

POLYURETHANE TO THE SURFACE(U) AKRON UNIV OH 44325
POLYMER SCIENCE F LIANG ET AL. DEC 83 TR-29

CLASSIFIED

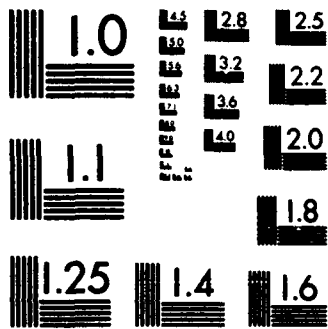
N00014-76-C-8488

F/G 11/1

| | | | | | | | | | | | | | | | | | | | | |
|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|
| | | | | | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | | | | |

END
X
etc

CONT



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 29 | 2. GOVT ACCESSION NO. | 3. RECIPIENT'S CATALOG NUMBER |
| 4. TITLE (and Subtitle) Effect of Amine Surface Treatment on the Adhesion of a Polyurethane to the Surface | | 5. TYPE OF REPORT & PERIOD COVERED Technical Report |
| 7. AUTHOR(s) F. Liang and P. Dreyfuss | | 6. PERFORMING ORG. REPORT NUMBER |
| 8. PERFORMING ORGANIZATION NAME AND ADDRESS Institute of Polymer Science The University of Akron Akron, Ohio 44325 | | 8. CONTRACT OR GRANT NUMBER(s) N00014-76-C-0408 |
| 11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Power Program Arlington, VA 22217 | | 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 092-555 |
| 14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) | | 12. REPORT DATE December, 1983 |
| | | 13. NUMBER OF PAGES 25 |
| | | 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) | | |
| 18. SUPPLEMENTARY NOTES "Adhesive Chemistry - Developments and Trends", L.-H. Lee, Ed., Plenum Press (in press). | | |
| 19. KEY WORDS (Continue on reverse side if necessary and identify by block number) adhesion, amine treatment, chrome steel, glass, polyurethane, tertiary amine | | |
| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number) → Amines in general and 3-aminopropyltriethoxysilane in particular were shown to improve the adhesion of a polyurethane to glass. At equivalent concentrations of amine in the solutions used to treat the glass the order of increase in the work of adhesion was 3-aminopropyltriethoxysilane >> 1,4-diaminobutane & p-phenylenediamine > piperazine >> aniline. The polyurethane was prepared from ARCO's hydroxyterminated polybutadiene, R-45HT, toluene diisocyanate, trimethylolpropane and N,N-bis(2-hydroxypropyl)aniline. The ratio $([-NCO]/[total\ OH])$ was kept constant and equal to 1.0. The swelling | | |

AD-A135591

DTIC ELECTE
S DEC 08 1983
E

DD FORM 1473 EDITION OF 1 NOV 68 IS OBSOLETE
1 JAN 73 S/N 0102-LF-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

DTIC FILE COPY

88 12 08 003

ratio, after curing, also remained constant. As the -NCO content compared to polymer-OH increased, the adhesion of the polyurethane to glass increased initially, passed through a maximum for prepolymers with 6% excess NCO, and then decreased again. Elongation at break behaved similarly but ultimate tensile strength reached a maximum and then stayed constant. The significance of these results is discussed. Adhesion of the polyurethane to chrome-plated steel did not show similar effects.

OFFICE OF NAVAL RESEARCH
Contract N00014-76-C-0408
Project NR 092-555

Technical Report No. 29

FRACTURE MECHANICS APPLIED TO ELASTOMERIC COMPOSITES

by

F. Liang and P. Dreyfuss

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

| | |
|--------------------|-------------------------------------|
| Accession For | |
| NTIS GRA&I | <input checked="" type="checkbox"/> |
| DTIC TAB | <input type="checkbox"/> |
| Unannounced | <input type="checkbox"/> |
| Justification | |
| By _____ | |
| Distribution/ | |
| Availability Codes | |
| Dist | Avail and/or Special |
| A-1 | |



December, 1983

Reproduction in whole or in part is permitted
for any purpose of the United States Government

Approved for Public Release; Distribution Unrestricted

EFFECT OF AMINE SURFACE TREATMENT ON
THE ADHESION OF A POLYURETHANE TO THE SURFACE

Fasi Liang and Patricia Dreyfuss

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

INTRODUCTION

This paper is a continuation of our investigation of the role amines play in adhesion. The overall investigation originated in repeated observations by ourselves and others that the presence of amine groups at an interface between a substrate and an adherend has a positive effect on the adhesion between the substrate and the adherend¹⁻⁴. In filled systems, mechanical properties compared to filled systems where the amines are absent are enhanced also. Previous work by Eckstein and Dreyfuss⁴⁻⁸ on peroxide cured bulk polybutadiene systems revealed both that the improvement in properties can be explained by the formation of chemical bonds through the amine group between the surface and the polymer and that the degree of improvement is related to the structure of the amine used.

In some applications of interest to us, notably solid fuel rocket propellants, polybutadiene is used as the soft segment of a polyurethane rather than as bulk polymer. Hence, our studies of the role of amines in adhesion have been extended to include systems with polyurethanes derived from functionalized liquid polybutadiene.

In polyurethane synthesis, amines are used both as chain extenders and as curing agents. The chemical reactions that occur and the products that form are well known⁹⁻¹¹. The questions that this study addressed were two. How does the structure of the amine used affect the adhesive properties of the resulting polyurethane and how can the observed effects be explained? This paper describes the synthesis and characterization of a new elastomeric polyurethane that shows remarkably high adhesion to glass and other substrates. A positive effect of amine surface treatment of the substrates on the adhesion of the polyurethane to the substrates is also reported. The results are interpreted in terms of the structure of the amines and of the polyurethane formed.

EXPERIMENTAL

Materials


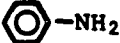
The materials used were: 1,4-diaminobutane, anhydrous piperazine *p*-phenylenediamine, and 2-ethyl- 2-(hydroxymethyl)-1,3-propanediol from Aldrich Chemical Company, Inc.; aniline ("Baker Analyzed" Reagent) from J. T. Baker Chemical Co.; 3-aminopropyltriethoxysilane from Petrarch Systems Inc.; TDI (80/20 mixture of 2,4 and 2,6 isomers of toluene diisocyanates) from BASF Wyandotte Corporation; Isonol-100 (N,N-bis-(2-hydroxypropyl)aniline) from Upjohn Polymer Chemicals; and hydroxyterminated polybutadiene resin (R-45HT) from ARCO Chemical Co. ARCO lists the properties given in Table 1 for the latter resin.

Table 1. Properties of ARCO's R-45HT

| | | |
|----------------------|-------------|---------------|
| Nonvolatile Material | wt% | 99.9 |
| Viscosity | poise 30°C | 50 |
| Hydroxyl Value | meq/gm | .083 |
| Molecular Weight | No. Average | 2800 |
| Moisture | wt. % | 0.05 |
| Iodine Number | | 398 |
| Trans-1,4 | 60%, | Cis-1,4 20%, |
| | | Vinyl-1,2 20% |

The amines were the same as those used in earlier studies⁴⁻⁸. Their properties are given in Table 2.

Table 2. List of Amines Used in Experiments

| Amine | Structure | b.p. (°C) | m.p. (°C) | Symbol |
|------------------------------|-------------------------------------------------------------------------------------|-----------|-----------|--------|
| 1,4-diaminobutane | $\text{NH}_2(\text{CH}_2)_4\text{NH}_2$ | 159 | 27 | AB |
| Piperazine |  | 145 | 109 | P |
| Aniline |  | 184 | -6.3 | A |
| <i>p</i> -Phenylenediamine | $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{NH}_2$ | 267 | 140 | PDA |
| 3-Aminopropyltriethoxysilane | $\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{OEt})_3$ | 122/30mm | | AS |

Preparation of Polyurethane

The polyurethane was prepared from ARCO's hydroxyterminated polybutadiene (R-45HT), toluene diisocyanate (TDI), trimethylolpropane and N,N-bis(2-hydroxypropyl)aniline using a slightly modified two stage procedure from that described by ARCO^{12,13}. The ratio $[-NCO]/[total\ OH]$ was kept constant and equal to 1.0 but the ratio $[-NCO]$ to hydroxyl number of R-45HT was varied in some experiments. For adhesion studies, a 6% excess $[-NCO]$ to hydroxyl number of R-45HT was used. The ratio of the substituted aniline to the triol was about 10 to 1 in most experiments. In one series, the latter ratio was varied.

The following equations were used to calculate the required amounts of diisocyanate and hydroxyl compounds.

- a) Amount of the TDI for selected % free isocyanate in first stage:

$$\frac{\text{Wt of TDI}}{100\text{g polybd}} = \frac{100(\text{Equiv. Wt of TDI})}{(\text{Equiv. Wt of polybd})} \times$$

$$\frac{100(\text{Equiv Wt of NCO}) + (\text{Equiv Wt of polybd}) (\% \text{ Free NCO})}{100(\text{Equiv Wt of NCO}) - (\text{Equiv Wt of TDI}) (\% \text{ Free NCO})}$$

Where Equivalent Weight of polybd = 100/hydroxyl value
 Equivalent Weight of NCO = 42
 Equivalent Weight of TDI = 87

- b) Amount of 2-ethyl-1,3-hexanediol(glycol) needed to react with prepolymer containing selected % free isocyanate from first stage:

$$\frac{\text{Weight of Glycol}}{100\text{g prepolymer}} = \frac{(\% \text{ Free NCO in prepolymer}) \times (\text{Equiv Wt of Glycol})}{42}$$

$$\text{Where Equiv Wt of Glycol} = \frac{1000 \times 56.1}{\text{hydroxyl number}}$$

$$= \frac{\text{Molecular Weight of Glycol}}{2}$$

In our experiments some of the calculated amount of diol was replaced by an equivalent amount (in terms of hydroxyl number) of triol. The total hydroxyl content of the mixture of triol and diol used in a particular experiment was equal to the hydroxyl content of the weight of glycol calculated as above for the selected % free isocyanate.

Surface Treatment of Substrates

Precleaned Opticlear soda lime microscope slides (75x25x1.06 mm) from KIMBLE were heated at 140°C for 1 hr., and kept in a dessicator over CaCl₂ until treated with the desired reagent. Amines used for surface treatment included p-phenylenediamine (PDA), 1,4-diaminobutane (AB), piperazine (P), aniline (A), and 3-aminopropyltriethoxysilane (AS). Glass slides were treated with amines at room temperature usually by immersing the slides for 5 min. in an amine-absolute ethanol solution. After removing the glass slides from the amine solution, the slides were dried in air and then heated for 30 min. at

60°C under vacuum before applying the elastomer layer. Pure ethanol treatment was carried out in the same manner. 3-Aminopropyltriethoxysilane was similarly applied except that a 50/50 mixture with water by volume was used instead of pure ethanol and after air drying the slides were heated at 100°C for 1 hr.

Small plates cut from Apollo mirror finish chrome ferro-type plates were similarly treated with amines. Before treatment the plates were cleaned with acetone and dried for 30 min. at 140°C.

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. in a heated press. Rubber sheets were cured in a vertical mold in a vacuum oven at 100°C for 5 hrs.

Measurement of Work of Adhesion (W_A)

180° peeling 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 was calculated from the time average of the peel force P per unit width of the detaching layer: $W = 2P$.

Tensile Tests

Tensile tests were carried out at room temperature and a crosshead speed of 50 cm/min using dumbbell specimens. Breaking elongation was calculated from the ratio $(L_D - L_0)/L_0$, where L_0 and L_D were the initial length and the length at break, respectively.

Swelling Ratio Measurements

Samples were cut from molded rod. The weight of a rod about 2.5 cm long and 0.6 cm in diameter was measured before, W_0 , and after, W_f , immersion in dioxane solvent at room temperature for 70 hrs. The swelling ratio, calculated from the relationship $(W_f - W_0)/W_0$ remained constant throughout all experiments.

Differential Scanning Calorimetry

Differential scanning calorimetry was carried out with a du Pont 990 Thermal Analyzer and its accessories, using a normal scanning speed of 10°C/min and a sample weight of approximately 14 mg.

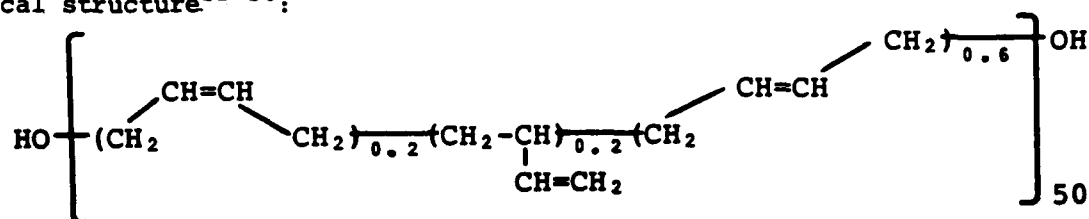
X-Ray Diffraction

Wide angle X-ray diffraction patterns were taken with a Phillips Universal Flat Plate Camera type PW 1030. The X-ray facility consisted of a Phillip's ultrastable generator model PW 1310/PW 1320.

RESULTS AND DISCUSSION

Effect of Free -NCO Content of Prepolymer on Properties of Polyurethane

According to ARCO, polybutadiene resin, R-45HT, has the following chemical structure¹²⁻¹³:



The hydroxyl functionality is slightly greater than 2.0. When excess isocyanate (TDI) is used in the preparation of a prepolymer in a two stage process, the hydroxyls are converted to urethane groups, $\text{R}'\text{NCO}\text{R}'$, which can then react with the excess isocyanate to form allophanates, $\text{R}'\text{NC}(\text{CO}_2\text{R})\text{NRH}$.

Since 2-9% excess isocyanate was used to prepare the polymers in this study, the polymers undoubtedly contained some allophanate groups. The effect of excess -NCO content compared to hydroxyl number of the polybutadiene on tensile properties of the polyurethane are shown in Figure 1. As the -NCO content increased, the ultimate tensile strength, σ , passed through a maximum at about 6% excess -NCO and then stayed constant. As shown in Table 3 Shore A Hardness increased continuously with % free NCO content.

Table 3. Effect of Free NCO Content of Prepolymer on Swelling Ratio and Shore A Hardness of Polyurethane^a

| Free NCO Content of Prepolymer | 2% | 3% | 4% | 6% | 7% | 9% |
|--------------------------------|----|------|------|------|------|------|
| Swelling Ratio | -- | 4.02 | 4.05 | 4.08 | 4.13 | 3.94 |
| Shore A Hardness | 33 | 36 | 43 | 60 | 64 | 76 |

^aThe ratio of glycol to triol was about 10 to 1 in these experiments.

Polymerizations were completed by chain extension and crosslinking using N,N-bis-2-hydroxyaniline and trimethylolpropane, usually in a 10:1 ratio.

PROPERTIES OF POLYMER

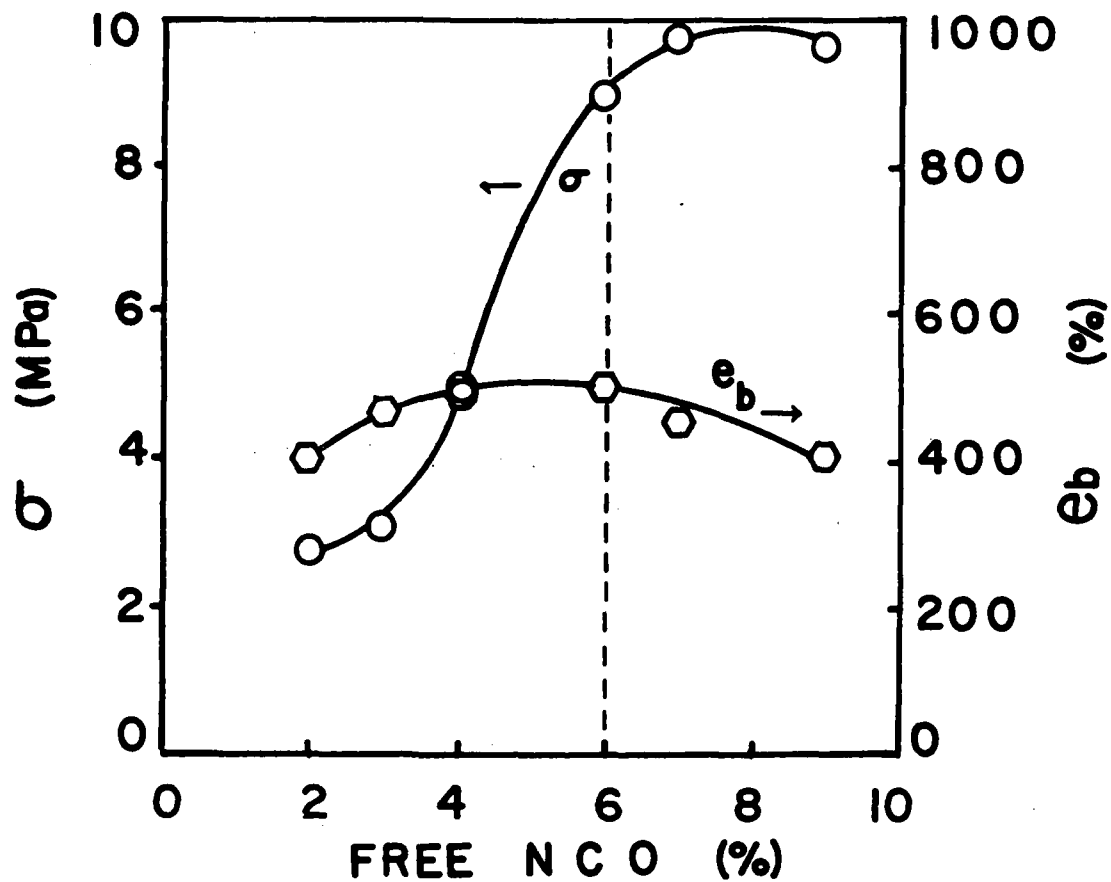


Fig. 1 Effect of free -NCO content of prepolymer on tensile strength (σ) and breaking elongation (e_b).

For these polymers, as shown in Table III, the swelling ratio remained constant. (The (total OH)/NCO ratio was constant and equal to 1.0.) As can be seen in Figure 1, elongation at break, e_b , passed through a maximum at about 6% excess -NCO and then decreased again.

Figure 2 shows the results of differential scanning calorimetry studies of these polymers. The glass transition temperature of the polybutadiene resin, R-45HT, is about -75°C . The glass transition temperature increases as the percentage of excess TDI used to make the polyurethane is increased. The behavior of T_g is similar to that of Shore A Hardness described above.

Wide angle X-ray photographs of a polyurethane whose prepolymer was prepared using 9% excess isocyanate groups did not show any evidence of crystallinity.

These effects occur because increasing the amount of TDI and chain extender with respect to the polybutadiene increases the relative concentration of urethane, allophanate, and other aromatic groups. This results in increased possibility for intermolecular hydrogen bonding, increased M_c , increased rigidity and increased elastomer strength.

Effect of Free -NCO Content of Prepolymer on Adhesion

The effect of free -NCO content of prepolymer on W_A to a glass substrate is shown in Figure 3. The results indicate that W_A increases initially as the -NCO content increases, reaches a maximum at ~6% free -NCO content and then decreases with further increases in -NCO content. As has already been mentioned above, increasing the free -NCO content of the prepolymer leads to an increase in the concentration of urethane groups in the elastomer backbone and results in increased intermolecular attractive forces in the elastomer. Reegen and Ilkka¹⁴ have made similar observations. They attributed the higher peel strength observed with increasing concentration of urethane groups to two factors: first, an increase in the true adhesion of the polyurethane and second, a more rigid and stiffer elastomer, which requires a greater force to bend it to an angle of 180° . In our experiments when the free -NCO content was over 6%, the rigidity of the elastomer increased so much that e_b and W_A decreased.

Effect of Water and Ethanol on Adhesion

A glass surface which has been exposed to the atmosphere is covered with a water film^{15,16}. When our polyurethane was applied to such a glass surface as shown in Figure 3 a much higher work of adhesion was obtained in comparison with a preheated glass surface. This can be explained as follows. The -NCO group can react with the water on the glass surface to form a primary amine, which on further reaction leads to urea linkages instead of the urethanes formed from alcohols. Urea groups are more polar than urethane groups and therefore promote higher adhesion than urethane groups.¹⁴

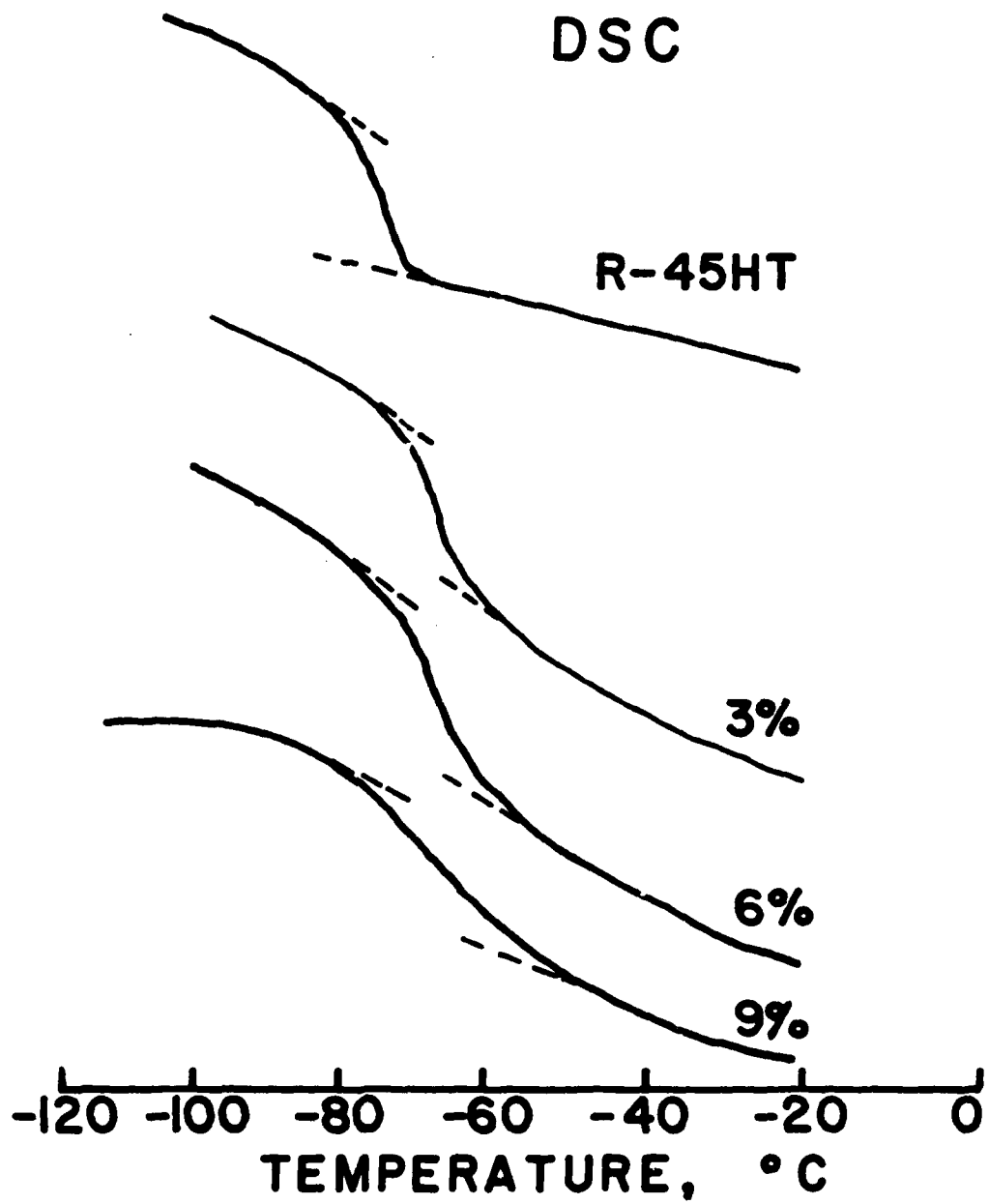


Fig. 2 Effect of concentration of excess TDI on glass transition temperature of resulting polyurethanes.

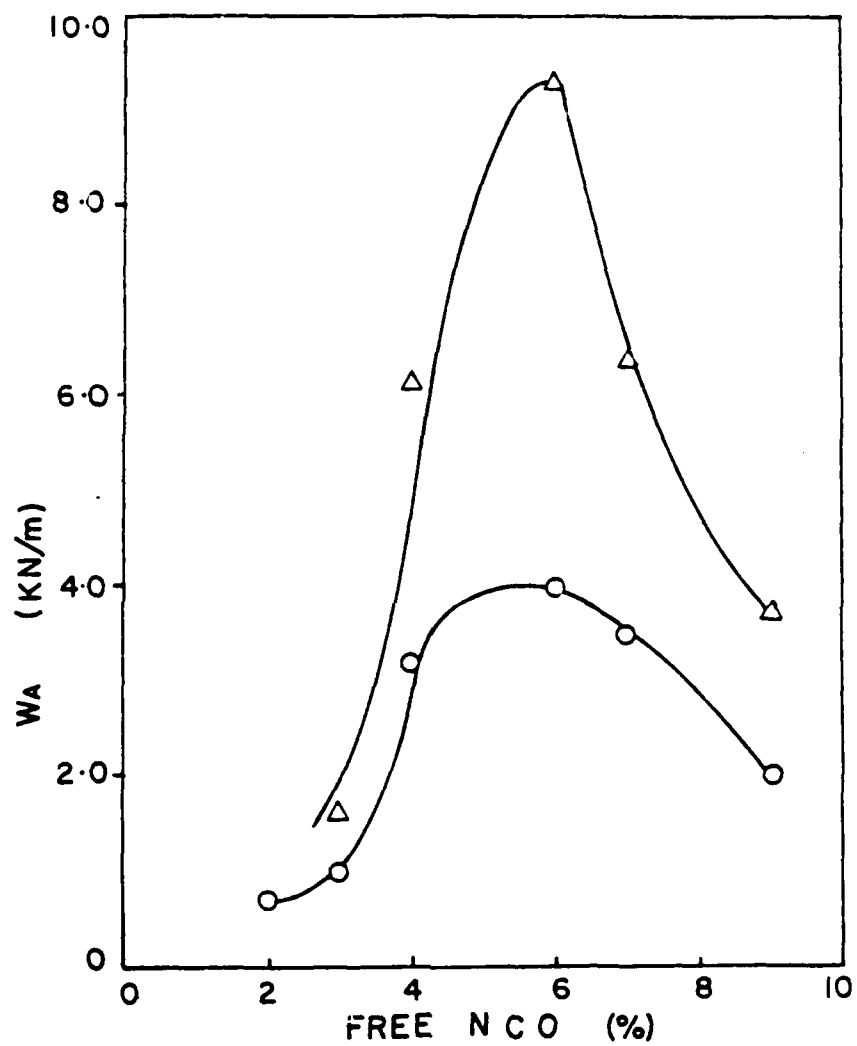
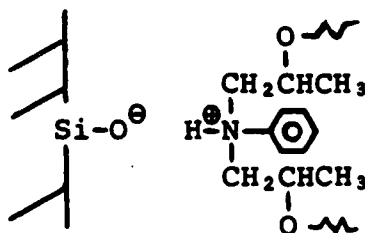


Fig. 3 Effect of free -NCO content of prepolymer on work of adhesion (W_A) of polyurethane to glass. Δ undried, O dried.

The formation of urea groups may not be the only explanation for the greatly enhanced adhesion of undried surfaces. The values of W_A observed for this polyurethane are substantially higher than those previously reported in the literature for other polyurethanes^{14,17}. We attribute the increased adhesion to the presence of tertiary amine groups from the *N,N*-bis(2-hydroxypropyl)aniline in the backbone of our polyurethane. These amine groups potentially can react with the acidic silanol groups present in the glass surface or perhaps even with surface moisture to form ionic bonds:



The presence of ionic groups in polyurethanes is known to drastically change the mechanical properties of polyurethanes¹⁸, but the remarkable effects on adhesion have not been reported previously. The presence of such ionic bonds is consistent with the fact that adhesion in these systems is markedly reduced by soaking a few days in water, which would solvate the ionic clusters¹⁸ and reduce their effectiveness in promoting adhesion. It is noteworthy that strong adhesive bonds reform on drying¹⁹.

Experiments intended to illustrate the effect of the concentration of tertiary amine groups on adhesion led to the remarkable changes in W_A shown in Figure 4. In this series of experiments the ratio of diol(tertiary amine) and triol was varied while a 6 percent excess isocyanate was maintained. Polymers with the greater percentage of diol were stronger and their swelling ratio was higher. Such systems have both an increased number of tertiary amine groups and are more chain extended than those prepared with the triol alone. Ahagon and Gent²⁰, among others, have shown that W_A decreases as the crosslink density of the polymer increases and the molecular weight between crosslinks decreases. Thus some of the increase in W_A with increased percent of diol is undoubtedly due to the decrease in crosslink density and polymer stiffness that accompanies the increase in diol. But the magnitude of the increase is greater than expected from this change alone. As stated above, we attribute the high strength of adhesion to the presence of ionic bonds. This interpretation is consistent with the observations of Kozakiewicz and Penczek²¹, who reported enhanced adhesion in systems shown to contain ionic bonds.

Preheated glass slides which had been immersed in absolute ethanol also led to a somewhat higher work of adhesion than untreated preheated slides, possibly due to an increased number of urethane groups at the interface.

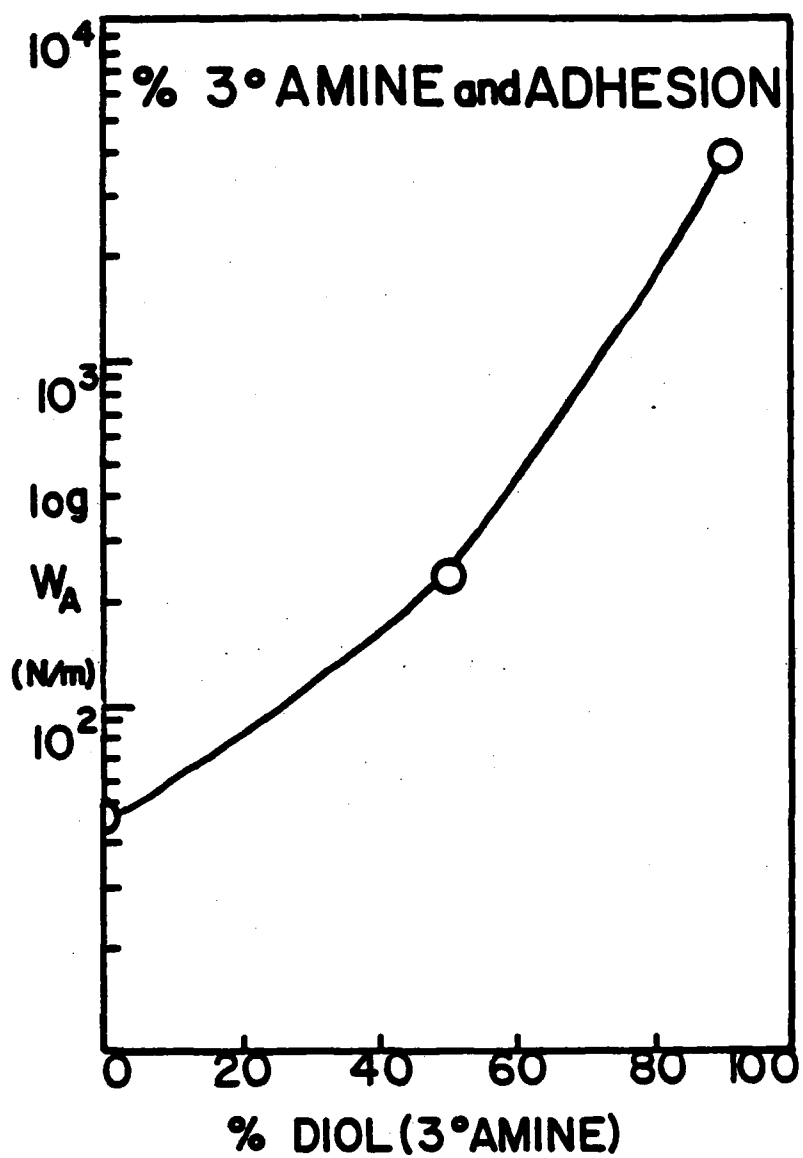
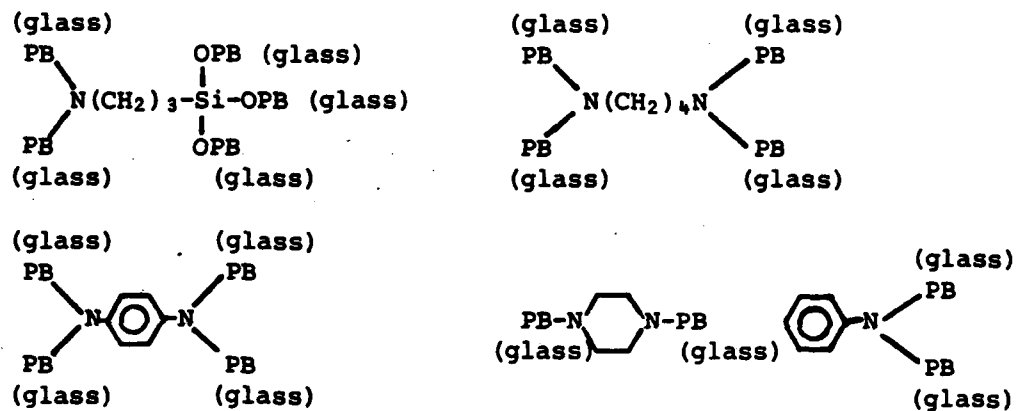


Fig. 4 Effect of concentration of diol (tertiary amine groups) on adhesion.

Effect of Amines on Adhesion

The values of the work of adhesion of our polyurethane to glass slides pretreated with different amine solutions are shown in Figures 5 and 6. The work of adhesion compared to untreated slides was increased in all cases except that of aniline. At equivalent concentration of amines, the order of enhancement in the work of adhesion was AS>>PDA~AB>P>>A. Cohesive failure of the adhesive bonds was observed for slides pretreated with AS. The results can be explained in terms of the different structures of the amines and the reactions that can occur with the amines. We conclude that just like in the work of Eckstein and Dreyfuss referred to above⁴⁻⁸, chemical bonds form from the surface through the amine to the substrate:



The degree of enhancement of adhesion is related to the number of bonds that can form between the surface and the adhesive. Aniline does not lead to reinforcement because it is monofunctional and the ring does not become part of the backbone.

The structures shown are intended to indicate that the amino groups can, in all cases, be bonded either to the glass or to the polybutadiene. The structures are not intended to suggest that bonding of the amine to the glass occurs only through the polybutadiene.

In the present case the chemical reactions occurring between the polybutadiene and the amines or glass are quite different from those described by Eckstein and Dreyfuss⁴⁻⁸, because in the present case no peroxide is present. All reactions occur among the functional endgroups. Bonding of the polybutadiene to the amines takes place as a result of the reaction of the isocyanate endgroups of the prepolymer with the amine to form a urea:



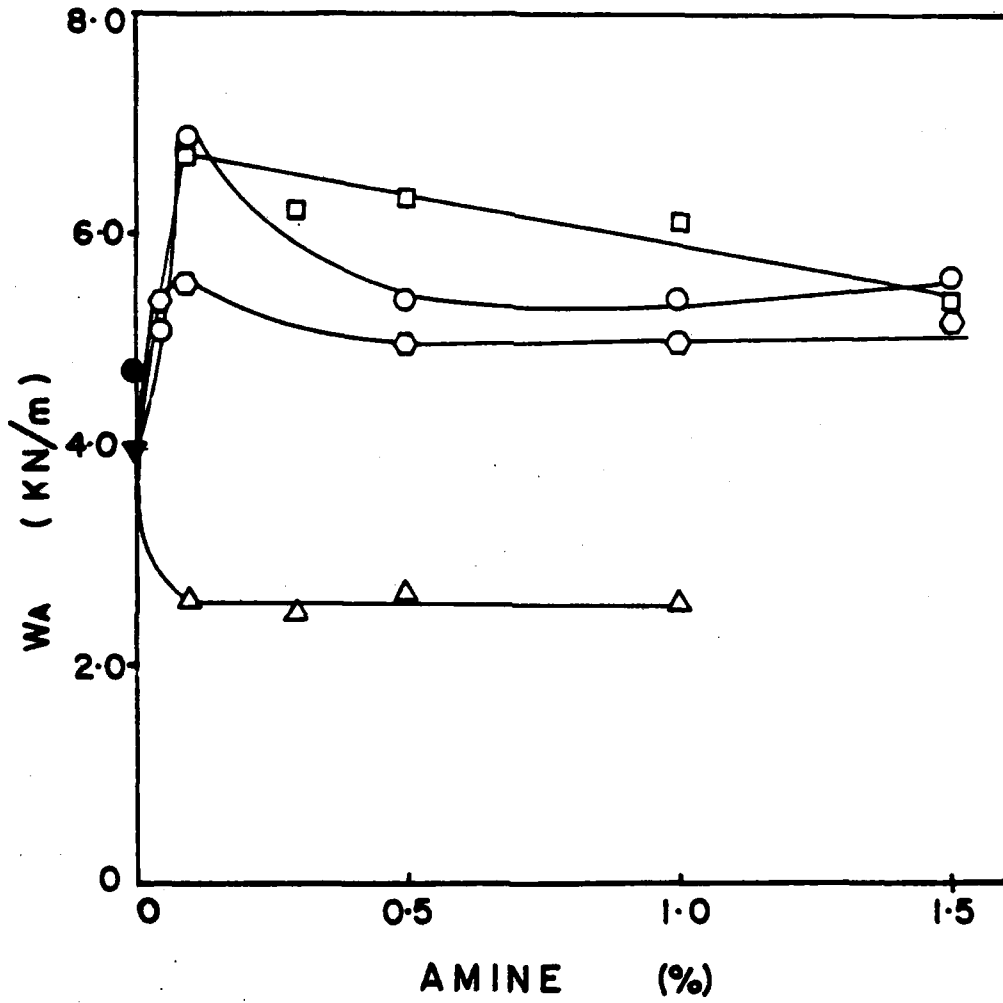


Fig. 5 Effect of concentration of amine on work of adhesion (W_A) of polyurethane to glass. \circ AB, \square PDA, \circ P, Δ aniline, \bullet ethanol, ∇ dried and untreated.

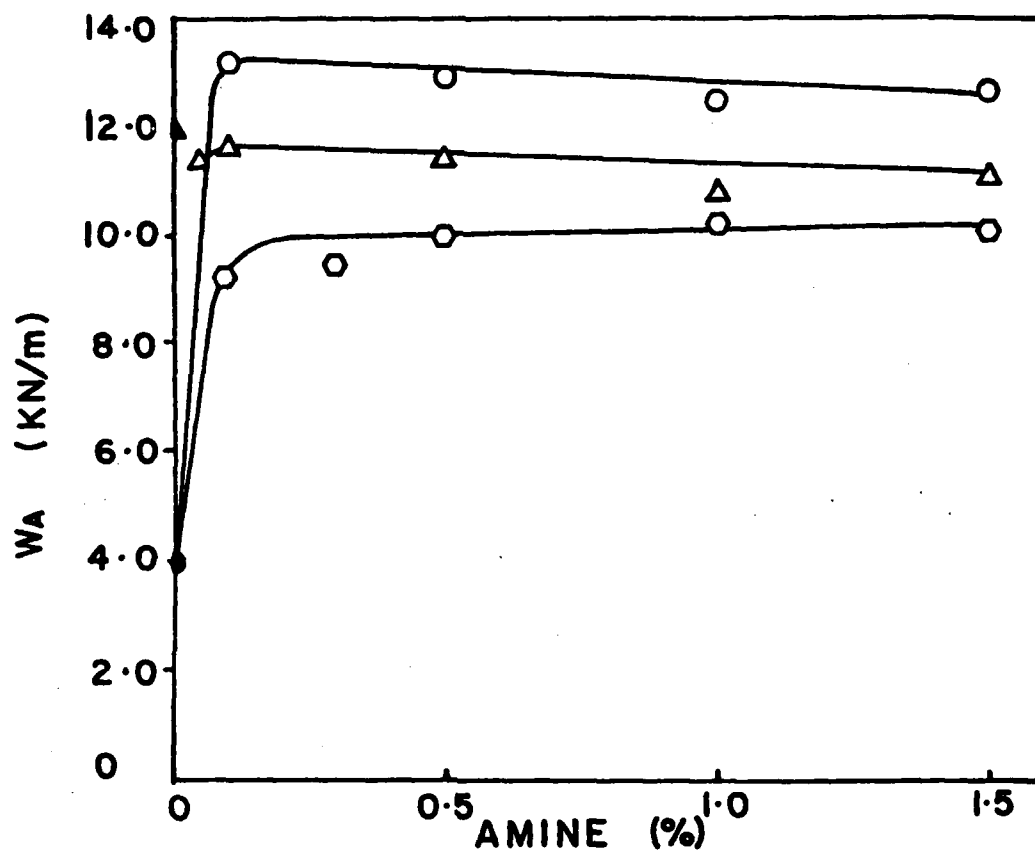
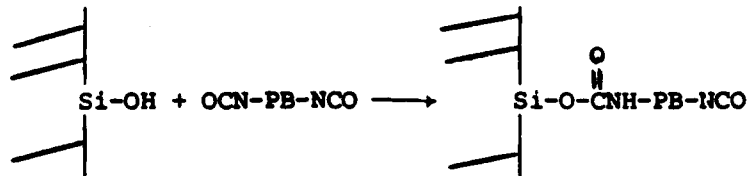
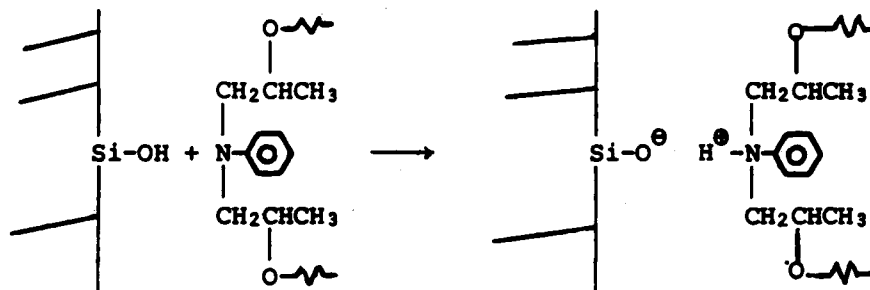


Fig. 6 Effect of concentration of AS on work of adhesion (W_A) of polyurethane to substrates. \circ glass treated with AS from 50/50 by volume water/ethanol, Δ chrome steel treated with AS, \circ glass treated with AS from acetone, Δ chrome steel treated with absolute ethanol, \bullet dried and untreated glass.

Bonding of the polybutadiene to the glass may occur by reaction of the prepolymer with silanol groups in the glass surface:



With the present polyurethane, as stated above in the section on the effect of water on adhesion, ionic bonds form between the tertiary amine groups of the polybutadiene polyurethane and the silanol groups:



The reactions that occur between the glass and the amines are probably the same as those already described by Eckstein and Dreyfuss⁴⁻⁸. All of the amines can react with the silanol groups on the glass surface to form ionic bonds similar to those shown above for the tertiary amine. Reactions of 1,4-diaminobutane and 3-aminopropyltriethoxysilane are probably facilitated by prior formation of carbamates. In addition, covalent bonds of a presently undefined structure probably form between the glass and the amine.

Adhesion of Polyurethane to Chrome Steel

Metals have a higher surface energy than glass. After treatment with ethanol, W_A of our polyurethane to preheated and clean chrome steel surfaces was much higher than to preheated glass surfaces. Treating the surface of the steel with amines before applying the elastomer did not enhance adhesion. Dried and untreated surfaces had W_A of about 3 kN/m. The results are included in Figure 6. Some preliminary experiments have been carried out on chrome steel surfaces treated with AS. W_A is not significantly increased but the bonds that form are extremely stable in water. They can be soaked for a month with no apparent change in W_A ¹⁹.

The chemical reactions occurring are probably similar to those described above for glass²². Supporting evidence that amino compounds are chemisorbed by metal oxide surfaces has recently been obtained by inelastic tunnelling spectroscopy²³. Further investigations are being carried out to find explanations for the differences observed in the effects of amine surface treatment of glass and of metal on the adhesion of this polyurethane to the substrate.

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. P. Dreyfuss, A. N. Gent and J. R. Williams, *J. Polym. Sci.: Polym. Phys. Ed.*, 18, 2135 (1980).
2. M. W. Ranney and C. A. Pagano, *Rubber Chem. Technol.*, 44, 1080 (1971).
3. M. W. Ranney, S. E. Berger and J. G. Marsden, Chapter 5 in "Composite Materials," 6, E. P. Plueddemann, Ed., Academic Press, N. Y., N. Y., 1974, p. 131.
4. E. P. Plueddemann, *Adhesives Age*, June, 1975, p. 38.
5. Y. Eckstein and P. Dreyfuss, "The Effect of Amine Structure and Concentration on the Strength of Adhesion," *J. Adhesion* (in press).
6. Y. Eckstein and P. Dreyfuss, "Effect of Amines on the Reaction of Peroxide with Olefinic Groups," *J. Adhesion* (in press).
7. Y. Eckstein and P. Dreyfuss, "Reactions of Amines with Triethylsilanol and/or Fumed Silica," *J. Adhesion* (in press).
8. Y. Eckstein and P. Dreyfuss, *J. Adhesion*, 13, 303 (1982).
9. P. Wright and A. P. C. Cumming, "Solid Urethane Elastomers," MacClaren and Sons, London (1969).
10. K. C. Frisch and S. L. Reegen, Eds., "Advances in Urethane Sciences and Technology," Technomic Publishing Co., Stamford, Conn. (1971).
11. R. J. Athey, Contribution No. 138, Division of Rubber Chemistry, American Chemical Society, Cincinnati, Ohio (1958).
12. poly bd^R liquid resins in urethane elastomers. Product Bulletin BD.3, ARCO Chemical Co., October, 1974.
13. poly bd^R resins, General Bulletin, ARCO Chemical Co., January, 1978.
14. S. L. Reegen and G. A. Ilkka, in "Adhesion and Cohesion," P. Weiss, Ed., Elsevier Pub. Co., Amsterdam, N. Y., 1962, p. 159.
15. E. Warburg and T. Ihmori, *Ann. d. Phys.*, 27, 481 (1886).
16. T. H. Elmer, "Glass Surfaces" in "Silylated Surfaces," D. E. Leyden and W. Collins, Eds., Gordon and Breach Science Pub., 1980.
17. A. N. Kuksin, Yu. S. Lipatov, L. M. Sergeeva and T. D. Kadurina, Chapter 26 in "Soviet Urethane Technology, Soviet Progress in Polyurethanes Series, 1, A. M. Schiller, Ed., Technomic Pub. Co., Westport, Conn., 1973, p. 171.

18. R. Rembaum, in *Advances in Urethane Science and Technology*, 2, K. C. Frisch and S. L. Reegen, Eds., Technomic Pub. Co., Stanford, Conn., 1971, p. 109.
19. F. Liang and P. Dreyfuss, to be published.
20. A. Ahagon and A. N. Gent, *J. Polym. Sci.: Polym. Phys. Ed.*, 13, 1285 (1975).
21. J. Kozakiewicz and P. Penczek, *Angew. Makromol. Chem.*, 78, 89 (1979).
22. F. J. Boerio, *ACS Organic Coatings and Plastics Chemistry Preprints*, 44, 625 (1981).
23. T. Furakawa, N. K. Eib, K. L. Mittal, H. R. Anderson, Jr., *SIA, Surf. Interface Anal.*, 4(6), 240 (1982).

DISTRIBUTION LIST

| | <u>No. Copies</u> | | <u>No. Copies</u> |
|--------------------------------------------------------------------------------------------------------------------------------------------|-------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------|
| Dr. L.V. Schmidt Assistant Secretary of the Navy (R,E, and S) Room 5E 731 Pentagon Washington, D.C. 20350 | 1 | Dr. F. Roberto Code AFRPL MKPA Edwards AFB, CA 93523 | 1 |
| Dr. A.L. Slafkosky Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380 | 1 | Dr. L.H. Caveny Air Force Office of Scientific Research Directorate of Aerospace Sciences Bolling Air Force Base Washington, D.C. 20332 | 1 |
| Dr. Richard S. Miller Office of Naval Research Code 413 Arlington, VA 22217 | 10 | Mr. Donald L. Ball Air Force Office of Scientific Research Directorate of Chemical Sciences Bolling Air Force Base Washington, D.C. 20332 | 1 |
| Mr. David Sfege Office of Naval Research Code 250 Arlington, VA 22217 | 1 | Dr. John S. Wilkes, Jr. FJSRL/NC USAF Academy, CO 80840 | 1 |
| Dr. R.J. Marcus Office of Naval Research Western Office 1030 East Green Street Pasadena, CA 91106 | 1 | Dr. R.L. Lou Aerojet Strategic Propulsion Co. P.O. Box 15699C Sacramento, CA 95813 | 1 |
| Dr. Larry Peebles Office of Naval Research East Central Regional Office 666 Summer Street, Bldg. 114-D Boston, MA 02210 | 1 | Dr. V.J. Keenan Anal-Syn Lab Inc. P.O. Box 547 Paoli, PA 19301 | 1 |
| Dr. Phillip A. Miller Office of Naval Research San Francisco Area Office One Hallidie Plaza, Suite 601 San Francisco, CA 94102 | 1 | Dr. Philip Howe Army Ballistic Research Labs ARRADCOM Code DRDAR-8LT Aberdeen Proving Ground, MD 21005 | 1 |
| Mr. Otto K. Heiney AFATL - DLDL Elgin AFB, FL 32542 | 1 | Mr. L.A. Watermeier Army Ballistic Research Labs ARRADCOM Code DRDAR-BLI Aberdeen Proving Ground, MD 21005 | 1 |
| Mr. R. Geisler ATTN: MKP/MS24 AFRPL Edwards AFB, CA 93523 | 1 | Dr. W.W. Wharton Attn: DRSNI-RKL Commander U.S. Army Missile Command Redstone Arsenal, AL 35898 | 1 |

DISTRIBUTION LIST

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

DISTRIBUTION LIST

| | <u>No. Copies</u> | | <u>No. Copies</u> |
|---------------------------------------------------------------------------------------------------------------------------------------|-------------------|-------------------------------------------------------------------------------------------------------------|-------------------|
| Mr. R. Brown Naval Air Systems Command Code 330 Washington, D.C. 20361 | 1 | Dr. J. Schnur Naval Research Lab. Code 6510 Washington, D.C. 20375 | 1 |
| Dr. H. Rosewasser Naval Air Systems Command AIR-310C Washington, D.C. 20360 | 1 | Mr. R. Beauregard Naval Sea Systems Command SEA 64E Washington, D.C. 20362 | 1 |
| Mr. B. Sobers Naval Air Systems Command Code 03P25 Washington, D.C. 20360 | 1 | Mr. G. Edwards Naval Sea Systems Command Code 62R3 Washington, D.C. 20362 | 1 |
| Dr. L.R. Rothstein Assistant Director Naval Explosives Dev. Engineering Dept. Naval Weapons Station Yorktown, VA 23691 | 1 | Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, PA 19112 | 1 |
| Dr. Lionel Dickinson Naval Explosive Ordnance Disposal Tech. Center Code D Indian Head, MD 20640 | 1 | Dr. H.G. Adolph Naval Surface Weapons Center Code R11 White Oak Silver Spring, MD 20910 | 1 |
| Mr. C.L. Adams Naval Ordnance Station Code PM4 Indian Head, MD 20640 | 1 | Dr. T.D. Austin Naval Surface Weapons Center Code R16 Indian Head, MD 20640 | 1 |
| Mr. S. Mitchell Naval Ordnance Station Code 5253 Indian Head, MD 20640 | 1 | Dr. T. Hall Code R-11 Naval Surface Weapons Center White Oak Laboratory Silver Spring, MD 20910 | 1 |
| Dr. William Tolles Dean of Research Naval Postgraduate School Monterey, CA 93940 | 1 | Mr. G.L. Mackenzie Naval Surface Weapons Center Code R101 Indian Head, MD 20640 | 1 |
| Naval Research Lab. Code 6100 Washington, D.C. 20375 | 1 | Dr. K.F. Mueller Naval Surface Weapons Center Code R11 White Oak Silver Spring, MD 20910 | 1 |

DISTRIBUTION LIST

| | <u>No. Copies</u> | | <u>No. Copies</u> |
|------------------------------------------------------------------------------------------------------|-------------------|----------------------------------------------------------------------------------------------------------------------|-------------------|
| Mr. J. Murrin Naval Sea Systems Command Code 62R2 Washington, D.C. 20362 | 1 | Dr. A. Nielsen Naval Weapons Center Code 385 China Lake, CA 93555 | 1 |
| Dr. D.J. Pastine Naval Surface Weapons Center Code R04 White Oak Silver Spring, MD 20910 | 1 | Dr. R. Reed, Jr. Naval Weapons Center Code 388 China Lake, CA 93555 | 1 |
| Mr. L. Roslund Naval Surface Weapons Center Code R122 White Oak, Silver Spring MD 20910 | 1 | Dr. L. Smith Naval Weapons Center Code 3205 China Lake, CA 93555 | 1 |
| Mr. M. Stosz Naval Surface Weapons Center Code R121 White Oak Silver Spring, MD 20910 | 1 | Dr. B. Douda Naval Weapons Support Center Code 5042 Crane, Indiana 47522 | 1 |
| Dr. E. Zimmet Naval Surface Weapons Center Code R13 White Oak Silver Spring, MD 20910 | 1 | Dr. A. Faulstich Chief of Naval Technology MAT Code 0716 Washington, D.C. 20360 | 1 |
| Dr. D. R. Derr Naval Weapons Center Code 388 China Lake, CA 93555 | 1 | LCDR J. Walker Chief of Naval Material Office of Naval Technology MAT, Code 0712 Washington, D.C. 20360 | 1 |
| Mr. Lee N. Gilbert Naval Weapons Center Code 3205 China Lake, CA 93555 | 1 | Mr. Joe McCartney Naval Ocean Systems Center San Diego, CA 92152 | 1 |
| Dr. E. Martin Naval Weapons Center Code 3858 China Lake, CA 93555 | 1 | Dr. S. Yamamoto Marine Sciences Division Naval Ocean Systems Center San Diego, CA 91232 | 1 |
| Mr. R. McCarten Naval Weapons Center Code 3272 China Lake, CA 93555 | 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

| | <u>No. Copies</u> | | <u>No. Copies</u> |
|----------------------------------------------------------------------------------------------------------------------------------|-------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------|
| Dr. J.F. Kincaid Strategic Systems Project Office Department of the Navy Room 901 Washington, D.C. 20376 | 1 | Dr. C.W. Vriesen Thiokol Elkton Division P.O. Box 241 Elkton, MD 21921 | 1 |
| Strategic Systems Project Office Propulsion Unit Code SP2731 Department of the Navy Washington, D.C. 20376 | 1 | Dr. J.C. Hinshaw Thiokol Wasatch Division P.O. Box 524 Brigham City, Utah 84302 | 1 |
| Mr. E.L. Throckmorton Strategic Systems Project Office Department of the Navy Room 1043 Washington, D.C. 20376 | 1 | U.S. Army Research Office Chemical & Biological Sciences Division P.O. Box 12211 Research Triangle Park NC 27709 | 1 |
| Dr. D.A. Flanigan Thiokol Huntsville Division Huntsville, Alabama 35807 | 1 | Dr. R.F. Walker USA ARRADCOM ORDAR-LCE Dover, MD 20701 | 1 |
| Mr. G.F. Mangum Thiokol Corporation Huntsville Division Huntsville, Alabama 35807 | 1 | Dr. T. Sinden Munitions Directorate Propellants and Explosives Defence Equipment Staff British Embassy 3100 Massachusetts Ave. Washington, D.C. 20003 | 1 |
| Mr. E.S. Sutton Thiokol Corporation Elkton Division P.O. Box 241 Elkton, MD 21921 | 1 | LTC B. Leving AFROL/LK Edwards AFB, CA 93523 | 1 |
| Dr. G. Thompson Thiokol Wasatch Division MS 240 P.O. Box 524 Brigham City, UT 84302 | 1 | Professor Alan N. Gent Institute of Polymer Science University of Akron Akron, OH 44325 | 1 |
| Dr. T.F. Davidson Technical Director Thiokol Corporation Government Systems Group P.O. Box 9253 Cogen, Utah 84409 | 1 | Mr. J. M. Frankle Army Ballistic Research Labs ARRADCOM Code ORDAR-BLI Aberdeen Proving Ground, MD 21005 | 1 |

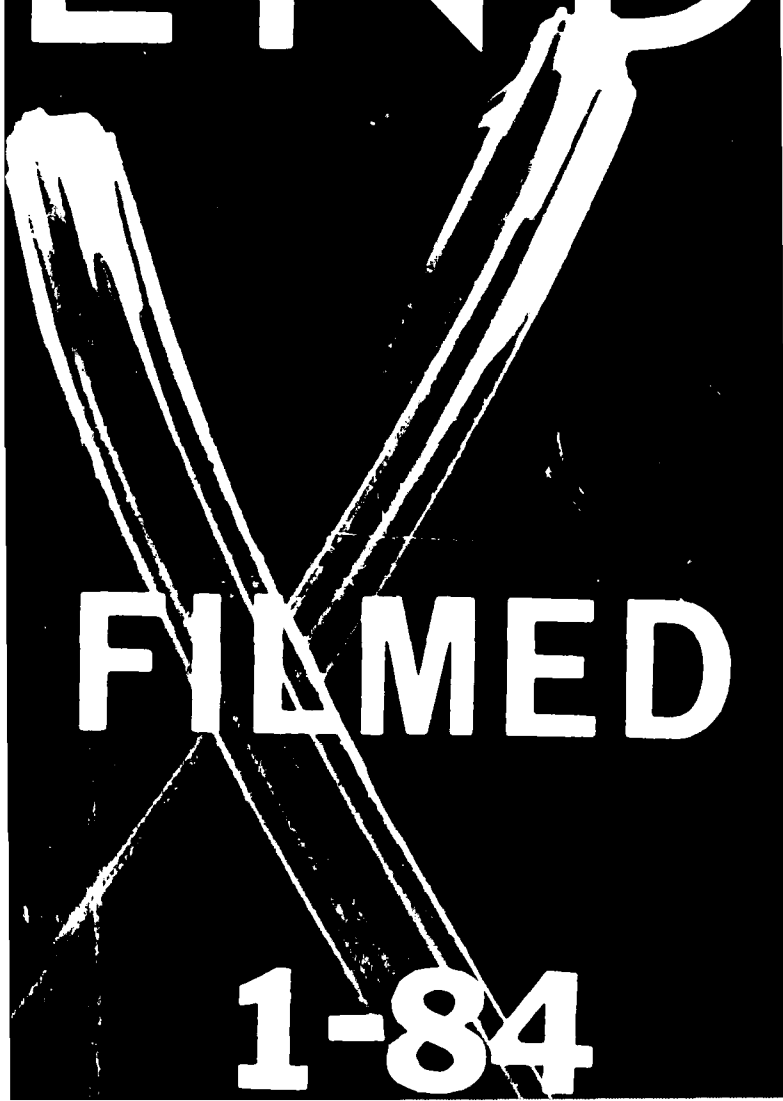
DISTRIBUTION LIST

| | <u>No. Copies</u> | | <u>No. Copies</u> |
|-------------------------------------------------------------------------------------------------------------------------------|-------------------|------------------------------------------------------------------------------------------------------------------------------|-------------------|
| Dr. Ingo W. May Army Ballistic Research Labs ARRADCOM Code DRDAR-BLI Aberdeen Proving Ground, MD 21005 | 1 | Dr. J. P. Marshall Dept. 52-35, Bldg. 204/2 Lockheed Missile & Space Co. 3251 Hanover Street Palo Alto, CA 94304 | 1 |
| Professor N.W. Tschoegl California Institute of Tech Dept. of Chemical Engineering Pasadena, CA 91125 | 1 | Ms. Joan L. Janney Los Alamos National Lab Mail Stop 920 Los Alamos, NM 87545 | 1 |
| Professor M.D. Nicol University of California Dept. of Chemistry 405 Hilgard Avenue Los Angeles, CA 90024 | 1 | Dr. J. M. Walsh Los Alamos Scientific Lab Los Alamos, NM 87545 | 1 |
| Professor A. G. Evans University of California Berkeley, CA 94720 | 1 | Professor R. W. Armstrong Univ. of Maryland Department of Mechanical Eng. College Park, MD 20742 | 1 |
| Professor T. Litovitz Catholic Univ. of America Physics Department 520 Michigan Ave., N.E. Washington, D.C. 20017 | 1 | Prof. Richard A. Reinhardt Naval Postgraduate School Physics & Chemistry Dept. Monterey, CA 93940 | 1 |
| Professor W. G. Knauss Graduate Aeronautical Lab California Institute of Tech. Pasadena, CA 91125 | 1 | Dr. R. Bernecker Naval Surface Weapons Center Code R13 White Oak, Silver Spring, MD 20910 | 1 |
| Professor Edward Price Georgia Institute of Tech. School of Aerospace Engin. Atlanta, Georgia 30332 | 1 | Dr. M. J. Kamlet Naval Surface Weapons Center Code R11 White Oak, Silver Spring, MD 20910 | 1 |
| Dr. Kenneth O. Hartman Hercules Aerospace Division Hercules Incorporated P.O. Box 210 Cumberland, MD 21502 | 1 | Professor J. D. Achenbach Northwestern University Dept. of Civil Engineering Evanston, IL 60201 | 1 |
| Dr. Thor L. Smith IBM Research Lab 042.282 San Jose, CA 95193 | 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

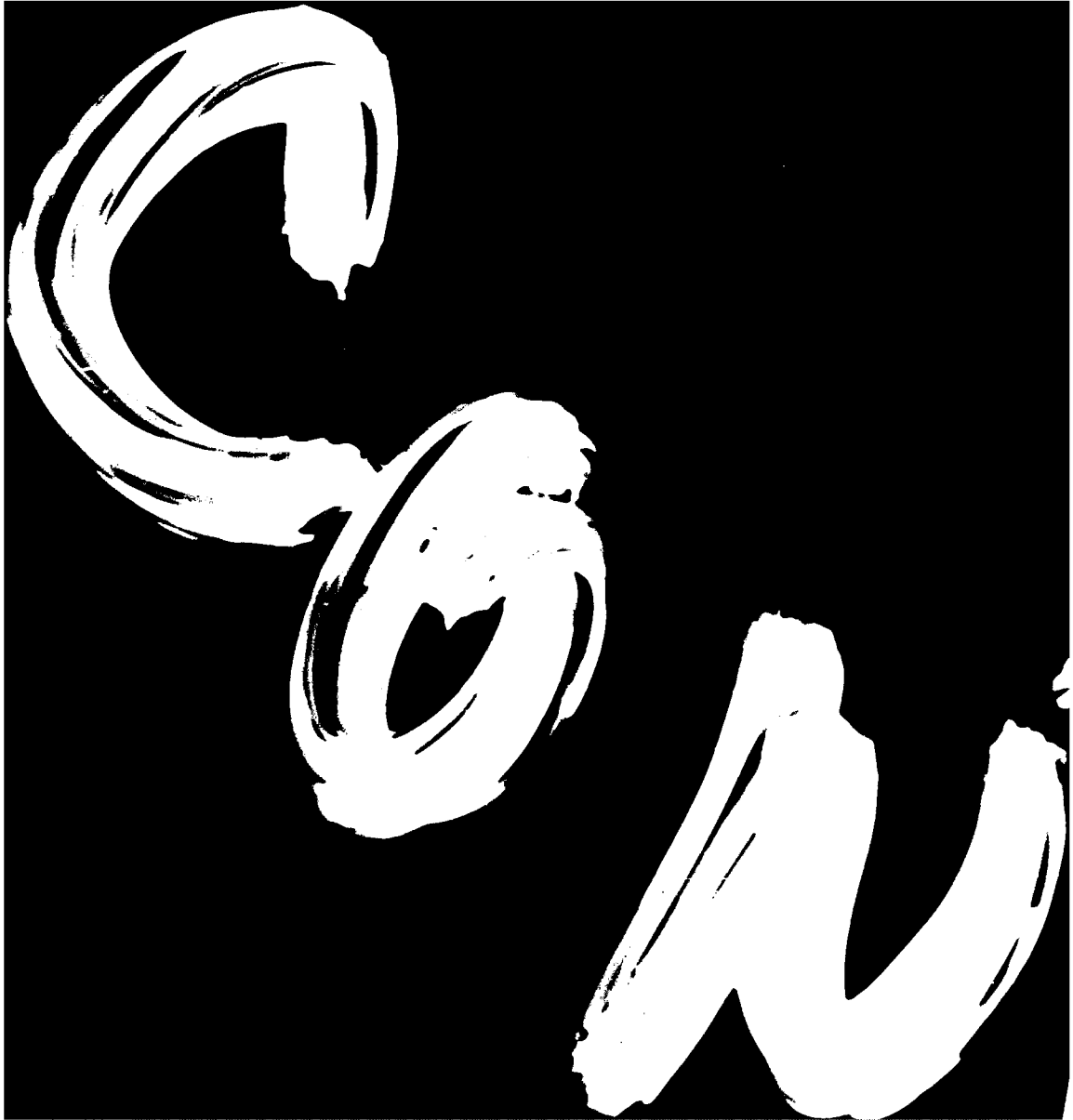
| | <u>No. Copies</u> | | <u>No. Copies</u> |
|----------------------------------------------------------------------------------------------------------------------------|-------------------|-----------------------------------------------------------------------------------------------------------|-------------------|
| Dr. S. Sheffield Sandia Laboratories Division 2513 P.O. Box 5800 Albuquerque, NM 87185 | 1 | ONR Resident Representative Ohio State University Res. Ctr. 1314 Kinnear Road Columbus, OH 43212 | 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 | | |

END



FILMED

1-84



EFFECT OF AMINE SURFACE TREATMENT ON THE ADHESION OF A
POLYURETHANE TO THE SURFACE(U) AKRON UNIV OH INST OF
POLYMER SCIENCE F LIANG ET AL. DEC 83 TR-29A

UNCLASSIFIED

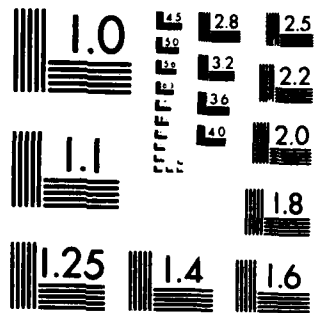
N00014-76-C-0408

F/G 11/1

NL



END
DATE
FILMED
6-84
DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963 A

SUPPLEMENTARY

INFORMATION

AD A135 591

ERRATA

The report, "Effect of Amine Surface Treatment on the Adhesion of a Polyurethane" by F. Liang and P. Dreyfuss, issued in December, 1983, should be Report No. 29A. The report has been re-numbered to eliminate duplication of an earlier report number.

LMED

— 8