorptive bond, which holds the poison to the catalyst, appears to be of a highly specific and chemical nature. The formation of such bonds is apparently dependent on definite types of electronic configurations both in the catalyst and poison.

One solution to this problem is simply to change the poison chemically to a shielded form that cannot form chemisorptive bonds with a catalyst. This is performed by saturating the poison's normal valency orbitals *via* stable bonding to other elements. This is illustrated by the following examples for catalytic hydrogenation on platinum below 100°C.



(2)

Using Maxted's approach of removing the catalytic poison by converting it to another oxidation state, previous work[3, 4] by the authors of this paper describes a method whereby the organic elastomer is treated with hydrogen peroxide prior to bonding with the RTV silicone. A bond between the RTV and the elastomer is obtained once hydrosilation-cure in the RTV has taken place. Presumably the vulcanizing ingredients and weathering additives of the organic elastomer were oxidized to give products that did not interfere with the platinum catalyst and that did not act as debonding agents. The reaction mechanisms of hydrogen peroxide in this situation are well documented by Weiss[5] and Baxendale.[6]

$$\text{e.g., } \underset{\text{alkylmercaptan}}{2RSH} \xrightarrow{H_2O_2} \underset{\text{alkyl disulfide}}{RSSR} \rightarrow RSOSOR \rightarrow RSO_2 \qquad (3)$$

To qualitatively identify the culprit of hydrosilation inhibition, the RTV silicone was mixed or placed in contact with all the possible causes of inhibition pertaining to the compounding of ECO elastomers.[7] In light of the lone pair poisoning by sulfur and nitrogen compounds demonstrated by Maxted[2] and since only ECO, compounded with 2-mercaptoimidazoline (NA-22)† and red lead oxide, in the cured and uncured state caused inhibition of the RTV silicone cure, it was concluded that the NA–22 and, possibly, the imidazolidinone (cure by-product) were the inhibitors. This assumes that any sulfur generated during the cure will be either combined with the ECO or present as lead sulfide (lead oxides, lead sulfide, and lead sulfate did not cause any inhibition).

Thus, upon oxidation of the adherend with 30 vol. % hydrogen peroxide prior to bonding, sufficient hydrosilation-cure took place to form a stable bond between the RTV polysiloxane and the ECO adherend. In this study using spectroscopic methods, the effects of the hydrogen peroxide treatment on the adherend were monitored in terms of hydrosilation kinetics and surface morphology and correlated with the bond strength obtained between the hydrosilation-cured adhesive and the ECO adherend.

EXPERIMENTAL

1. Material preparation and characterization

a) *Epichlorohydrin ethylene oxide copolymer (ECO) compound* Three uncured compounds based upon ECO were prepared containing only the vulcanizing agent and hydrocarbon processing aid. The red lead acid acceptor and processing aid quantities were the same for each compound. The recipes were as follows:

	Parts per hundred polymer		
Hydrin 200 (ECO)	100	100	100
Red lead	5	5	5
ZO–9 (hydrocarbon processing aid)	1	1	1
NA–22 (2-mercaptoimidazoline)	0.5	1.0	1.5
	106.5	107.0	107.5

These compounds were cured for 13, 31 and 53 minutes at 155°C, the cure temperature being obtained from the exotherm temperature of a differential thermal analysis of the uncured compound. Carbon black, silica and other fillers were not added since they did not contribute to the inhibition of RTV hydrosilation cure. Great care was taken to process these compounds in exactly the same way to provide a constant ECO surface. Inhibition would

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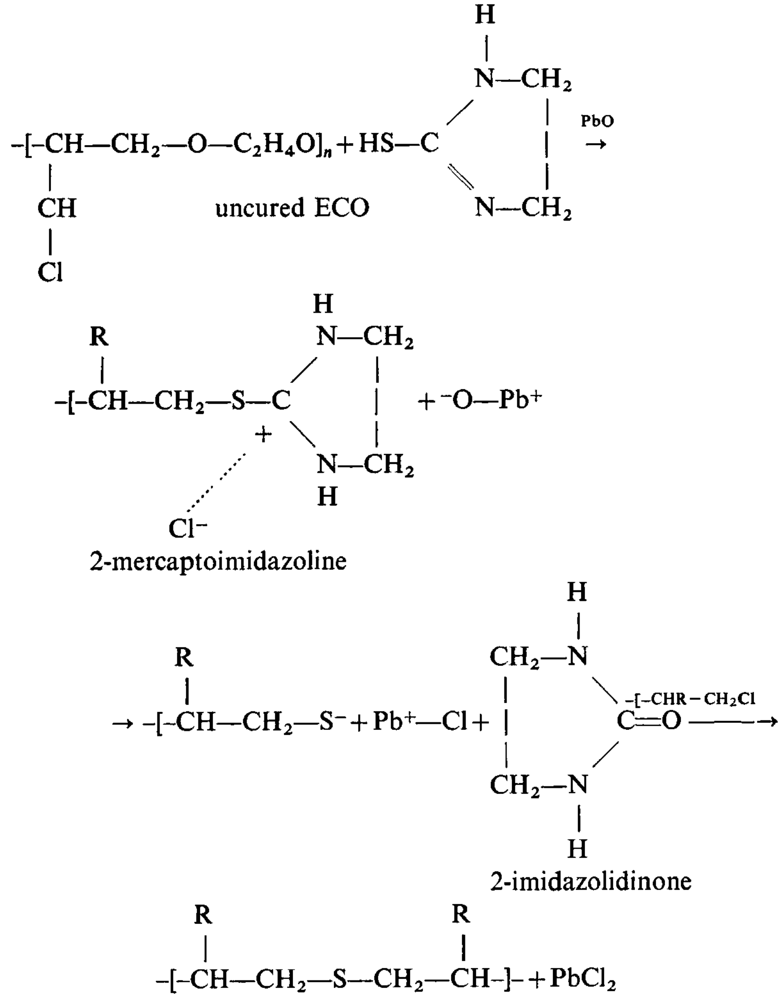
† NA–22, Tradename, E. I. du Pont de Nemours & Company.

only be caused by the vulcanizing agent and by-products of cure as indicated earlier[7] and depicted in Eq. (4) below.

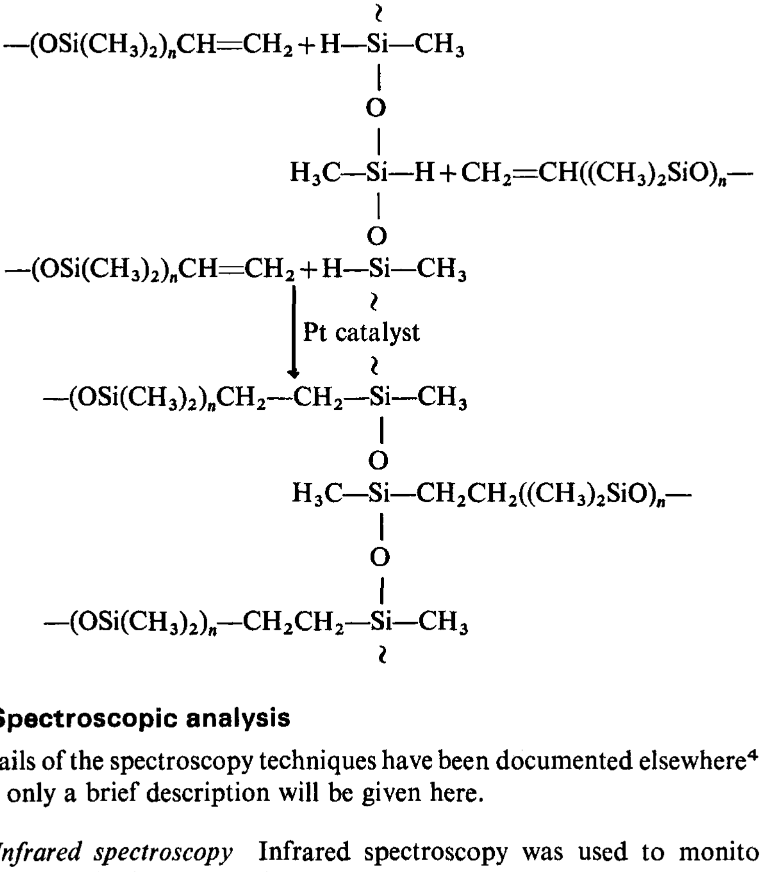


(4)

b) *RTV Polysiloxane* This is a two component system (e.g., General Electric Co. RTV 600 series) consisting of, as the first component, vinyl chain-stopped dimethyl polysiloxane, finely divided quartz, colbalt-based pigment, and a platinum catalyst and, as the second component, a vinyl chain-stopped dimethyl polysiloxane, quartz and a dimethyl hydrogen siloxane copolymer.

The first component is added to the second one in a 10:1 ratio by weight. The rate of cure is a function of the platinum catalyst concentration and temperature. The cure may vary from 24 hours at room temperature to

30 minutes at 100°C. The general cure of hydrosilation proceeds by anti-Markovnikoff addition. Trifunctional crosslinking takes place due to the few in-chain vinyl and Si-H groups.[8]



$$\begin{array}{rcl}
 & \wr & \\
-(OSi(CH_3)_2)_nCH{=}CH_2 + H- & Si & -CH_3 \\
 & | & \\
 & O & \\
 & | & \\
H_3C- & Si & -H + CH_2{=}CH((CH_3)_2SiO)_n- \\
 & | & \\
 & O & \\
-(OSi(CH_3)_2)_nCH{=}CH_2 + H- & Si & -CH_3 \\
 & \wr & \\
 & \Big\downarrow\ \text{Pt catalyst} & \\
 & \wr & \\
-(OSi(CH_3)_2)_nCH_2-CH_2- & Si & -CH_3 \\
 & | & \\
 & O & \\
H_3C- & Si & -CH_2CH_2((CH_3)_2SiO)_n- \\
 & | & \\
 & O & \\
 & | & \\
-(OSi(CH_3)_2)_n-CH_2CH_2- & Si & -CH_3 \\
 & \wr &
\end{array} \tag{5}$$

2. Spectroscopic analysis

Details of the spectroscopy techniques have been documented elsewhere[4, 9, 10] and only a brief description will be given here.

a) *Infrared spectroscopy* Infrared spectroscopy was used to monitor the RTV hydrosilation-cure by itself and in contact with ECO-based compounds. The Beckman IR-12 was used for both transmission and multiple internal reflectance (MIR) techniques. Data obtained from both techniques correlated well and led to the same conclusions. After mixing the RTV silicone in a 10:1 ratio of vinyl to silane components, a thin film was smeared onto a KBr salt plate or KRS-5 crystal (subsequently followed by the ECO sheet stock) and the IR spectrum recorded by monitoring the 900 cm^{-1} Si—H wagging and the 700 cm^{-1} CH_3 rocking (internal thickness standard) absorbances (Figure 1) with time at the beam temperature of 39.5°C.

b) *Ultraviolet spectroscopy* The actual 2-mercaptoimidazoline content of the elastomers was measured by first isopropanol soxhlet-extracting the thiourea and measuring the C=S $n \rightarrow \pi^*$ transition of the extracted material at 270 nm by ultraviolet spectroscopy using a Cary 16 spectrometer. A blank of isopropanol-extracted uncured ECO containing only red lead and the processing aid was used to balance any absorption at 270 nm due to these components. A working curve of absorbance against the NA-22 concentration enabled the amount of extracted NA-22 to be calculated.

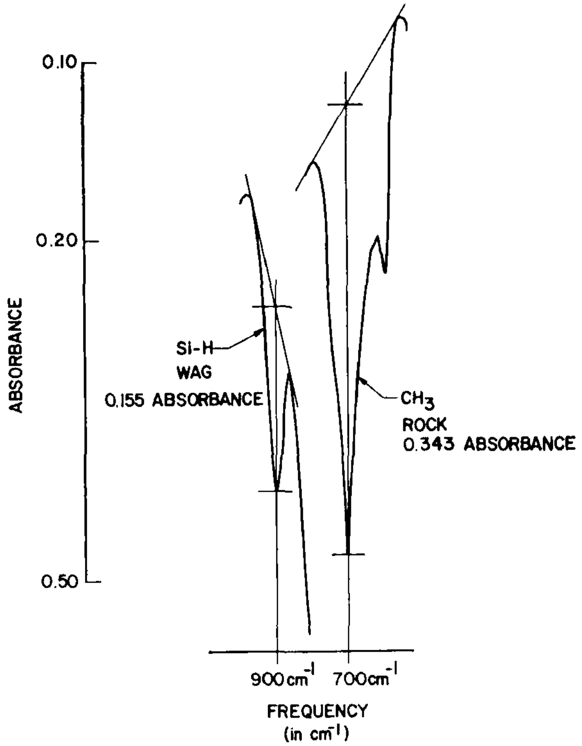


FIGURE 1 Infrared absorbances (Si—H wagging and CH_3 rocking modes) used to quantitatively monitor the RTV hydrosilation cure.

c) *X-ray photoelectron spectroscopy (ESCA)* ECO sheet samples were wrapped around the outside of a small cylinder and placed into the Varian Induced Electron Spectrometer (VIEE-15). The source was aluminum K-α x-rays operated at 9 kV, 70 MA with an analyzer acceptance energy of 100 eV. The "2p" core electron emission was monitored from the sulfur atoms on the elastomer surface. The data was gathered by 620i computer in a repetitive scan mode. For the sulfur region, 250 scans were taken; and for oxygen and carbon, 50 scans were taken. The scan time was 25 seconds; the scan width was 25 volts; and the number of channels of memory/region was 250.

3. Scanning electron microscopy

A Cambridge "Stereo Scan"—Mark II was used at 20 kV. The surfaces of the ECO specimens were coated with chromium. The presence of artifacts was checked by viewing specimens coated with carbon and copper on a cold stage. ECO specimens containing different 2-mercaptoimidazoline concentrations and with and without the peroxide surface treatment were photomicrographed at 500×, 2000× and 5000× magnification to monitor surface phenomena differences such as blister formation, cracks and particulate inclusions.

4. Mechanical testing in peel

In order to correlate the effect of the partially oxidized 2-mercaptoimidazoline (NA–22) in the ECO compounds upon hydrosilation-cure, peel testing was chosen for its simplicity and its well documented analytical procedure to evaluate the adhesive bond produced between the silicone adhesive and cured ECO adherend.

Peel testing was performed on an Instron machine. Two 1-inch wide, 6-inch long and $\frac{1}{16}$-inch thick pieces of cured ECO were cleaned, roughened and treated with 30 vol. % hydrogen peroxide solution for various times. The samples were then rinsed in distilled water and dried at 40°C in an air circulating oven. They were then primed with a silane and room temperature air-dried at 60% RH for 1 hour to allow the silane to hydrolyze.

Mixed, deaerated RTV polysiloxane was then coated onto both samples which were then mated together to give a bonded "T" peel specimen. The adhesive thickness was controlled by using 0.5 mm spacers. The adhesive was cured at room temperature for 40 hours prior to testing. "T" peel specimens were made with ECO strips having different peroxide treatment times and NA–22 concentrations. Figure 2 illustrates the specimen configuration used to test at five different temperatures with a constant rate (1.0 in/min) using five specimens for each temperature condition. The temperature of the specimen was obtained by using dry ice, liquid N_2 or oven heat and was measured with an iron-constantan thermocouple. The peel rate at room temperature (27°C) was also varied for one set of specimens. The peel force was taken as the value when the load became independent of strain. This generally occurred after 2–3 inches of the specimen had separated. The data was reduced by using the time–temperature superposition principle and correlated with the instrumental analytical data.

Gent *et al.*[11] describe the relationship of peel strength to peel rate and temperature using the time–temperature superposition principle. A form of the Williams, Landel and Ferry equation was used to obtain the equivalency factor a_t, i.e.,

$$\log a_t = \frac{-17.5\,(T\text{–}Tg)}{51.6+T\text{–}Tg}$$

where Tg is the glass transition temperature of the adhesive and T is the test temperature. The same principle may also be applied to the tensile strength of adhesive joints.[12]

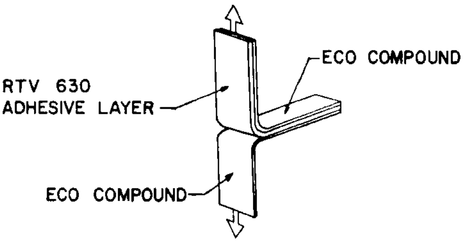


FIGURE 2 Schematic of "T" peel test configuration.

RESULTS AND DISCUSSION

The rate of hydrosilation-cure occurring in the mixed RTV polysiloxane was measured by the disappearance of the normalized Si—H bending absorption. This absorbance ratio data, plotted as $\log_{10}$ of the ratio versus time, obeyed first-order kinetics with respect to the silane.[9] The resulting specific reaction rate constants obtained at various temperatures showed an Arrhenius relationship for both the inhibited and uninhibited reactions (Figure 3). Hydrosilation cure was inhibited by NA–22 or the imidazolidinone addition to the RTV 630. Inhibition of cure did not appear to affect its energy of activation as measured by the slope of Figure 3. Thus poisoning of the platinum catalyst in the hydrosilation cure is indicated to occur via the cure mechanism of Chalk and Harrod[13] and the inhibition or poisoning concept of Maxted.[2]

The effect of poison concentration on the hydrosilation-cure was determined by varying the amount of 2-mercaptiomidazoline (NA–22) contained in the RTV silicone. Figure 4 shows that the inhibition effect on the reaction rates is larger than when imidazolidinone was used. Monitoring the reaction rate for various amounts of the inhibitor at 38.5°C and 23°C yielded similar effects of catalyst poison concentration as indicated by the slope in Figure 4.

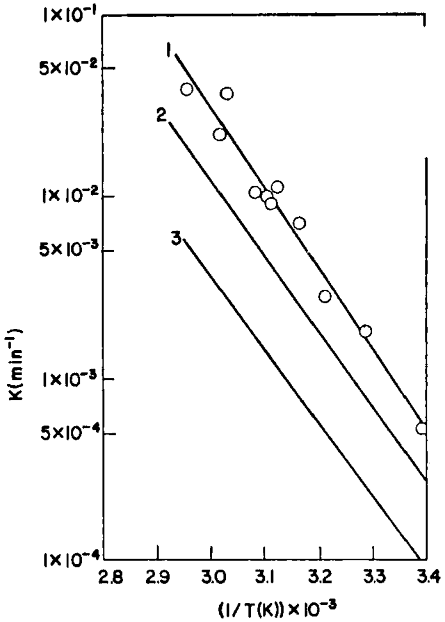


FIGURE 3 Effect of temperature on reaction rate constant for unpoisoned and poisoned hydrosilation cure: 1-RTV 630; 2-RTV 630+0.52% NA-22; 3-RTV 630+0.52% imidazolidinone.

The slopes obey the equation $K = K_0\, e^{-3.1\,(C)}$ where $K =$ the reaction rate constant for the inhibited reaction, $K_0 =$ the reaction rate constant for the uninhibited reaction and (C) is the weight per cent concentration of the inhibitor.

This dependency of inhibition concentration on reaction rate is somewhat different from the one observed by Maxted.[2] He reported a linear relationship, $K = K_0(1-\alpha C)$, where α is a sensitivity constant. The sensitivity constant for the exponential equation is the slope of the curve. 2-imidazolidinone had a sensitivity constant of 1.29, being less than half that for the 2-mercaptoimidazoline.

Using the i.r. multiple internal reflectance technique in conjunction with the equivalent data obtained by the i.r. thin film transmission method, the hydrosilation-cure of the polysiloxane adhesive was monitored in contact with the three ECO compounds in both the cured and uncured states. From the calculated reaction rate constants, the amount of thiourea (NA–22) inhibiting hydrosilation was measured from Figure 4 which correlated hydrosilation reaction rate constant with inhibitor concentration. Thus, the reaction rate constant obtained for the RTV 630 in contact with the ECO reflects the concentration of NA–22 inhibitor on the ECO surface. These data

(Table I) showed that the surface concentration of the NA-22 in the ECO compounds was similar to the bulk NA-22 concentration obtained by the ultraviolet spectroscopic technique.

In order to remove the inhibiting effect of the excess NA-22 in the ECO compounds, they were surface oxidized with 30 vol. % hydrogen peroxide and dried. The hydrosilation reaction was again monitored by the MIR technique in contact with the oxidized ECO surface and the bulk NA-22 contents of the oxidized elastomers were measured by the ultraviolet spectroscopic technique.

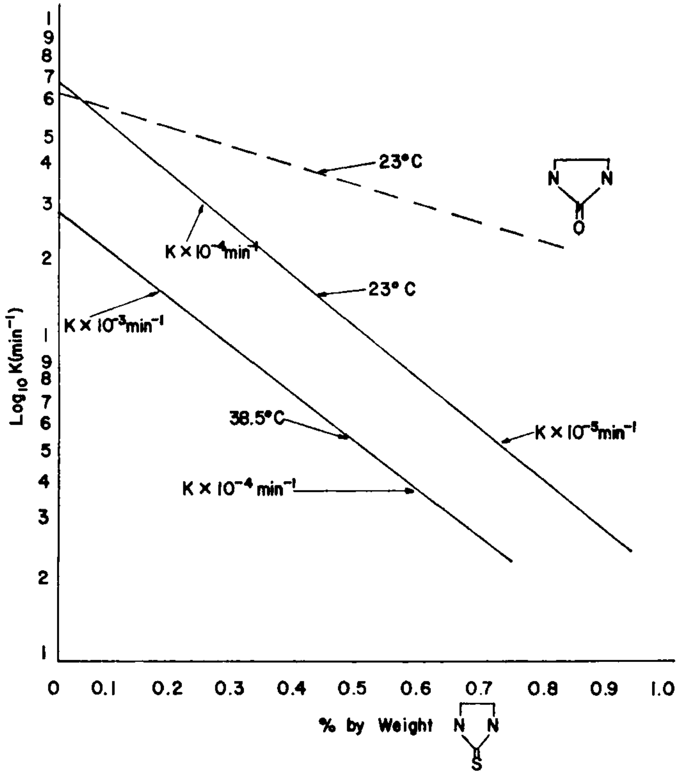


FIGURE 4 Effect of 2-mercaptoimidazoline poison concentration on hydrosilation reaction rate constant at 23 and 38.5°C. Also shown for comparison is the effect of imidazolidinone at 23°C. Note the change in log scales between the top two and lowermost curves.

The data are summarized in Table 2. The NA-22 concentration on the ECO surface was much less than that in the bulk as indicated by the higher hydrosilation reaction rate constants. The data also shows that the inhibitor was never completely removed from the ECO surface except for the case of the 15 minute H_2O_2 treatment of the 53 minute cured ECO compound initially containing 0.5 p.p.h. NA-22.

Note also that the bulk NA–22 concentration and the estimated surface NA–22 concentrations were the same for both the 30 minute H_2O_2-treated, 53 minute-cured ECO compound initially containing 1.0 p.p.h. NA–22, and the 13 minute-cured ECO compound of the same initial NA–22 concentration and H_2O_2 treatment time. Since the oxidized ECO NA–22 bulk concentrations are much lower than those expected for purely a surface oxidation effect, a diffusion process is suggested for the peroxide attack upon the ECO compounds. Although the above data suggests a diffusion attack of the NA–22 by the peroxide, the physical nature of this process was not clearly indicated until the ECO specimens were photomicrographed. Figure 5 shows the unoxidized, cured ECO compound containing particulate material. After treatment with 30 vol. % H_2O_2 several physical changes were noted on comparing the oxidized surface of Figure 6 with Figure 5. First, the particulate matter (probably NA–22) disappeared and penetration of the peroxide through the ECO surface oxidized the NA–22 under the surface. This resulted in oxygen outgassing and consequent bubbling of the surface which eventually produced corrugations and cavities of 1–2 μ. Thus, a new surface was provided for repetition of this process. Further evidence of peroxide attack of the NA–22 was provided by photoelectron spectroscopy (ESCA).[10]

TABLE I

Correlation of NA–22 content given by hydrosilation inhibition (Figures 3 and 4) with the bulk NA–22 content obtained by u.v. spectroscopy

ECO compound cure cycle	NA–22 content in ECO compound as given by hydrosilation inhibition of the polysiloxane ($k_{39.5°C}$) (%)	Bulk NA–22 content given by u.v. spectroscopy (%)
13 min at 155°C cure 1 p.p.h. NA–22	0.61	0.59
31 min at 155°C cure 1 p.p.h. NA–22	0.55	0.53
53 min at 155°C cure 1 p.p.h. NA–22	0.50	0.48
53 min at 155°C cure 0.5 p.p.h. NA–22	0.36	0.32
53 min at 155°C cure 1.5 p.p.h. NA–22	1.00	0.98
Uncured 1 p.p.h. NA–22	0.97	0.95

An analysis of the ESCA scans is summarized in Table III. The values in the first column are binding energies, which have been corrected for calibration and charging effects by subtraction of 2.9 eV(10); the binding energies (BE) for O(1S) and C(1S) have not been corrected. Four different sulfur species are resolvable. The second column lists the percentage of the total sulfur "2p" area due to each of the species. From the binding energies the residual charge on the sulfur atom was estimated by utilizing calibration data.[10]

TABLE II

NA-22 concentration of oxidized ECO compounds

ECO compound history	Surface concentration of NA-22 given by the reaction rate constant for hydrosilation at 39°C (Figures 3 and 4) (%)	Bulk concentration of NA-22 (%)
Uncured 0.5 p.p.h. NA-22 +15 min H_2O_2	0.42	0.47
Uncured 1.0 p.p.h. NA-22 +15 min H_2O_2	0.42	0.79
Cured 53 min at 155°C 1.0 p.p.h. NA-22 +15 min H_2O_2	0.08	0.40
Cured 53 min at 155°C 1.0 p.p.h. NA-22 +30 min H_2O_2	0.05	0.34
Cured 53 min at 155°C 0.5 p.p.h. NA-22 +15 min H_2O_2	0.00	0.18
Cured 53 min at 155°C 1.5 p.p.h. NA-22 +15 min H_2O_2	0.54	0.72
Cured 13 min at 155°C 1.0 p.p.h. NA-22 +30 min H_2O_2	0.05	0.34

The species with a residual charge of 0.4 to −0.5 (BE ~ 161) is probably lead sulfide, while a residual charge of +0.13 is probably due to a R—SH or perhaps a R—S—S—R— group. The species with residual charge of 0.60 to 0.74 could be either a R—SO_2—M or a SO_3^{2-} group. Finally, the higher residual charge group at +1.4 (BE = 169) is most likely an SO_4^{2-} group.

By comparing the uncured, cured, and cured/peroxide-treated samples in Table III, it is clear that the peroxide-treated elastomer contained the highest

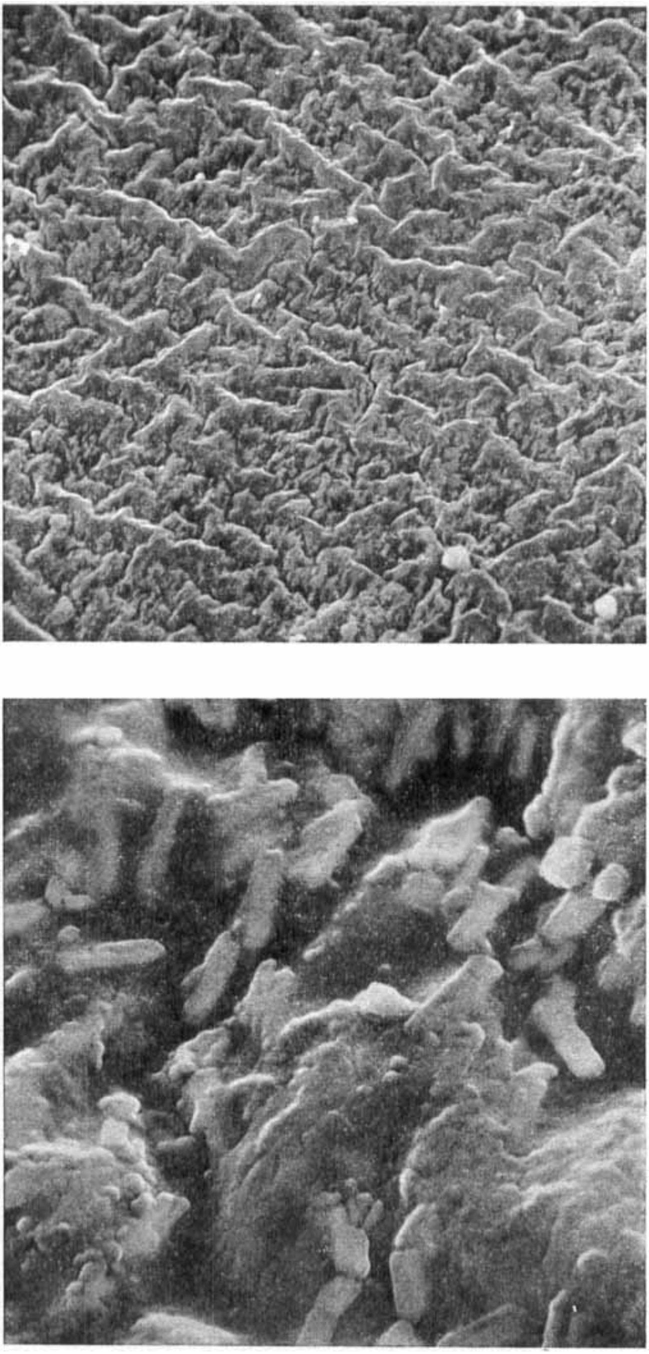


FIGURE 5 Scanning electron micrographs of unoxidized, cured ECO compound containing 1 p.p.h. NA-22. Note the particulate matter on the surface. Top ×470, bottom ×4700.

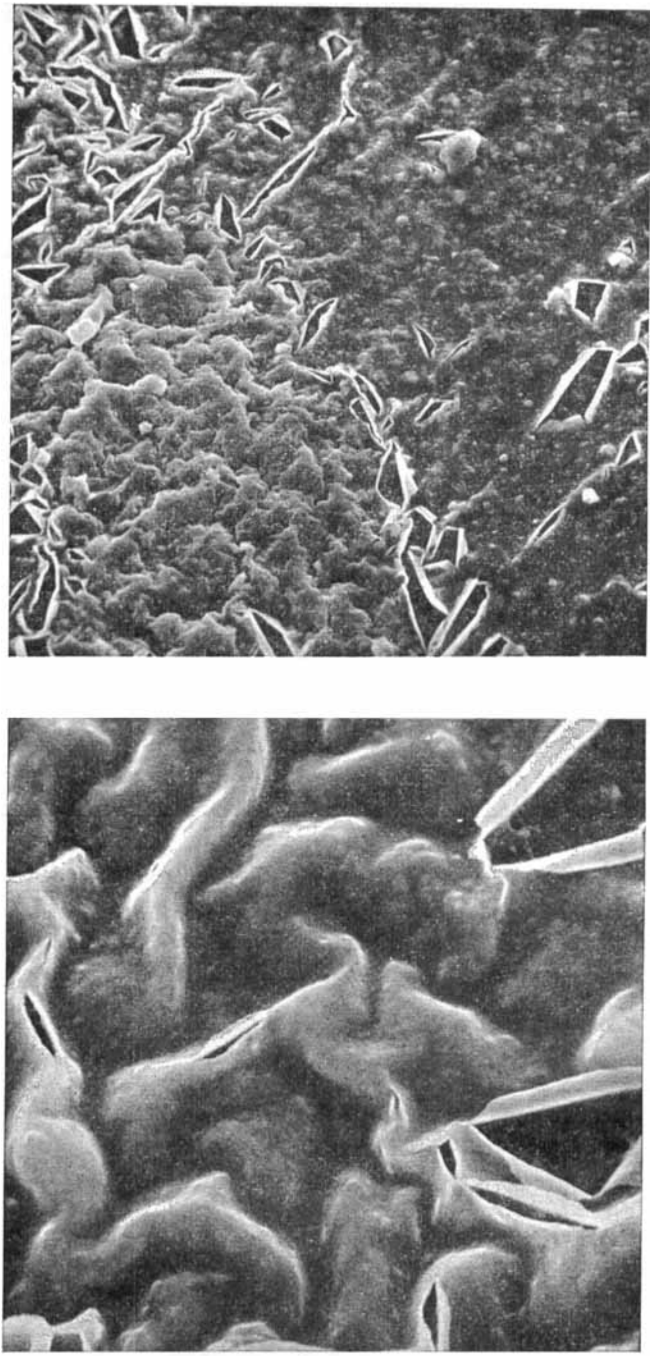


FIGURE 6 Scanning electron micrographs of oxidized, cured ECO compound (containing initially 1 p.p.h. NA–22) after 15-minute H_2O_2 treatment. Note absence of particles seen in Figure 6 and surface tears caused by oxygen outgassing. Top ×460, bottom ×1900.

amount (~ 70% relative peak area) of bonded sulfur in an oxidized state. Since this is much higher than the corresponding value for the cured elastomer (~ 50%), and since it is known that the peroxide treatment will not degrade the cured elastomer,[7] the increase in oxidized sulfur emission is most likely due to peroxide oxidation of the 2-mercaptoimidazoline (NA–22), which remains unreacted after the elastomer cure. Such a treatment thus diminishes the C=S bond by oxidation and effectively reduces the catalyst poisoning reaction $(\mathrm{C{=}S+Pt}\overset{/}{\underset{\backslash}{-}})$ at the ECO/polysiloxane interface.

TABLE III

Sulfur, oxygen and carbon binding energies for ECO surfaces from ESCA

Sample history	BE S ("2p") eV	Relative area (%)	Residual charge	BE for O (1s) eV	BE for C (1s) eV
Cured ECO (originally containing 1.0 p.p.h. NA–22) after H_2O_2 treatment for 15 min	1) 168.9	17	1.4	532.50	284.75, 286.50[b]
	2) 165.6	52	0.64		
	3) 163.3	19	0.13		
	4) 160.7	22	−0.46		
Uncured ECO containing 1.0 p.p.h. NA–22	1) 169.1	2	1.43	532.70	285.00, 286.80
	2) 165.8	30	0.60		
	3) 163.3	7.5	0.13		
	4) 160.4	60	−0.53		
Cured ECO originally containing 21.0 p.p.h. NA–22	2) 166.0	50	0.74	532.60	285.05
	4) 161.0	43	−0.40		
	— 158.2[a]	6	—		

[a] Not likely to be a S species, but included in area measurement.

[b] Shoulder on side of larger C peaks, possibly due to C=S and C=O.

Since surface oxidation removes the hydrosilation inhibitor, a suitable bond should now be obtainable between the adhesive and adherend. To examine this supposition, 180° "T" peel tests were carried out involving the following ECO surface oxidized samples:

1) 0.5 p.p.h. NA–22; cured 53 minutes at 155°C; treated for 30 minutes with H_2O_2.

2) 1.0 p.p.h. NA–22; cured 53 minutes at 155°C; treated for 5 minutes with H_2O_2.

3) 1.0 p.p.h. NA–22; cured 53 minutes at 155°C; treated for 15 minutes with H_2O_2.

4) 1.0 p.p.h. NA–22; cured 53 minutes at 155°C; treated for 30 minutes with H_2O_2.

5) 1.5 p.p.h. NA–22; cured 53 minutes at 155°C; treated for 30 minutes with H_2O_2.

Hydrosilation inhibition was observed in the 1.0 p.p.h. NA–22 specimens, H_2O_2-treated for 5 minutes, and the 1.5 p.p.h. NA–22 specimens, H_2O_2-treated for 30 minutes (Tests 1 and 5). This may be rationalized by comparing the hydrosilation rate constants obtained with the RTV in contact with the oxidized ECO or by comparing the surface NA–22 concentrations obtained from Figure 4 data. Figure 7 shows that the hydrosilation rate constant with the 30-minute H_2O_2-treated, 1.5 p.p.h. NA–22 ECO is the same as that for 5-minute, H_2O_2-treated, 1.0 p.p.h. NA–22 ECO. Note that the shapes of the curves in Figure 7 seem to depend on the initial amount of NA–22 present in the ECO. For the 1.5 p.p.h. NA–22 plot, the rate constant increases at a faster rate for increasing H_2O_2 treatment time, whereas for the 0.5 p.p.h. and the 1.0 p.p.h. NA–22 ECO cured for 53 minutes, the reaction rate constant increases at a slower rate for increasing H_2O_2 treatment time.

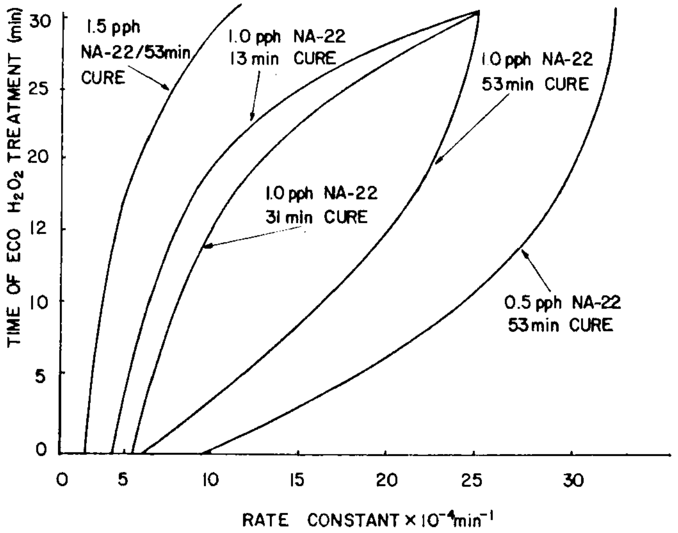


FIGURE 7 Dependence of hydrosilation rate constants on H_2O_2 treatment times for ECO compounds having different initial NA–22 concentration and cure times.

Figure 8 shows the "T" peel results in the form of $300P/T$°K plotted against $\log_{10} Ra_T/a_T 27$°C, where P is grams/cm peel force, 300 is the °K reference temperature, T°K is the test temperature, R is the rate of specimen separation and a_T is the correlation factor. The data from the ECO peel specimens (Tests 1, 4 and 5) having a 30-minute hydrogen peroxide ECO surface treatment prior to bonding, will be considered first. The specimens, having initially 0.5 p.p.h. NA–22 before ECO cure, gave the highest peel strengths, at any given temperature or rate, as compared to the peel strengths for the specimens initially containing 1.0 p.p.h. and 1.5 p.p.h. before ECO cure. The glass/rubber transition of the bond as gaged by the upswing of the curve was also higher than that for the specimens initially containing 1.0 p.p.h. NA–22. The data from the 1.0 p.p.h. and 1.5 p.p.h. NA–22 specimens differed only slightly, the 1.0 p.p.h. specimen had a higher bond strength but only a slightly

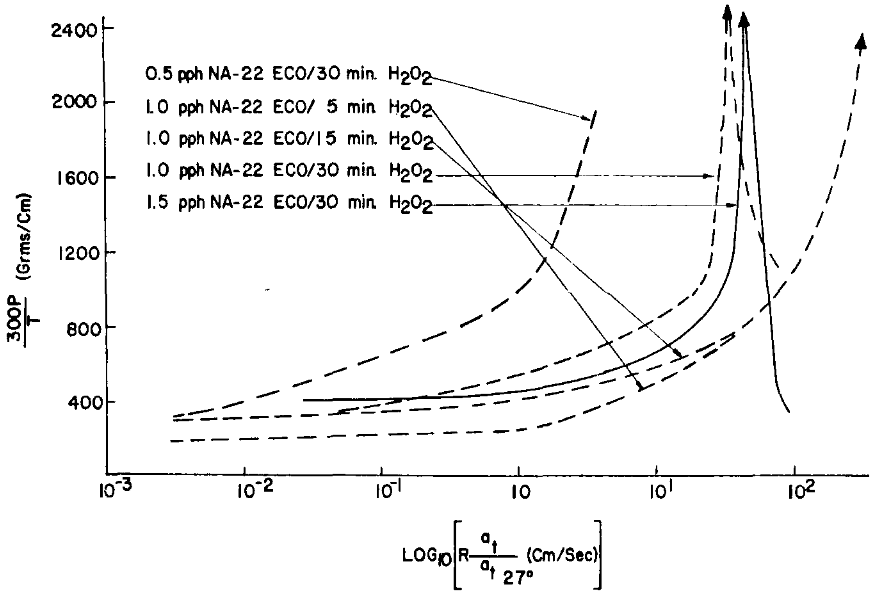


FIGURE 8 Rate–Temperature dependency of peel force for H_2O_2-treated ECO specimens having different initial inhibitor concentrations and oxidation treatment times.

higher glass–rubber transition compared to those of the 1.5 p.p.h. NA–22 specimens. The H_2O_2-treated, 1.5 p.p.h. NA–22 specimens exhibited surface RTV cure inhibition; thus, the 30-minute H_2O_2 surface treatment time was insufficient to oxidize enough residual NA–22 to prevent observable cure inhibition. No observable inhibition was detected in any of the 0.5 p.p.h. or 1.0 p.p.h. NA–22 specimens after the 30-minute hydrogen peroxide treatment.

Let us now consider the peel specimens initially containing 1.0 p.p.h. NA–22 in the ECO prior to curing. These ECO specimens were treated for

5, 15 and 30 minutes with 30 vol. % H_2O_2 prior to bonding (Tests 2, 3 and 4). The 5-minute, H_2O_2-treated peel specimens had the lowest bond strengths for any temperature or rate, but had the same glass–rubber transition as the 15-minute, H_2O_2-treated specimens. Except at a high temperature or low rate, the 30-minute H_2O_2-treated specimens had the highest bond strengths. They also had the highest glass–rubber transition. The difference between the glass–rubber transitions for the 15-minute and 30-minute H_2O_2-treated, 1.0 p.p.h. NA–22 specimens was greater than that between the 30-minute H_2O_2-treated 1.0 p.p.h. and 1.5 p.p.h. NA–22 specimens. Inhibited RTV polysiloxane was also observed in the 5- and 15-minute-treated 1.0 p.p.h. NA–22 specimens.

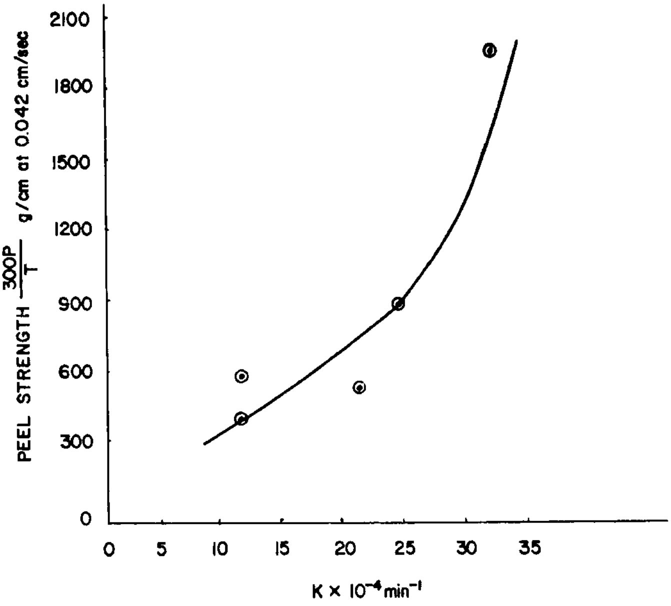


FIGURE 9 Correlation between residual peel strength and hydrosilation rate constant which is proportional to NA–22 poison content. The peel temperature was 300°K and the peel rate 0.042 cm/second.

On comparing the peel strength data to the data obtained by scanning electron microscopy, several generalizations can be made. The 0.5 p.p.h. NA–22 specimens had the highest peel strength and glass–rubber transition. Scanning electron photomicrographs of the ECO surface of these specimens before bonding showed no islands of NA–22, whereas the 1.0 p.p.h. NA–22 ECO surfaces showed some small islands of NA–22, especially after the 5-minute H_2O_2 treatment time. Therefore, low peel from specimens prepared from the latter condition is expected due to the islands of NA–22 which inhibit the RTV cure and introduce weak regions. This effect is increased with the 1.5 p.p.h. specimens due to the NA–22 islands becoming larger and more frequent so that even the 30-minute H_2O_2 treatment results in low peel strength and glass–rubber transition.

Finally, Figure 9 summarizes the correlation between residual NA–22 content, given by hydrosilation rate constants, and the peel strength for 300°K and 0.042 cm/second (1 inch/min) peel rate. For any initial NA–22 content the peel strength between ECO and the RTV polysiloxane increases with decreasing NA–22 content as given by an increase in the hydrosilation reaction rate constant. Thus, for good bond strength, no NA–22 should be present on the ECO surface to be bonded with the RTV hydrosilation-cured polysiloxane.

Looking back over this study, it is clear that an alternative solution to the poisoning problem exists; namely, one could increase the catalyst concentration. This is not practical economically, particularly since all one needs to do is apply a simple surface treatment to prevent cure inhibition. In this particular RTV system, the bulk adhesive is poisoned by the adherend surface alone. Presumably the poison must diffuse into the adhesive. This effect was observed but not quantified in our study. We should also point out that this type of poisoning problem also arises in polyester systems in which dimethyl methyl phosphonate (DMMP) is added to provide fire retardency. Cure inhibition results because the cobalt naphthenate, which is used as a free radical promoter with methyl ethyl ketone peroxide, is poisoned. The DMMP chelates with the cobalt preventing free radical generation at room temperature. In this case, an addition of excess promotor solves the problem and also provides a process control bonus.

CONCLUSIONS

Inhibition of hydrosilation-cure in an adhesive may be prevented by removing the inhibitor using methods such as surface oxidation of the adherend prior to bonding.

The resultant bond strength obtained from the polysiloxane adhesive after oxidation of the hydrosilation inhibitor correlated with the degree of hydrosilation-cure. Very little NA–22 was required to cure the ECO compounds and the residual surface amount of NA–22 was almost entirely removed by H_2O_2 treatment of the ECO surface prior to bonding with the polysiloxane adhesive.

References

1. George F. Schmitt, Jr., *Material Parameters that Govern the Rain Erosion Behavior of Polymer Coatings and Composites at Subsonic Velocities*, Technical Report AFMS-TR-197, December 1971.
2. E. B. Maxted, The poisoning of metallic catalysts, *Advances in Catalysis* **3** (1951).
3. R. Fountain and G. M. McLaughlin, United States Patent 3,749,617 (1973).
4. R. Fountain and J. L. Kardos, *High Temperature Elastomeric Bonding for Rain Erosion Boots*, presented at Rubber Convention, 1972, Institute of Rubber Industry, Brighton, United Kingdom, May 1972.
5. J. Weiss, The free radical mechanism in the reactions of hydrogen peroxide, *Advances in Catalysis* **4** (1952).
6. J. H. Baxendale, Decomposition of hydrogen peroxide by catalysts, *Advances in Catalysis* **4** (1952).
7. R. Fountain, Doctoral Thesis, Washington University, January 1973.
8. J. C. Watt, Silicone liquid rubbers, *Chemistry in Britain* **6** (12) (December 1970).
9. R. Fountain and J. L. Kardos (to be published).
10. R. Fountain and J. L. Kardos, *Polymer Letters* **12**, 161 (1974).
11. A. N. Gent and R. P. Petrich, *Proc. Roy. Soc.* (*London*) **A310**, 433 (1969).
12. A. N. Gent, *J. Polymer Sci.*, *A*-2 **9**, 283 (1971).
13. A. J. Chalk and J. F. Harrod, *J. Amer. Chem. Soc.* **87**, 16 (1965).