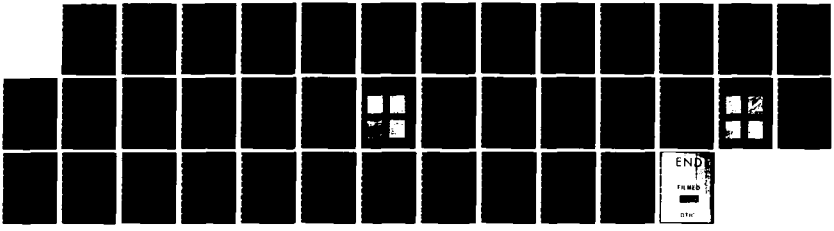
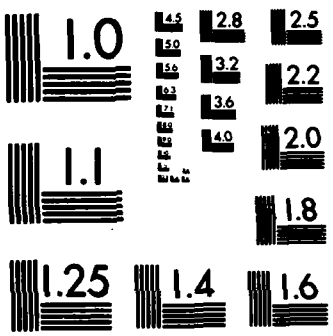
AD-A137 489 DURABILITY OF ADHESIVE BONDS BETWEEN GLASS OR METAL SUBSTRATES AND A POLYBUTADIENE-POLYURETHANE(U) AKRON UNIV OH INST OF POLYMER SCIENCE F LIANG ET AL. FEB 84 1/1

UNCLASSIFIED TR-31 N00014-76-C-0408 F/G 13/8 NL





MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

(12)

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: Technical Report -31	2. GOVT ACCESSION NO.: AD-A137489
3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle): Durability of Adhesive Bonds Between Glass or Metal Substrates and a Polybutadiene-Polyurethane	5. TYPE OF REPORT & PERIOD COVERED: Technical Report
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): F. Liang and P. Dreyfuss	8. CONTRACT OR GRANT NUMBER(s): N00014-76-C-0408
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Institute of Polymer Science, The University of Akron, Akron, Ohio 44325	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: NR 092-555
11. CONTROLLING OFFICE NAME AND ADDRESS: Office of Naval Research, Power Program, Arlington, VA 22217	12. REPORT DATE: February, 1984
	13. NUMBER OF PAGES: 35
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report): Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

According to attached distribution list.
Approved for public release; distribution unrestricted.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

DTIC ELECTE FEB 03 1984 S D E

18. SUPPLEMENTARY NOTES

J. Appl. Polym. Sci. (in press).

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

adhesion, aluminum, amine treatment, chrome steel, durability, interfacial ionic bonds, polyurethane, surface roughness, tertiary amine

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The durability of polybutadiene-polyurethane joints to glass or metals in water at room and elevated temperatures was studied. The effects of silane pretreatment of the surface and of surface morphology on adhesion were examined. The durability of the joint was related to the number of chemical bonds that could form between the polyurethane and the surface and to the type of surface treatment given to the surface. Proper treatment led to significant enhancement of durability of the joints. The polyurethane was prepared from ARCO's hydroxyterminated polybutadiene (R-45HT), toluene

AD A137489

DTIC FILE COPY

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

84 02 00 034

OFFICE OF NAVAL RESEARCH

Contract N00014-76-C-0408

Project NR 092-555

Technical Report No. 31

DURABILITY OF ADHESIVE BONDS BETWEEN GLASS OR METAL SUBSTRATES AND A POLYBUTADIENE-POLYURETHANE

BY

F. Liang and P. Dreyfuss

Institute of Polymer Science
The University of Akron
Akron, Ohio 44325

Accession For	
NTIS GRA&I	☒
DTIC TAB	☐
Unannounced	☐
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

February, 1984

Reproduction in whole or in part is permitted

for any purpose of the United States Government

Approved for Public Release; Distribution Unrestricted

Adhesives are being used increasingly in engineering applications. One problem frequently encountered is that the mechanical properties of the bond component rapidly deteriorates upon exposure of the joint to its normal operating environment. Water (moisture) is one of the most hostile and common environments to which adhesive joints are exposed. This paper is concerned with the durability of polyurethane joints subjected to wet climate conditions. In order to accelerate such exposure the joints were immersed in water at elevated temperature. The effect of silanes and surface morphology of etched substrates on joint durability was examined.

Experimental

Materials

The materials used were 3-aminopropyltriethoxysilane (AS), (γ-glycidoxypropyl)trimethoxysilane (GS), 3-chloropropyltrimethoxysilane (CS), and 3-mercaptopropyltrimethoxysilane (MS) from Petrarch Systems Inc.; TDI (80/20 mixture of 2,4- and 2,6-isomers of toluene diisocyanates) from BASF Wyandotte Corporation; Isonal-100 (N,N-bis-(2-hydroxylpropylaniline) from Upjohn Polymer Chemicals; MICRO laboratory cleaner from International Product Corp.; and hydroxy-terminated polybutadene resin (R-45HT) from ARCO Chemical Co. The properties of R-45HT were listed in earlier studies.[1]

Precleaned opticlear soda lime microscope slides (25 x 25 x 1.06 mm) were from KIMBLE. Mirror finish chrome ferro-type stainless steel places were from Appolo. The aluminum alloy was 300 3-H-14.

Preparation of Polyurethane

The polyurethane was prepared from hydroxyterminated polybutadiene (R-45HT), TDI and N,N-bis(2-hydroxypropyl) aniline. The ratio [-NCO]/total [-OH] was kept constant and equal to 1. 6% excess [-NCO] to hydroxyl number of R-45T was used. The equations for calculating the required amounts of diisocyanate and N,N-bis(2-hydroxypropyl) aniline and the procedure were the same as in previous studies[1].

Surface treatment of substrates

All amounts are in parts by weight unless otherwise stated.

Glass. Unabraded glass slides were heated at 140°C for 1 hr. and kept in a dessicator over $CaCl_2$ until treated with the desired reagent.

Surface abraded slides were ground with #600 aluminum oxide abrasive from BARNES Engineering Company, rinsed with distilled water, and immersed for 24 hrs. at room temperature in a mixture of MICRO laboratory cleaner with H_2O (50/50 by weight). The solution was heated to 90°C for 1 hr and then the slides were rinsed with distilled water, immersed in 90°C distilled water for 1 hr., rinsed with cold distilled water, dried at 140°C for 1 hr. and kept in a dessicator over $CaCl_2$.

Metals. Small plates (Approximately 75 x 25 x 1 mm) cut from the ferro-type plates were treated by one of four different methods before applying the chemical and elastomer layers:

1. Cleaned with petroleum ether or acetone and dried at 60°C for 40 minutes.
2. Cleaned as in 1; immersed for 10 minutes at 90°C in a solution

of concentrated hydrochloric acid (50 parts) and distilled water (50 parts); rinsed with cold distilled water; and dried at 60°C for 40 minutes.

3. Cleaned as in 1; immersed for 20 minutes at 80°C in a solution of oxalic acid (9 parts), sulfuric acid (1 part), and distilled water (80 parts); and rinsed and dried as in 2.
4. Cleaned as in 1; immersed at 70-75°C for 5 minutes in a solution of hydrochloric acid (83.3% by volume), phosphoric acid (12.5% by volume); and rinsed and dried as in 2.

The surfaces of aluminum plates of similar size were prepared by one of four methods:

5. Cleaned with petroleum ether and dried at 60°C for 40 minutes.
6. Abraded with fine sandpaper; and cleaned and dried as in 5.
7. Cleaned as in 5; immersed for 10 minutes in a 70°C solution of distilled water (30 parts), sulfuric acid (10 parts), sodium dichromate (1 part); and cleaned and dried as in 2.
8. Cleaned as in 5; immersed in 15% NaOH at 40°C for 5 minutes; rinsed with distlled water; and then method 7 without the petroleum ether step.

Application of silane solution

The silanes were applied at room temperature by immersing the substrates for 5 min. in a 0.5% by weight solution of the silane in a 50/50 mixture by volume of ethanol and water. Several drops of hydrochloric acid ($pH \sim 4$) as a catalyst for silane were added also except when the silane was AS. After removing the substrates from the silane solution, they were dried in air and then heated for 30 minutes at 100°C before applying the elastomer layer.

Application of elastomer layer and curing

For adhesion studies appropriately treated substrates were placed in a Teflon coated compression mold and the prepolymer containing the glycol was poured on. The top plate of the mold was covered with a sheet of washed, dried and pressed cotton cloth. The sample was cured at 100°C for 4 hrs. at 25 psi per 5 inch ram in a preheated PHI press. Rubber sheets were cured in a vertical mold in a Vacuum Oven at 100°C for 5 hrs.

Measurement of work of adhesion

180° peel tests were carried out on strips of cloth backed elastomer layer after trimming them to a uniform width of 2 cm. on the substrate. The cloth-backed elastomer layer was peeled off the substrate at a constant rate of 0.5 cm/min. The work of adhesion per unit area of interface W_A was calculated from the time average of the peel force P per unit width w of the detaching layer $W_A = 2P/w$.

Tensile tests

Tensile tests were carried out at room temperature and a cross head speed of 50 cm/min. using dumbbell specimens. Breaking elongation was calculated from the ratio $(L_b-L_o)/L_o$, where L_o and L_b were the initial length and the length at break, respectively.

Contact angle measurements

Contact angle measurements were carried out at room temperature with a contact angle goniometer manufactured by KERNCO Instrument Co. For each liquid five drops were placed on a substrate, and contact angle readings were taken from both left and

right sides of the liquid-air-solid interface. Readings were recorded at 10 and 20 minutes after the drops were placed on the substrate.

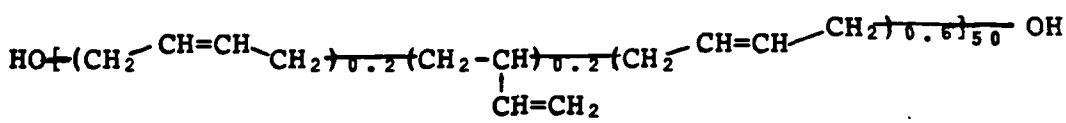
Electron microscopy

The electron microscopy was carried out with scanning electron microscope model JSM-U3.

Results and Discussion

Effect of water on bulk properties of polyurethane

According to ARCO hydroxyl terminated polybutadiene resin, R-45HT has the following chemical structure[2,3].



In contrast to the two principal classes of polyurethanes, from polyethers and from polyesters, the polyurethanes formed from polybd resin display certain properties and performance characteristics attributable to the hydrocarbon backbone. The most outstanding of these characteristics are outstanding low temperature properties and good hydrolytic stability. The glass transition temperature of the polyurethane derived from a prepolymer containing 6% Free NCO is about -65°C[1]. As shown in Fig. 1, when this polyurethane was immersed in distilled water at 70°C, the ultimate tensile strength σ_b, and the elongation at break, eb, decreased slightly with increasing immersion time. After soaking for 55 days at 70°C σ_b decreased by about 30%, while e_b decreased by about 25%.

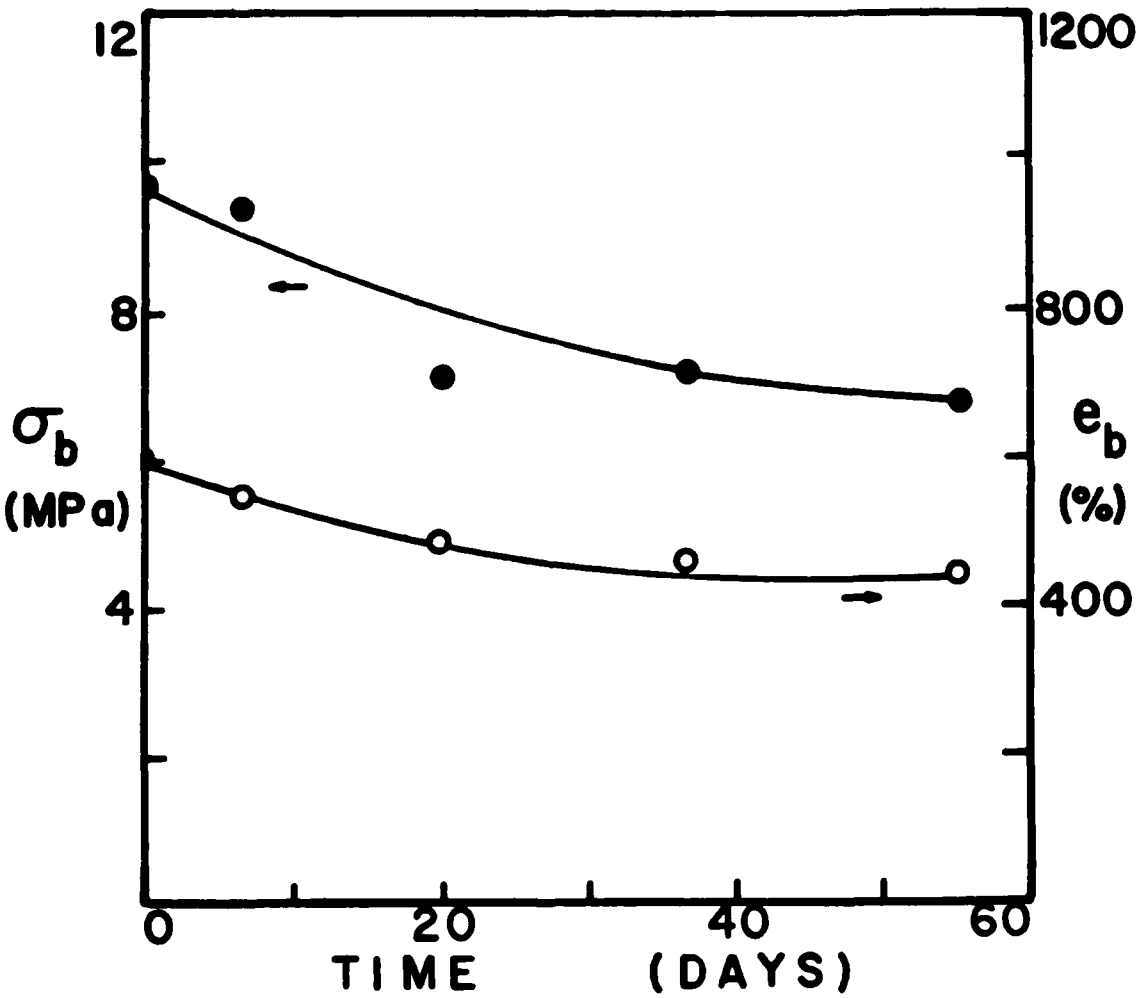
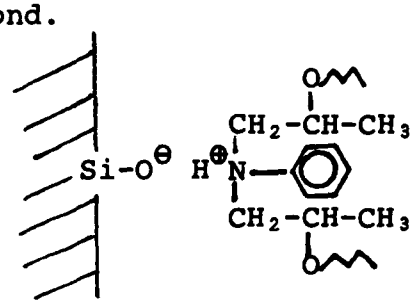


Fig. 1 - Effect of water on ultimate tensile strength (σ_b) and breaking elongation (e_b).

Adhesion of polyurethane to smooth glass surfaces

Warburg and Ihmori[4] recognized that glass surfaces, which have been exposed to room air, are covered by a water film. Infrared adsorption spectra of physically adsorbed water in porous silica show that the water is hydrogen bonded both intermolecularly and to hydroxyl groups on the silica surface[5]. When the polyurethane elastomer of this study is applied to a glass surface, the tertiary amine groups from the N,N-bis(2-hydroxypropyl)aniline in the back bone of the polyurethane can react with the acidic silanol groups present in the glass surface or perhaps even with surface moisture to form an ionic bond.



Our earlier studies indicated that high adhesion results. But as shown in Fig. 2 the work of adhesion fell dramatically, when glass/polyurethane peel test specimens were immersed in distilled water at room temperature. In order to improve the wet adhesion, glass slides were treated with AS, GS, or MS before applying the polyurethane. The dry adhesion increased remarkedly. At equivalent concentrations of silanes the order of enhancement in the work of adhesion was AS > MS > GS. Cohesive failure was observed for glass slides pretreated with AS and MS. As in our earlier studies, results can be explained in terms of the different structures of silanes[1,6-9] AS has two reactive hydrogen atoms that can react

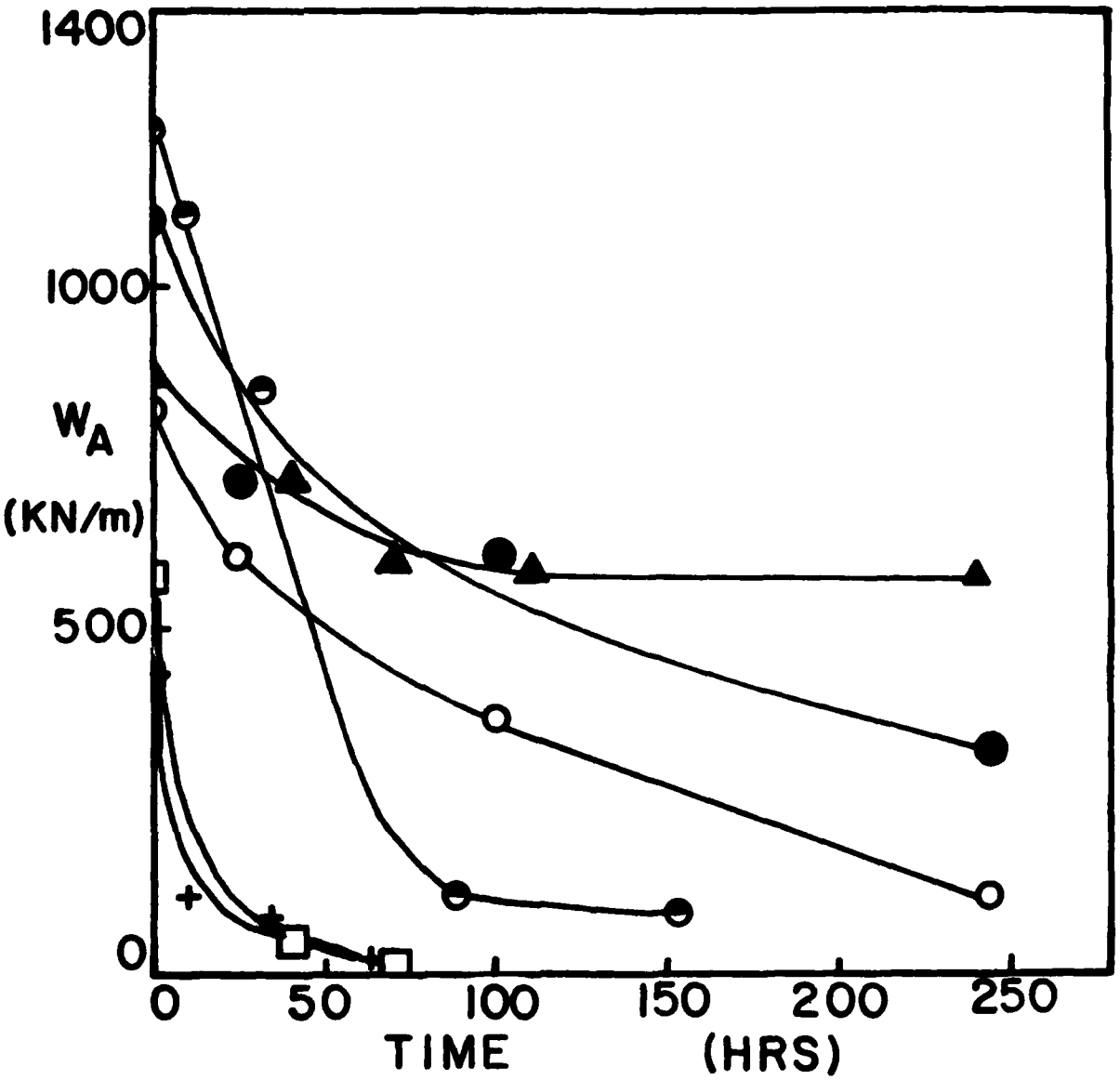
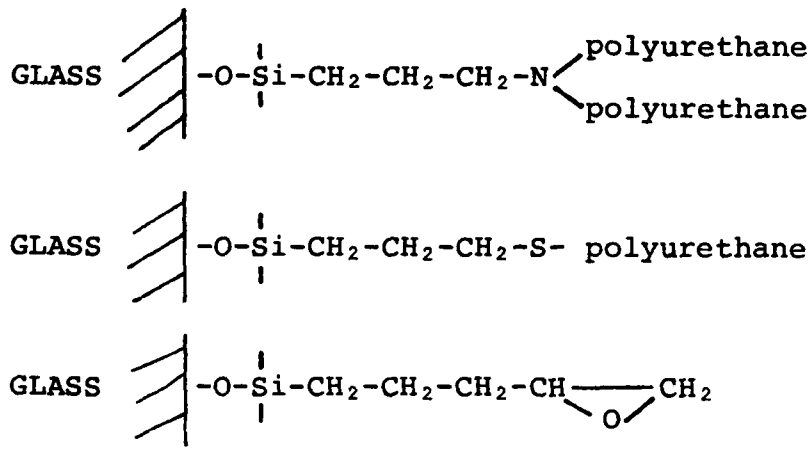


Fig. 2 - Effect of different treatments of glass surface on work of adhesion, W_A. ⊖ treated with AS, ● treated with MS, O treated with GS, ▲ abraded and treated with AS, □ abraded with #600 abrasive, + untreated.

with the -NCO group of the prepolymer, MS has just one reactive hydrogen atom and GS has none. The degree of enhancement of adhesion is related to the number of bonds that can form between the silane and polyurethane.



The glycidoxy group might react with the hydrogen atom that is present in the polyurethane backbone by a ring opening reaction but this reaction is much more difficult than the one between -NCO and -NH.

The wet adhesion was slightly improved for silane treated glass surfaces, but the durability of the joints still decreased considerably after soaking for several days. At equivalent concentrations of silane, the order of decrease in the work of adhesion was AS > GS > MS.

The polyurethane based on polybd resin R-45HT has good hydrolytic stability. Thus the losses in the work of adhesion after immersion in water must result from the adverse effect of

water on the interface rather than on the bulk properties of the polyurethane. Thermodynamic calculations indicate that if only secondary forces are acting across a glass/adhesive interface, water will virtually always desorb an organic adhesive from the glass surface[10]. In our experiments the presence of ionic bonds can result in markedly reduced adhesion in the presence of water, which would solvate the ionic clusters[11]. Also according to Plueddeman[12], a flexible polymer like polybutadiene cannot form water resistant bonds to a hydrophilic mineral surface even with added silane coupling agents. As individual siloxane bonds are hydrolyzed, the silanols retract from the surface and are no longer available for new bond formation. Water gradually interposes itself throughout the interface until adhesion is completely lost.

From our observations, it seems that silane coupling agents do not exclude water from the interface but somehow function to retain adhesion in the presence of water. As shown in Fig. 2 at equivalent concentrations of silane, the order of decrease in the work of adhesion was AS > GS > MS. With the GS or MS treated glass surface, a fully condensed polysiloxane has some polarity arising from the terminal epoxy or mercapto groups, but these groups do not usually take part in hydrogen bond formation. The cured material would not be expected to show highly polar interaction with water. In the case of AS, the terminal amine group has a strong tendency to absorb water by hydrogen bonding and that could

lead to bond rupture and the poorer wet adhesion, compared to GS or MS pretreated glass surfaces, observed for AS pretreated glass surfaces.

When AS treated glass slide samples were prepeeled to some extent, a thin layer of elastomer was left on the glass surface due to cohesive failure. Upon immersion in distilled water for several days, the adhesion between the thin layer and the glass' surface was completely lost but the thin layer remained firmly attached to the elastomer. The initial W_A of AS treated glass surfaces to the polyurethane was 1234 KN/M^2; after soaking for 155 hr in distilled water at room temperature the W_A became 88 KN/M^2. When the specimens were dried in vacuum at room temperature for 4 days, the W_A increased to 1000 KN/M^2. Similar partial recovery in strength of adhesive joints after drying has been reported previously for bonds between polyethylene and glass or steel[12] and between epoxy adhesives and aluminum[13]. Permanent loss in bond strength has been ascribed to covalent bond rupture[13] whereas recoverable loss in bond strength is variously attributed to reforming of hydrogen bonds[13] and an equilibrium of bonding and debonding in the presence of water[12]. In the present case strength recovery can be attributed to reformation of ionic bonds.

Adhesion of polyurethane to abraded glass surfaces

The durability studies of Gledhill and Kinloch support the conclusions reached above[14]. They conclude that in order to improve durability of adhesive joints to water either the water must be

prevented from reaching the interface or water resistant interfacial bonds must be formed. Formation of such bonds requires that special care should be taken to prepare the surface prior to joint preparation. Abrading a surface could be advantageous in two ways. First, the surface area would be increased and provide more sites for formation of chemical bonds. Second, a suitably abraded surface could provide sites for mechanical interlocking of the adhesive to the substrate. In the present study, grinding a glass surface with #600 abrasive from Barnes Engineering Company, gave high dry adhesion but had no effect on improving wet adhesion. (See Figure 2) If the ground glass surface was treated with AS before applying the polyurethane, the durability of the joint in the presence of water was much improved. Anchoring of the organic polymer in a rough surface improved dry adhesion but it was not effective at improving wet adhesion. When there were micropits along with an increased number of active chemical groups on the substrate surface as in the case of the AS pretreated ground glass surface, the wet adhesion was much improved.

Adhesion of chrome steel to polyurethane

Figures 3 and 4 show that after immersion in distilled water for several days the W_A of a petroleum ether cleaned chrome steel surface to polyurethane was decreased markedly. When the metal surface was pretreated with GS, CS, or MS, the treatments were similarly ineffective at improving the durability of the joints in water. (See Figure 3). Pretreatment

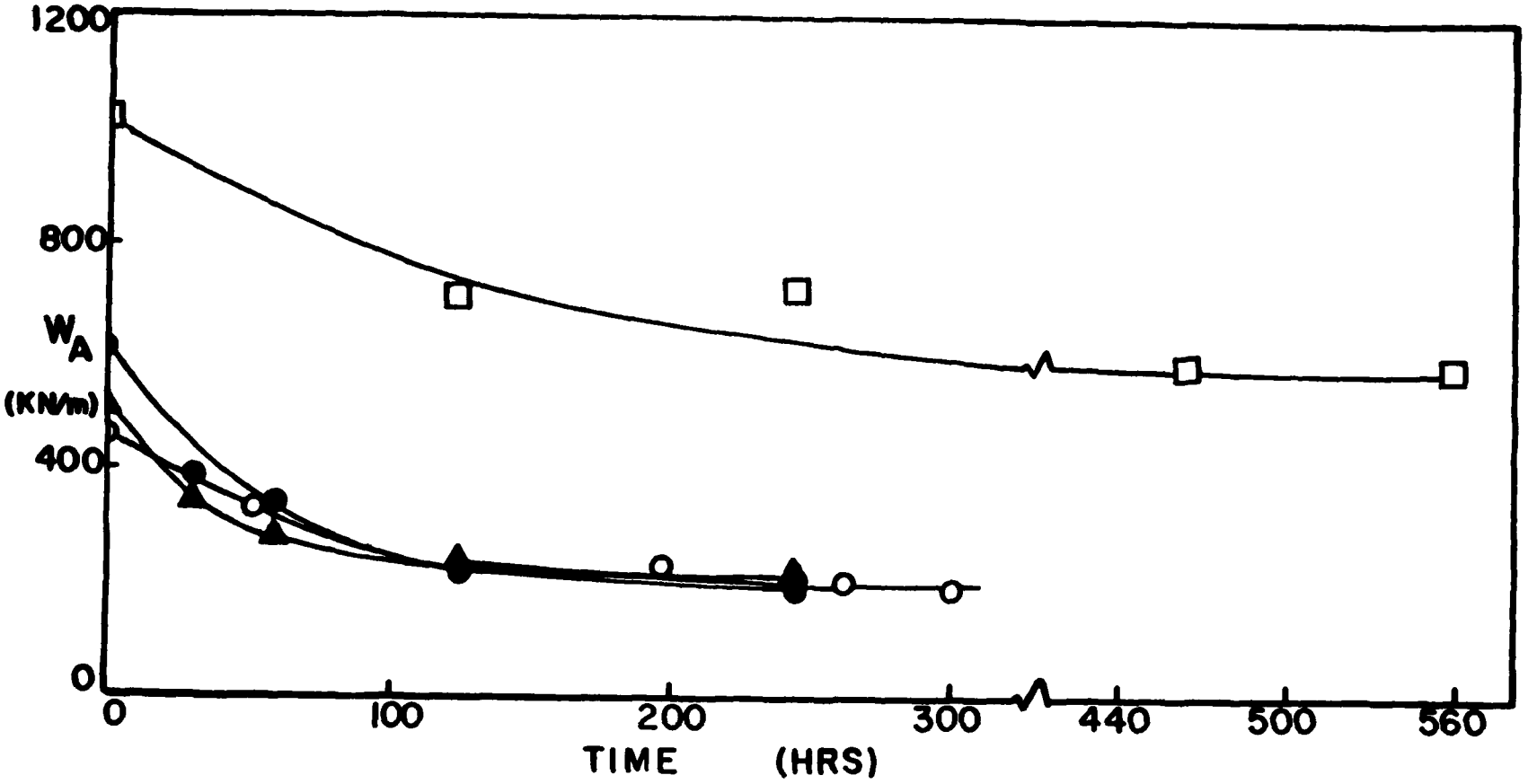


Fig. 3 - Effect of silane treatment of chrome steel surfaces on W_A.

□ treated with AS, ● treated with MS, O treated with GS,

▲ treated with CS.

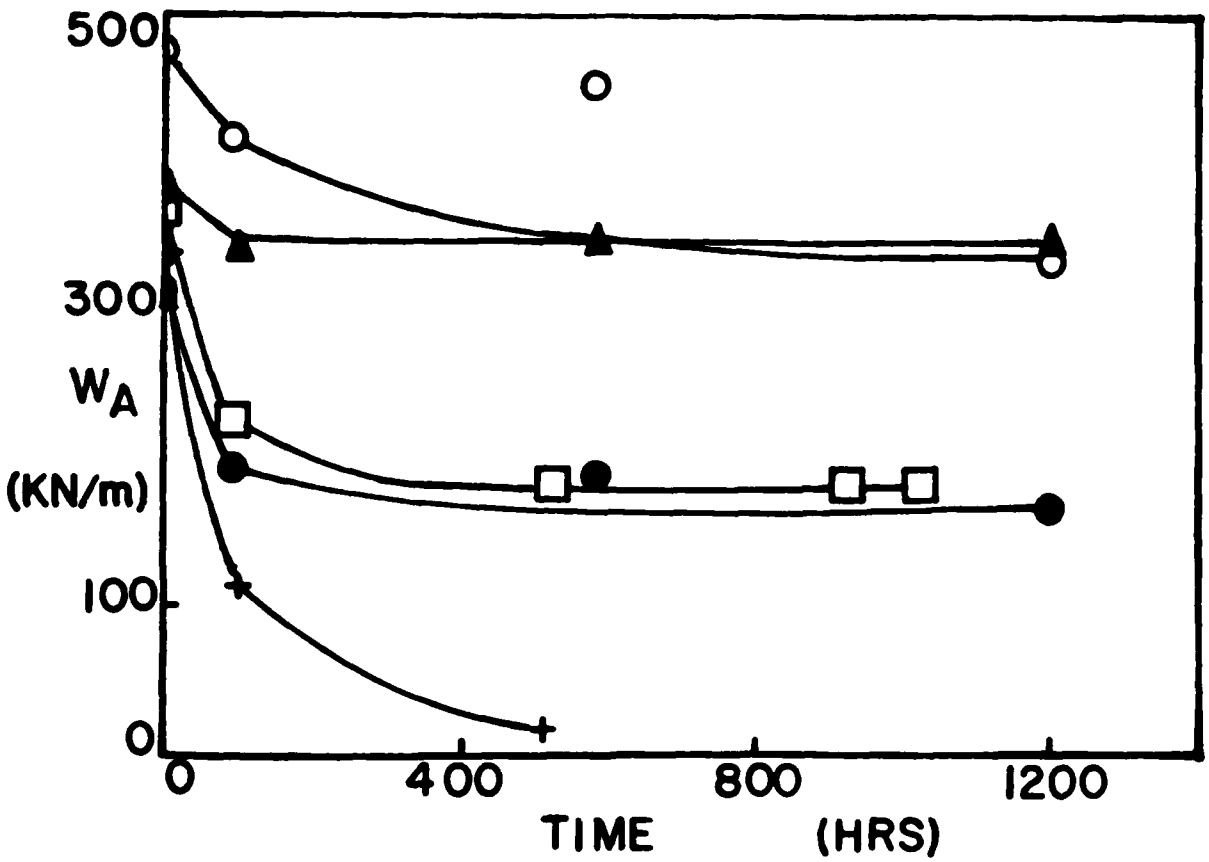


Fig. 4 - Effect of acid etching of chrome steel surface on W_A. O etched with $HCl \cdot HF \cdot H_3PO_4$ (method 4), ▲ etched with $H_2C_2O_4 \cdot H_2SO_4 \cdot H_2O$ (method 3) and treated with prepolymer containing 0.5% GS, □ etched with $H_2C_2O_4 \cdot H_2SO_4 \cdot H_2O$ (method 3), ● etched with $HCl \cdot H_2O$ (method 2), + cleaned with petroleum ether (method 1).

with AS was very effective. The AS treated chrome steel surface gave a high W_A, even after immersion in distilled water for 23 days; its W_A after 23 days was still higher than the initial W_A of surfaces pretreated with the other silanes. GS, MS, CS have less effect on the steel surface than AS. The amino group of the latter silane can be chemisorbed by metal oxide surfaces[15], and contribute to the high W_A observed.

The influence of chrome steel surface preparation

Surface preparation of substrates for joining adhesively plays a dominant and most important part in the reliability of the finished product. The prime purpose for surface preparation is to develop a bonding surface that will result in an optimum bond and provide the best service protection possible in the expected service environment.

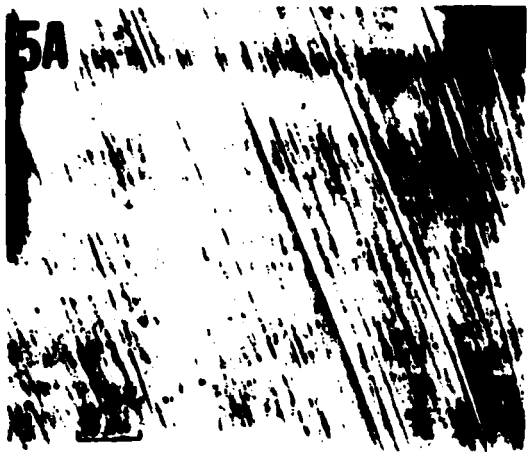
Etching. Chrome steel surfaces were subjected to the surface treatments 2, 3, and 4 described in the experimental section. The effect of different surface treatment on the work of adhesion W_A of a chrome surface to polyurethane is shown in Fig. 4. $HCl/HF/H_3PO_4$ treated chrome steel surface gave the highest W_A, HCl/H_2O and $H_2C_2O_4/H_2SO_4/H_2O$ treatment had similar effects on the W_A. Their wet adhesion was much improved compared to the unetched surface, probably as a result of mechanical interlocking of the

surface and the adhesive. In addition chemical treatment may have altered the surface to increase its free energy and make it more receptive to the adhesive. The usual result of chemical surface treatments of metals with acids in the presence of air is metal oxide formation[16].

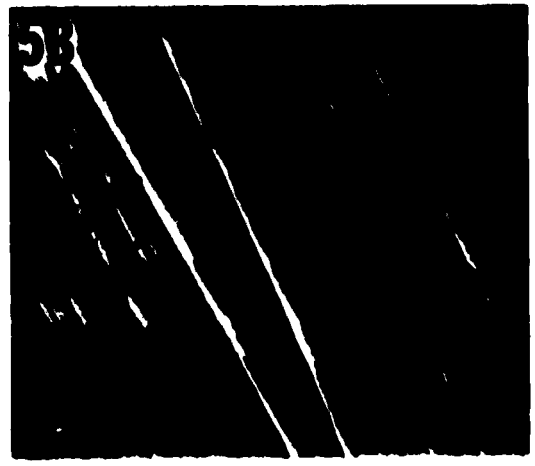
Experimental observations support the above conclusions. The morphology of the etched chrome steel surfaces is shown in Figure 5. As a result of acid etching, the surface profile was actually quite rough on a micro scale. $HCl/HF/H_3PO_4$ etching resulted in more micro etch pits than other treatments did. The $H_2C_2O_4/H_2SO_4/H_2O$ etched surface was smooth and micropit free. Probably the etching condition was too mild.

Chemical surface treatment not only produces micro etching pits but also increases the chemical polarity of the surface. Contact angles for water and glycerol on the etched metal surfaces are shown in Table 1. Chromium is resistant to the attack of a wide variety of chemicals at normal temperatures but it can react with many of these at elevated temperature[10,17].

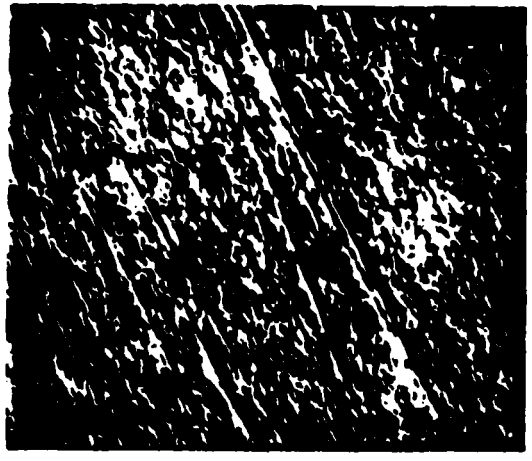
When the $H_2C_2O_4/H_2SO_4/H_2O$ treated surface was pretreated with GS before applying the elastomer, the wet adhesion was



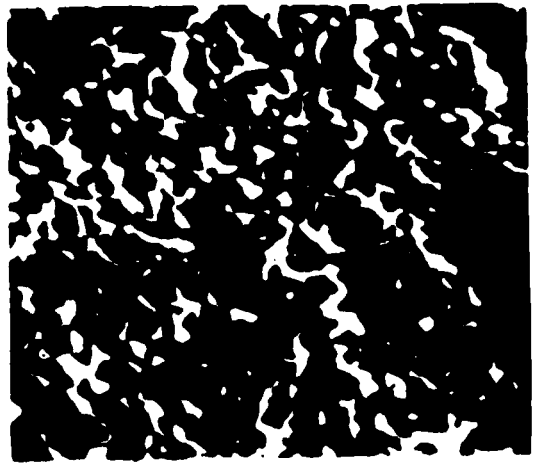
C_5H_{12}



$HCl \cdot H_2O$



$H_2C_2O_4 \cdot H_2SO_4 \cdot H_2O$



$HCl \cdot HF \cdot H_3PO_4$

Fig. 5 - Electronmicrographs of etched chrome steel surfaces.

TABLE I

Contact Angle on Metal Surfaces

Method of Surface Treatment	Contact Angle	
Chrome Steel	Water	Glycerol
Cleaned with petroleum ether	51	52
Etched with $HF \cdot HCl \cdot H_3PO_4$	31	55
Etched with $HCl \cdot H_2O$	28	54
Etched with $H_2C_2O_4 \cdot H_2SO_4 \cdot H_2O$	34	46
Aluminum		
Cleaned with petroleum ether	60	44
Etched with 15% NaOH	49	35
Etched with $Na_2CrO_4 \cdot H_2SO_4 \cdot H_2O$	50	28
Etched with 15% NaOH and $Na_2CrO_4 \cdot H_2SO_4 \cdot H_2O$	52	29

enhanced significantly. The reasons for the improvement are probably similar to those given above in the section dealing with silane treatment of glass surfaces.

Etching of chrome steel plus silane in the resin recipe. Silane coupling agents are usually applied to a substrate surface as a pretreatment from dilute aqueous solution. In this part of our study silane was added to the prepolymer at a concentration of 0.5g silane/100g prepolymer. The prepolymer containing silane and glycol was applied to a $HF/H_3PO_4/HCl$ etched chrome steel surface. The effect of different silanes of the work of adhesion is shown in Fig. 6. The durability of the joint in the presence of water was much improved. Even after immersion in distilled water for over two months, there was only a slight decrease in W_A. The improved durability is attributed to increasing the extent of covalent bond formation between silane and acid etched metal surfaces compared to unetched surfaces. Polyurethane containing 0.5% GS gave the highest W_A and that containing 0.5% MS provided the lowest W_A. Probably part of the MS was consumed by reaction of -SH with NCO. The $CH_2CH_2CH_2Cl$ group might to some extent form hydrogen bonds with the tertiary amine groups in the backbone of polyurethane, decrease the diffusion of GS into the interface, and result in the intermediate strength of adhesion.

The adhesion of aluminum to polyurethane

Aluminum is always covered with an oxide layer. The bonding interface of aluminum is not the metal itself but a variety of

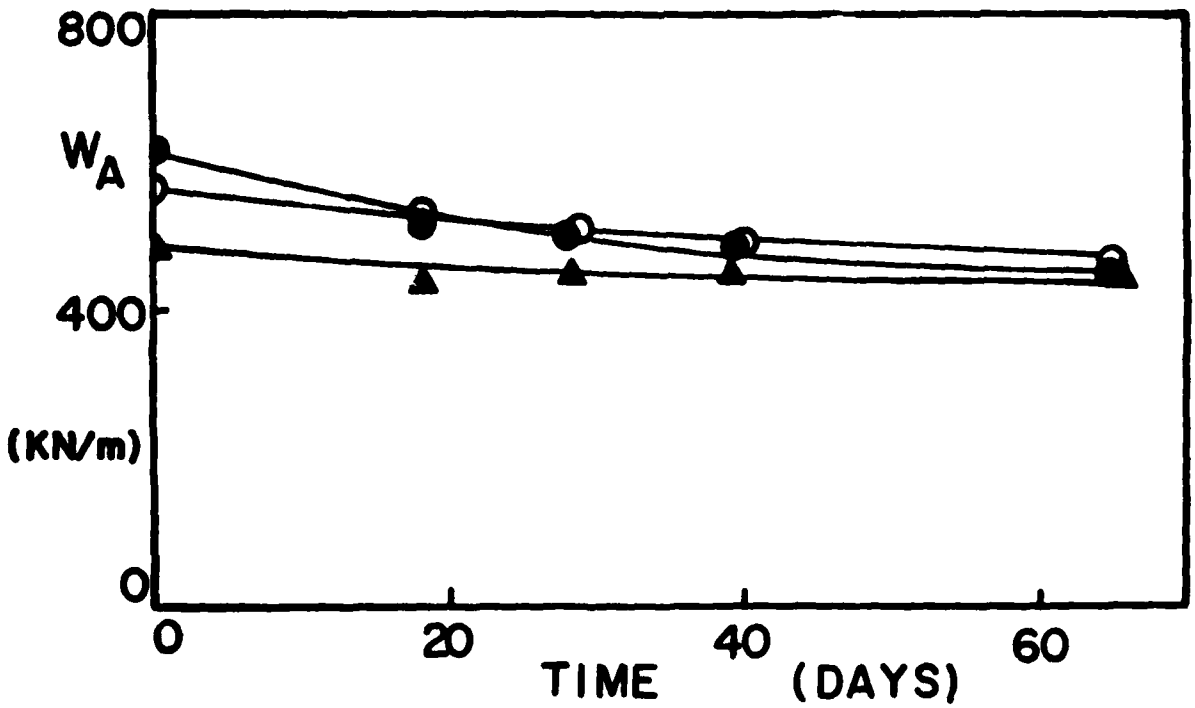


Fig. 6 - Effect of silane treatment of $HF \cdot HCl \cdot H_3PO_4$ etched chrome steel surfaces on W_A. ● treated with GS, O treated with CS, ▲ treated with MS.

aluminum oxide structures whose physical and chemical constitution can be altered through a variety of chemical procedures[10]. Bondability depends on the structure of the oxide layer. Water is absorbed on the surface of nonhydroscopic oxides like (Al_2O_3) as hydroxyl groups (∿M-OH) and as molecular water held by H-bonding to the surface hydroxyls.

Etching of aluminum. One of the methods to assess the quality of a pretreated surface is to make an adhesive joint. The work of adhesion, W_A, of different pretreated aluminum surfaces to polyurethane is shown in Fig. 7. Abraded aluminum surfaces gave high initial W_A, but during immersion in distilled water the rate of loss of W_A was similar to petroleum cleaned aluminum. Aluminum treated with aluminum surface treatment No. 8 gave much better wet adhesion than the others.

Figure 8 shows the change of morphology at different stages of pretreatment. The "as received" state of the aluminum surface is not structured but it is contaminated. After cleaning with petroleum ether the "clean" surface still has some loose particles (Fig. 8A). The alkaline degreased surface shows an irregular structure with pits and some loose particles on the surface (Fig. 8B). A Na_2CrO_4/H_2SO_4 etched surface gave a smooth etched surface with micro pits (Fig. 8C) and the alkaline cleaned-acid etched surface provided a concave, hilly micro morphology with oxide pits (Fig. 8D). In our experiments acid etching was influenced by alkaline precleaning. A smooth surface gave a low peel strength whilst a

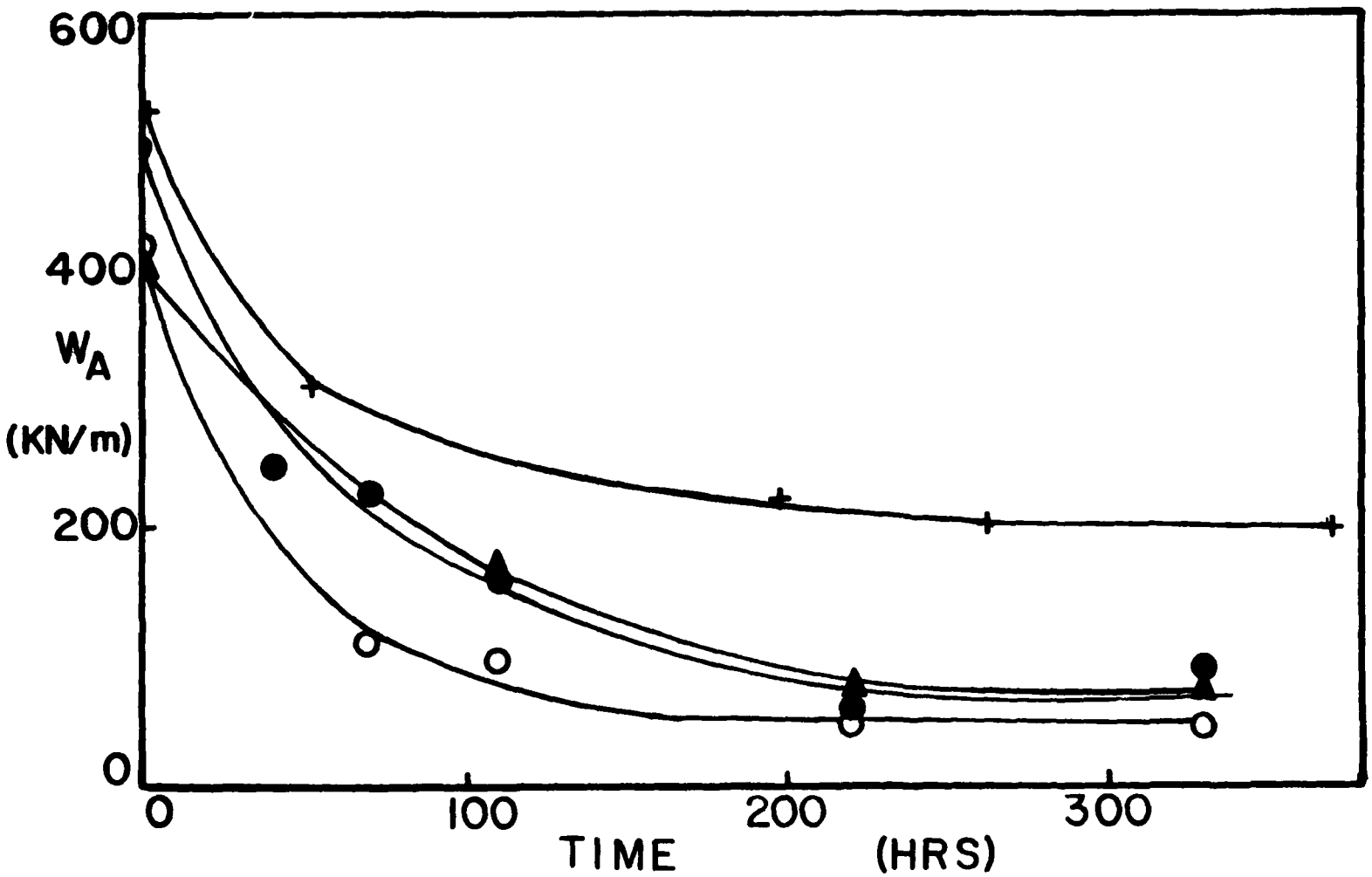
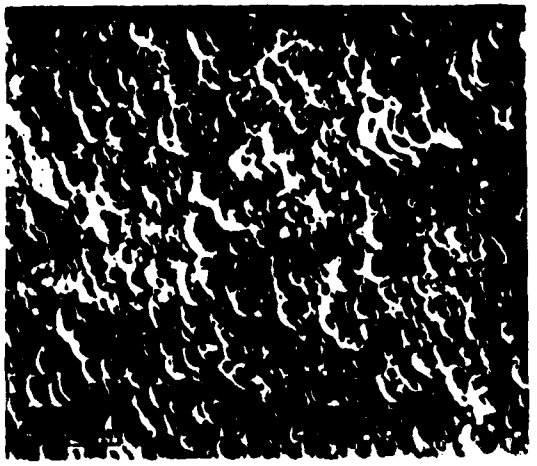
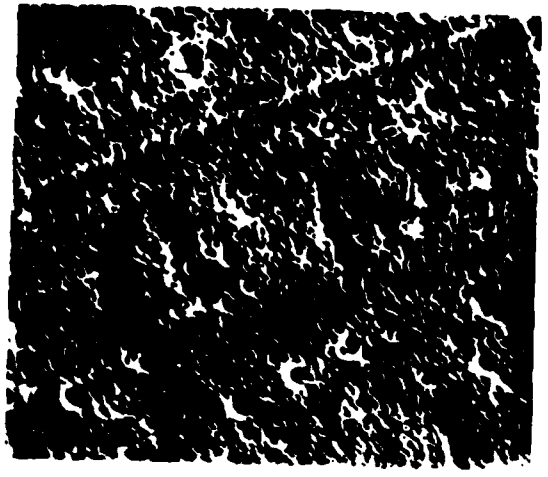


Fig. 7 - Effect of etching of aluminum on W_A + etched with 15% NaOH, $Na_2CrO_4 \cdot H_2SO_4 \cdot H_2O$ (method 8), ▲ etched with $Na_2Cr_2O_4 \cdot H_2SO_4 \cdot H_2O$ (method 7), ● brushed with sand paper (method 6), O cleaned with petroleum ether (method 5).

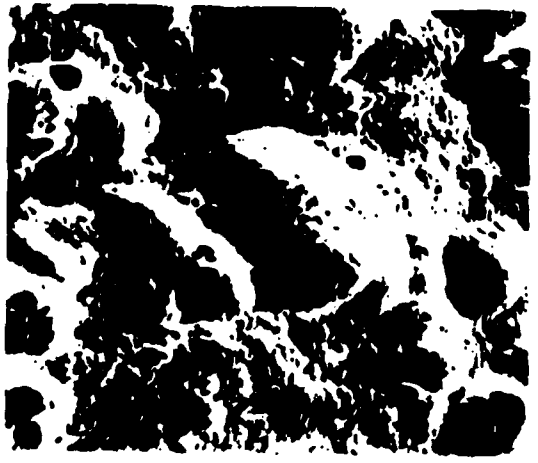
C_5H_{12}



15 % NaOH



$Na_2CrO_4 \cdot H_2SO_4 \cdot H_2O$



$NaOH,\ Na_2CrO_4 \cdot H_2SO_4 \cdot H_2O$

Fig. 8 - Electronmicrographs of surface aluminum at different stages of pretreatment.

microscopically rough surface provided high peel strength. It seems the anchoring of the adhesive plays an important role.

Acid etching plus silane pretreatment. Bond failure in the presence of water is due to adsorption of water on the aluminum surface. In order to improve the durability of bond strength, in the presence of water, acid etched aluminum surfaces were treated with 0.5% silane. The effect of different silanes on the work of adhesion, W_A, of aluminum to polyurethane is shown in Fig. 9. Their wet adhesion was much improved; even after immersion in 70°C distilled water for 264 hrs, W_A decreased just slightly. At equivalent concentrations of silane, the order of durability of bond strength in the presence of water was AS > MS > GS. Trialkoxysilane chemically bonds to polyurethane by reaction of the organic functional group such as $-NH_2$, -SH etc., with an -NCO group of the prepolymer and may form metalosiloxane bonds to the aluminum surface. The degree of durability of the adhesion bond is related to the number of bonds that can form between the silane and polyurethane.

Base cleaning plus acid etching plus silane pretreatment of aluminum. The influence of alkaline cleaning in addition to acid etching is given in Fig. 10. Alkaline cleaned-acid etched aluminum surfaces gave higher W_A's than just acid etched surfaces. Durability was also better. As before the reasons for the observed behavior probably include both improved mechanical interlocking and a greater number of interfacial covalent bonds.

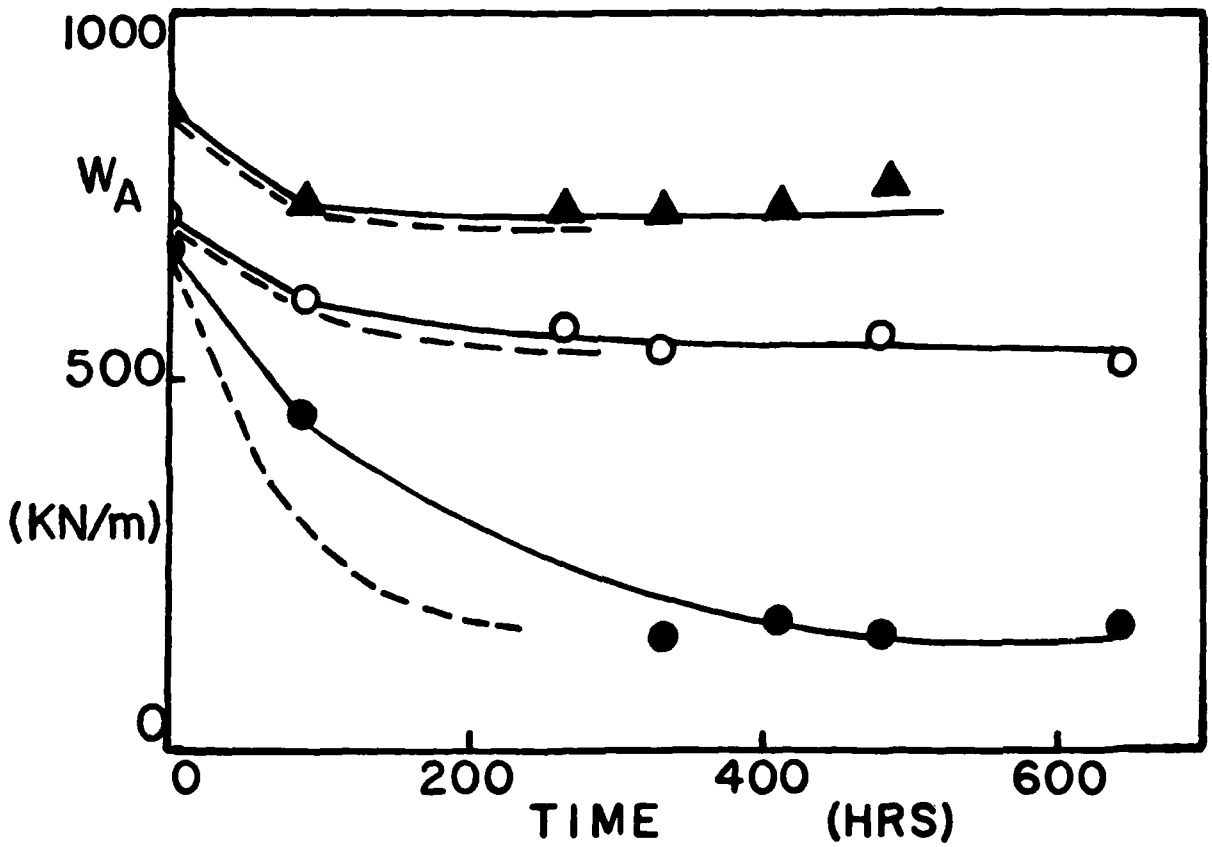


Fig. 9 - Effect on W_A of silane treatment on acid etched aluminum surfaces. ▲ treated with AS, O treated with MS, ● treated with GS. —— 25°C, --- 70°C.

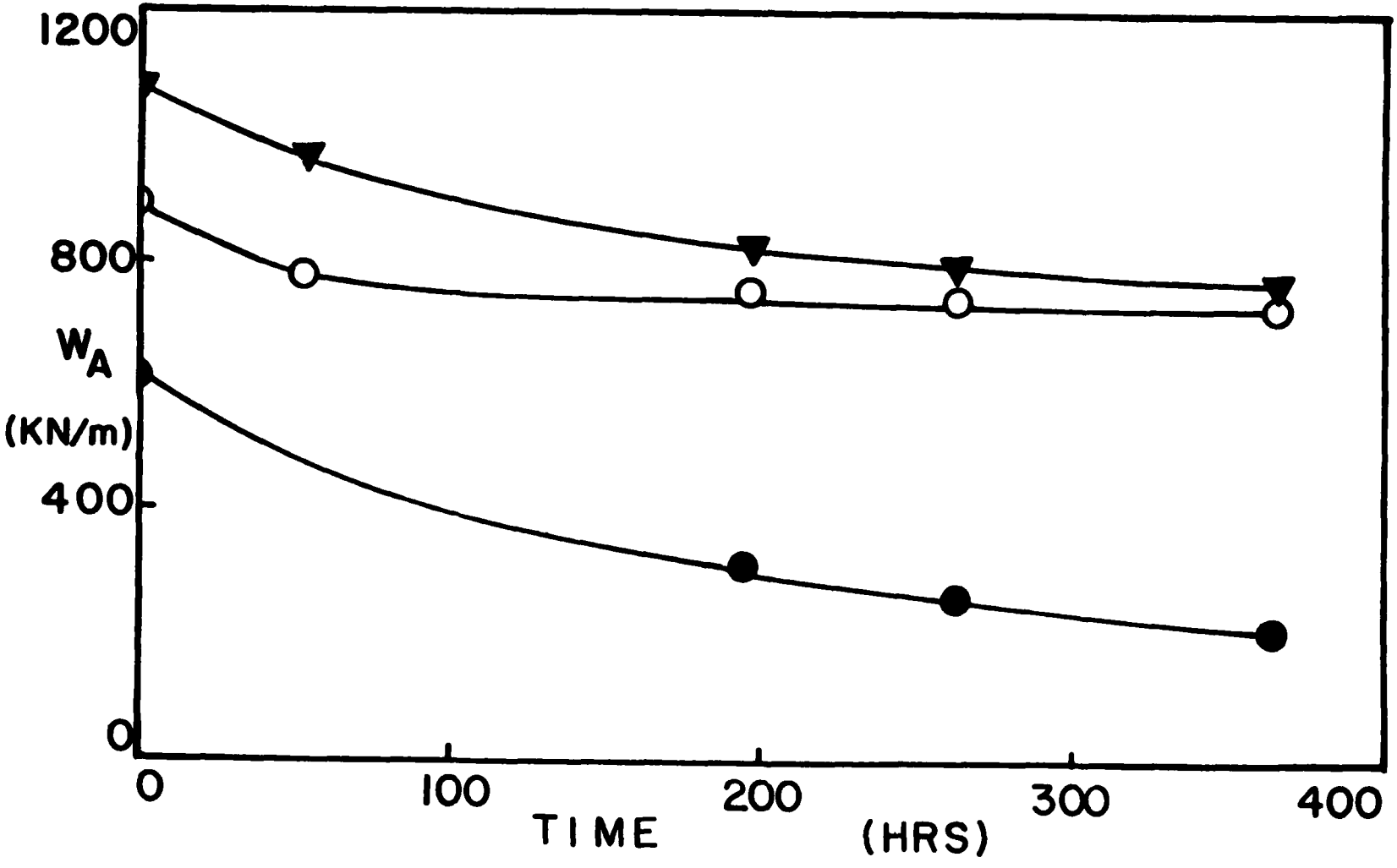


Fig. 10-Effect on W_A of silane treatment of NaOH cleaned and acid etched aluminum surfaces. ▲ treated with AS, O treated with MS, ● treated with GS.

Conclusion

The water durability of joints between glass or metal substrates and polyurethane can be greatly improved by proper surface preparation combined with the use of silane pretreatments. 3-Aminopropyltriethoxysilane is a very effective primer.

Acknowledgement

This work forms part of a program of research on the adhesion of elastomers supported by a research grant from the Office of Naval Research. One of us (F.L.) is grateful to the Education Ministry of the People's Republic of China for opportunity to carry out this work.

References

1. F. Liang and P. Dreyfuss, Organic Coatings and Applied Polymer Science Proceedings, 48, 18 (1983).
2. "Polybd^R liquid Resin in urethane elastomers", product bulletin B.D. 3, ARCO Chemical Co., October, 1974.
3. "Polybd^R resin", General Bulletin, ARCO Chemical Co., January, 1978.
4. E. Warburg and T. Ihmori, Ann. d. Phys. 27, 481 (1886).
5. T. H. Elmer in "Silylated Surfaces", D. E. Leyden and W. Collens, Eds., Gordon and Breach Science Publishers, N.Y., 1980, p. 11.
6. Y. Eckstein and P. Dreyfuss, J. Adhesion, 13, 303 (1982).
7. Y. Eckstein and P. Dreyfuss, J. Adhesion, 15, 163 (1983).
8. Y. Eckstein and P. Dreyfuss, J. Adhesion, 15, 179 (1983).

9. Y. Eckstein and P. Dreyfuss, J. Adhesion, 15, 193 (1983).

10. A. J. Kinloch, W. A. Dukes and R. A. Gledhill, in "Adhesion Science and Technology", L. H. Lee, Ed., Plenum Press, N.Y., N.Y. 1975, p. 597.

11. R. Rembaum, in "Advances in Urethane Science and Technology", 2, K. K. Frisch and S. L. Reegen, Eds, Technomic Pub. Co. Stanford, Conn., 1971, p. 109.

12. E. P. Plueddemann, J. Adhesion, 2, 184 (1970).

13. R. I. Butt and J. L. Cotter, J. Adhesion, 8, 11 (1976).

14. R. A. Gledhill and A. J. Kinloch, Adhesion, 1974, 315.

15. T. Furakawa, N. K. Eib, K. L. Mittal, H. R. Anderson, Jr., SIA Surf. Interface Anal., 4(6), 240 (1982).

16. C. V. Cagle, "Adhesive Bonding", McGraw Hill Book Co., N.Y., N.Y. 1968, p. 87.

17. J. C. Bailar, H. J. Emeléus, Sir Ronald Nyholm and A. F. Trotman-Dickenson, Eds., "Comprehensive Inorganic Chemistry", 3, Pergamon Press, distributed by Compendium Publishers, Elmsford, N.Y., 1973.

18. J. D. Minford, Adhesives Age, March, 1978, p. 17.

DISTRIBUTION LIST

	No. Copies
Dr. L.V. Schmidt Assistant Secretary of the Navy (R,E, and S) Room 5E 731 Pentagon Washington, D.C. 20350	1
Dr. A.L. Slafkosky Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Dr. Richard S. Miller Office of Naval Research Code 413 Arlington, VA 22217	10
Mr. David Siegel Office of Naval Research Code 250 Arlington, VA 22217	1
Dr. R.J. Marcus Office of Naval Research Western Office 1030 East Green Street Pasadena, CA 91106	1
Dr. Larry Peebles Office of Naval Research East Central Regional Office 666 Summer Street, Bldg. 114-D Boston, MA 02210	1
Dr. Phillip A. Miller Office of Naval Research San Francisco Area Office One Hallidie Plaza, Suite 601 San Francisco, CA 94102	1
Mr. Otto K. Heiney AFATL - DLDL Elgin AFB, FL 32542	1
Mr. R. Geisler ATTN: MKP/MS24 AFRPL Edwards AFB, CA 93523	1
Dr. F. Roberto Code AFRPL MKPA Edwards AFB, CA 93523	1
Dr. L.H. Caveny Air Force Office of Scientific Research Directorate of Aerospace Sciences Bolling Air Force Base Washington, D.C. 20332	1
Mr. Donald L. Ball Air Force Office of Scientific Research Directorate of Chemical Sciences Bolling Air Force Base Washington, D.C. 20332	1
Dr. John S. Wilkes, Jr. FJSRL/NC USAF Academy, CO 80840	1
Dr. R.L. Lou Aerojet Strategic Propulsion Co. P.O. Box 15699C Sacramento, CA 95813	1
Dr. V.J. Keenan Anal-Syn Lab Inc. P.O. Box 547 Paoli, PA 19301	1
Dr. Philip Howe Army Ballistic Research Labs ARRADCOM Code DRDAR-BLT Aberdeen Proving Ground, MD 21005	1
Mr. L.A. Watermeier Army Ballistic Research Labs ARRADCOM Code DRDAR-BLI Aberdeen Proving Ground, MD 21005	1
Dr. W.W. Wharton Attn: DRSMI-RKL Commander U.S. Army Missile Command Redstone Arsenal, AL 35898	1

DISTRIBUTION LIST

	No. Copies
Dr. R.G. Rhoades Commander Army Missile Command DRSMI-R Redstone Arsenal, AL 35898	1
Dr. W.D. Stephens Atlantic Research Corp. Pine Ridge Plant 7511 Wellington Rd. Gainesville, VA 22065	1
Dr. A.W. Barrows Ballistic Research Laboratory USA ARRADCOM DRDAR-BLP Aberdeen Proving Ground, MD 21005	1
Dr. C.M. Frey Chemical Systems Division P.O. Box 358 Sunnyvale, CA 94086	1
Professor F. Rodriguez Cornell University School of Chemical Engineering Olin Hall, Ithaca, N.Y. 14853	1
Defense Technical Information Center DTIC-DDA-2 Cameron Station Alexandria, VA 22314	12
Dr. Rocco C. Musso Hercules Aerospace Division Hercules Incorporated Alleghany Ballistic Lab P.O. Box 210 Washington, D.C. 21502	1
Dr. Ronald L. Simmons Hercules Inc. Eglin AFATL/DLDL Eglin AFB, FL 32542	1
Dr. E.H. Debutts Hercules Inc. Baccus Works P.O. Box 98 Magna, UT 84044	1
Dr. James H. Thacher Hercules Inc. Magna Baccus Works P.O. Box 98 Magna, UT 84044	1
Mr. Theordore M. Gilliland Johns Hopkins University APL Chemical Propulsion Info. Agency Johns Hopkins Road Laurel, MD 20810	1
Dr. R. McGuire Lawrence Livermore Laboratory University of California Code L-324 Livermore, CA 94550	1
Dr. Jack Linsk Lockheed Missiles & Space Co. P.O. Box 504 Code Org. 83-10, Bldg. 154 Sunnyvale, CA 94088	1
Dr. B.G. Craig Los Alamos National Lab P.O. Box 1663 NSP/DOD, MS-245 Los Alamos, NM 87545	1
Dr. R.L. Rabie WX-2, MS-952 Los Alamos National Lab. P.O. Box 1663 Los Alamos NM 37545	1
Dr. R. Rogers, WX-2 Los Alamos Scientific Lab. P.O. Box 1663 Los Alamos, NM 87545	1

DISTRIBUTION LIST

	No. Copies
Mr. R. Brown Naval Air Systems Command Code 330 Washington, D.C. 20361	1
Dr. H. Rosenwasser Naval Air Systems Command AIR-310C Washington, D.C. 20360	1
Mr. B. Sobers Naval Air Systems Command Code 03P25 Washington, D.C. 20360	1
Dr. L.R. Rothstein Assistant Director Naval Explosives Dev. Engineering Dept. Naval Weapons Station Yorktown, VA 23691	1
Dr. Lionel Dickinson Naval Explosive Ordnance Disposal Tech. Center Code D Indian Head, MD 20640	1
Mr. C.L. Adams Naval Ordnance Station Code PM4 Indian Head, MD 20640	1
Mr. S. Mitchell Naval Ordnance Station Code 5253 Indian Head, MD 20640	1
Dr. William Tolles Dean of Research Naval Postgraduate School Monterey, CA 93940	1
Naval Research Lab. Code 6100 Washington, D.C. 20375	1

	No. Copies
Dr. J. Schnur Naval Research Lab. Code 6510 Washington, D.C. 20375	1
Mr. R. Beauregard Naval Sea Systems Command SEA 64E Washington, D.C. 20362	1
Mr. G. Edwards Naval Sea Systems Command Code 62R3 Washington, D.C. 20362	1
Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, PA 19112	1
Dr. H.G. Adolph Naval Surface Weapons Center Code R11 White Oak Silver Spring, MD 20910	1
Dr. T.D. Austin Naval Surface Weapons Center Code R16 Indian Head, MD 20640	1
Dr. T. Hall Code R-11 Naval Surface Weapons Center White Oak Laboratory Silver Spring, MD 20910	1
Mr. G.L. Mackenzie Naval Surface Weapons Center Code R101 Indian Head, MD 20640	1
Dr. K.F. Mueller Naval Surface Weapons Center Code R11 White Oak Silver Spring, MD 20910	1

DISTRIBUTION LIST

	No. Copies
Mr. J. Murrin Naval Sea Systems Command Code 62R2 Washington, D.C. 20362	1
Dr. D.J. Pastine Naval Surface Weapons Cneter Code R04 White Oak Silver Spring, MD 20910	1
Mr. L. Roslund Naval Surface Weapons Center Code R122 White Oak, Silver Spring MD 20910	1
Mr. M. Stosz Naval Surface Weapons Center Code R121 White Oak Silver Spring, MD 20910	1
Dr. E. Zimmet Naval Surface Weapons Center Code R13 White Oak Silver Spring, MD 20910	1
Dr. D. R. Derr Naval Weapons Center Code 388 China Lake, CA 93555	1
Mr. Lee N. Gilbert Naval Weapons Center Code 3205 China Lake, CA 93555	1
Dr. E. Martin Naval Weapons Center Code 3858 China Lake, CA 93555	1
Mr. R. McCarten Naval Weapons Center Code 3272 China Lake, CA 93555	1

	No. Copies
Dr. A. Nielsen Naval Weapons Center Code 385 China Lake, CA 93555	1
Dr. R. Reed, Jr. Naval Weapons Center Code 388 China Lake, CA 93555	1
Dr. L. Smith Naval Weapons Center Code 3205 China Lake, CA 93555	1
Dr. B. Douda Naval Weapons Support Center Code 5042 Crane, Indiana 47522	1
Dr. A. Faulstich Chief of Naval Technology MAT Code 0716 Washington, D.C. 20360	1
LCDR J. Walker Chief of Naval Material Office of Naval Technology MAT, Code 0712 Washington, D.C. 20360	1
Mr. Joe McCartney Naval Ocean Systems Center San Diego, CA 92152	1
Dr. S. Yamamoto Marine Sciences Division Naval Ocean Systems Center San Diego, CA 91232	1
Dr. G. Bosmajian Applied Chemistry Division Naval Ship Research & Development Center Annapolis, MD 21401	1
Dr. H. Shuey Rohn and Haas Company Huntsville, Alabama 35801	1

DISTRIBUTION LIST

	No. Copies
Dr. J.F. Kincaid Strategic Systems Project Office Department of the Navy Room 901 Washington, D.C. 20376	1
Strategic Systems Project Office Propulsion Unit Code SP2731 Department of the Navy Washington, D.C. 20376	1
Mr. E.L. Throckmorton Strategic Systems Project Office Department of the Navy Room 1048 Washington, D.C. 20376	1
Dr. D.A. Flanigan Thiokol Huntsville Division Huntsville, Alabama 35807	1
Mr. G.F. Mangum Thiokol Corporation Huntsville Division Huntsville, Alabama 35807	1
Mr. E.S. Sutton Thiokol Corporation Elkton Division P.O. Box 241 Elkton, MD 21921	1
Dr. G. Thompson Thiokol Wasatch Division MS 240 P.O. Box 524 Brigham City, UT 84302	1
Dr. T.F. Davidson Technical Director Thiokol Corporation Government Systems Group P.O. Box 9263 Ogden, Utah 84409	1
Dr. C.W. Vriesen Thiokol Elkton Division P.O. Box 241 Elkton, MD 21921	1
Dr. J.C. Hinshaw Thiokol Wasatch Division P.O. Box 524 Brigham City, Utah 83402	1
U.S. Army Research Office Chemical & Biological Sciences Division P.O. Box 12211 Research Triangle Park NC 27709	1
Dr. R.F. Walker USA ARRADCOM DRDAR-LCE Dover, NJ 07801	1
Dr. T. Sinden Munitions Directorate Propellants and Explosives Defence Equipment Staff British Embassy 3100 Massachusetts Ave. Washington, D.C. 20008	1
LTC B. Loving AFROL/LK Edwards AFB, CA 93523	1
Professor Alan N. Gent Institute of Polymer Science University of Akron Akron, OH 44325	1
Mr. J. M. Frankle Army Ballistic Research Labs ARRADCOM Code DRDAR-BLI Aberdeen Proving Ground, MD 21005	1

DISTRIBUTION LIST

	No. Copies
Dr. Ingo W. May Army Ballistic Research Labs ARRADCOM Code DRDAR-BLI Aberdeen Proving Ground, MD 21005	1
Professor N.W. Tschoegl California Institute of Tech Dept. of Chemical Engineering Pasadena, CA 91125	1
Professor M.D. Nicol University of California Dept. of Chemistry 405 Hilgard Avenue Los Angeles, CA 90024	1
Professor A. G. Evans University of California Berkeley, CA 94720	1
Professor T. Litovitz Catholic Univ. of America Physics Department 520 Michigan Ave., N.E. Washington, D.C. 20017	1
Professor W. G. Knauss Graduate Aeronautical Lab California Institute of Tech. Pasadena, CA 91125	1
Professor Edward Price Georgia Institute of Tech. School of Aerospace Engin. Atlanta, Georgia 30332	1
Dr. Kenneth O. Hartman Hercules Aerospace Division Hercules Incorporated P.O. Box 210 Cumberland, MD 21502	1
Dr. Thor L. Smith IBM Research Lab D42.282 San Jose, CA 95193	1

	No. Copies
Dr. J. P. Marshall Dept. 52-35, Bldg. 204/2 Lockheed Missile & Space Co. 3251 Hanover Street Palo Alto, CA 94304	1
Ms. Joan L. Janney Los Alamos National Lab Mail Stop 920 Los Alamos, NM 87545	1
Dr. J. M. Walsh Los Alamos Scientific Lab Los Alamos, NM 87545	1
Professor R. W. Armstrong Univ. of Maryland Department of Mechanical Eng. College Park, MD 20742	1
Prof. Richard A. Reinhardt Naval Postgraduate School Physics & Chemistry Dept. Monterey, CA 93940	1
Dr. R. Bernecker Naval Surface Weapons Center Code R13 White Oak, Silver Spring, MD 20910	1
Dr. M. J. Kamlet Naval Surface Weapons Center Code R11 White Oak, Silver Spring, MD 20910	1
Professor J. D. Achenbach Northwestern University Dept. of Civil Engineering Evanston, IL 60201	1
Dr. N. L. Basdekas Office of Naval Research Mechanics Program, Code 432 Arlington, VA 22217	1
Professor Kenneth Kuo Pennsylvania State Univ. Dept. of Mechanical Engineering University Park, PA 16802	1

DISTRIBUTION LIST

	No. Copies
Dr. S. Sheffield Sandia Laboratories Division 2513 P.O. Box 5800 Albuquerque, NM 87185	1
Dr. M. Farber Space Sciences, Inc. 135 Maple Avenue Monrovia, CA 91016	1
Dr. Y. M. Gupta SRI International 333 Ravenswood AVenue Menlo Park, CA 94025	1
Mr. M. Hill SRI International 333 Ravenswood Avenue Menlo Park, CA 94025	1
Professor Richard A. Schapery Texas A&M Univ. Dept of Civil Engineering College Station, TX 77843	1
Dr. Stephen Swanson Univ. of Utah Dept. of Mech. & Industrial Engineering MEB 3008 Salt Lake City, UT 84112	1
Mr. J. D. Byrd Thiokol Corp. Huntsville Huntsville Div. Huntsville, AL 35807	1
Professor G. D. Duvall Washington State University Dept. of Physics Pullman, WA 99163	1
Prof. T. Dickinson Washington State University Dept. of Physics Pullman, WA 99163	1
ONR Resident Representative Ohio State University Res. Ctr. 1314 Kinnear Road Columbus, OH 43212	1

END

FILMED

02-84

DTIC