



AD A 094756

12

OFFICE OF NAVAL RESEARCH

Contract <sup>15</sup> N00014-76-C-0408

Project NR 092-555

<sup>14</sup> Technical Report No. 9

LEVEL II

EFFECT OF INTERFACIAL BONDING ON THE STRENGTH OF ADHESION  
OF ELASTOMERS, I. SELF-ADHESION.

by

R.-J. Chang and A. N. Gent,

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

January, 1981

DTIC  
ELECTE  
S FEB 09 1981 D  
E

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

Approved for Public Release; Distribution Unlimited

DBG FILE COPY

401067

81 2 09 078

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report 9	2. GOVT ACCESSION NO. AD-AC94	3. RECIPIENT'S CATALOG NUMBER 756
4. TITLE (and Subtitle) Effect of Interfacial Bonding on the Strength of Adhesion of Elastomers I. Self-Adhesion		5. TYPE OF REPORT & PERIOD COVERED Technical Report
		6. PERFORMING ORG. REPORT NUMBER N00014-76-C-0408
7. AUTHOR(s) R.-J. Chang and A. N. Gent		8. CONTRACT OR GRANT NUMBER(s) NR 092-555
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
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Power Program Arlington, Virginia 22217		12. REPORT DATE January 30, 1981
		13. NUMBER OF PAGES 42
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) Approved for public release; distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES Submitted for publication in: Journal of Polymer Science: Polymer Physics Edition		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Adhesion, Bonding, Crosslinking, Elastomers, Fracture, Interface, Strength		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Two partially-gelled (crosslinked) layers of elastomer were pressed into intimate contact and the gelation reaction was then taken to completion. By varying the extent of initial gelation, the degree of chemical interlinking was varied from zero, when two fully-reacted sheets were pressed together, up to a level charac- teristic of the final density of molecular linking within each layer, when they were brought together before any reaction had		

DD FORM 1473

JAN 73

EDITION OF 1 NOV 65 IS OBSOLETE

S/N 0102-LF-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

occurred. The strength of adhesion between the layers was measured under threshold conditions, i.e., at low rates of peel, at high temperatures, and, in some instances, with the layers swollen with a compatible liquid. Linear relations were obtained between the threshold work of detachment per unit of interfacial area and the amount of chemical interlinking, deduced from the kinetics of molecular linking within each layer. At any degree of interlinking, ranging from zero to the fully interlinked state, the work of detachment was lower for networks composed of shorter molecular chains, in accordance with the Lake-Thomas theory for the threshold strength of elastomer networks. By extrapolation to the fully interlinked state, the strength of adhesion corresponding to cohesive rupture was inferred. These values agreed with measured tear strengths for polybutadiene gelled by a free-radical process. For a sulfur crosslinking system, and for both free-radical and sulfur crosslinking of poly(ethylene-co-propylene), the threshold tear strength of the elastomer was found to be much higher than the extrapolated value from adhesion measurements. This discrepancy is ascribed to roughness of the tear plane in relatively strong elastomers, in contrast to the smooth separation of flat adhering layers. Adhesion of fully-crosslinked sheets was generally low, 1 - 2 J/m<sup>2</sup>. Higher values, 5 - 25 J/m<sup>2</sup>, were found with sulfur crosslinking systems, especially those yielding a high proportion of polysulfidic crosslinks. Interlinking via polysulfide crosslink interchange reactions is suggested in these case.

Introduction

The relationship between the mechanical strength of an adhesive joint and the density of chemical bonds across the interface is still somewhat uncertain. Previous work with a simple elastomer layer bonded to a silane-treated glass plate suggested that a direct proportionality exists under near-equilibrium conditions, i.e., at low rates of detachment and at high temperatures (1). The strength of the joint, expressed as the work required to separate unit area of the joint, varied from 1-3 J/m<sup>2</sup> when no covalent bonds were present at the interface up to about 50 J/m<sup>2</sup> when interlinking by a free-radical process was inferred between reactive groups in the elastomer and in the silane on the glass surface. However, although the effect of chemical bonding was demonstrated unequivocally, and shown to be large under near-equilibrium conditions, a quantitative relationship between adhesion strength and the density of interfacial bonds could not be established because no absolute measurements of bond density were made. Attempts to carry out such measurements are in progress now, using radioactive tagging techniques (2) but

Accession For	
NTIS CHEM	X
DTIC TAB	
Unannounced	
Justification	
By	
Distribution/	
Availability Codes	
Dist	
<b>A</b>	

they are still far from complete. An experimental study has therefore been carried out using a somewhat simpler model of an adhesive joint that has several advantages, including the major one that the density of interlinking between the two components can be inferred with some confidence from the known chemistry of homogeneous gelation (crosslinking) reactions within elastomers.

The test procedure is as follows: two identical layers of an elastomer are prepared, partially crosslinked to the same extent. These layers are then pressed into intimate contact and the crosslinking reaction is taken to completion, Figure 1. By varying the extent of crosslinking before the layers are brought into contact, the degree of chemical interlinking between the layers can be varied over the entire range, from zero, when two fully-crosslinked sheets were pressed together, up to a level characteristic of the final density of crosslinking within a sheet when the layers are brought together before any crosslinking takes place. Moreover, the density of crosslinking within simple elastomer systems can be determined by a variety of techniques at various stages in the crosslinking process. In this way the density of interlinking can be deduced for elastomer layers bonded together as described.

Other advantages accrue with this simple experimental system. Because the two-layer testpiece is symmetrical, no shrinkage stresses are developed on warming or cooling. Furthermore, the testpiece can be swollen uniformly by compatible liquids so that the dissipative properties of the elastomer are minimized, without introducing stresses at the interface. Thus, measurements of the mechanical strength can be made using swollen testpieces to test the hypothesis that a constant low value is attained in the absence of mechanical energy dissipation within the adherends and that it is this threshold value which is directly related to the degree of interfacial bonding (1).

Measurements of the threshold strength of adhesion are reported here for two simple elastomers, poly butadiene and poly(ethylene-co-propylene), with two crosslinking systems, a peroxide recipe yielding intermolecular C-C bonds via a free-radical reaction and an accelerated-sulfur recipe yielding sulphidic intermolecular bonds. Various amounts of interfacial bonding were introduced between two layers of each elastomer, as described above. The final degree of crosslinking of the layers was also varied.

### Experimental

Two simple hydrocarbon elastomers were used in the experiments. The first was an anionically-polymerized polybutadiene (Diene 35 NFA, Firestone Rubber and Latex Company), reported to contain 36 per cent cis, 54 per cent trans, and 10 per cent vinyl butadiene units, and to have a weight-average molecular weight of about 230,000 (3). This material is relatively pure, non-crystallizing, and has a low glass-transition temperature of about  $-90^{\circ}\text{C}$ , so that near-equilibrium behavior can be obtained at moderately high temperatures and low rates of deformation. The second elastomer was an ethylene-propylene copolymer containing about 45 per cent by weight of ethylene (Vistalon 404, EXXON Chemical Company). In this case, a terpolymer (Vistalon 4608, containing about 3.2 per cent of a diene comonomer) was used for crosslinking with sulfur. The mix formulations used are given in the Appendix.

Flat sheets about 0.5 mm thick were prepared from each mix by premolding them for a few minutes at  $80^{\circ}\text{C}$  between films of polyethylene terephthalate (Mylar, Type 300A, E. I. du Pont de Nemours and Company). After this premolding step, the elastomer sheets were crosslinked to a certain degree by heating them for a time  $t_1$  in a heated press at  $150^{\circ}\text{C}$ . After 24 hours at room temperature, the Mylar films were removed and two sheets, crosslinked to the same degree, were immediately pressed into intimate contact and subjected to further



crosslinking by a further period  $t_2$  of heating at  $150^\circ\text{C}$ . The total time of heating  $t_1 + t_2$  was chosen so that the crosslinking process was substantially complete after this time, Figure 1. Only slight pressure was exerted on the sheets during this second crosslinking stage, in order to minimize elastic deformation.

Two measurements were employed to provide estimates of the degree of crosslinking at various times of reaction and hence of the degree of interlinking when two sheets were brought together after partial crosslinking and then crosslinked to completion. The first consisted of measurements of the stress-strain relations in simple extension. The results were plotted in the form suggested by the predicted tensile stress-strain relation for a material that conforms to the Mooney strain energy function for rubberlike materials (4),

$$f/2A_0 (\lambda - \lambda^{-2}) = C_1 + C_2/\lambda \quad (1)$$

where  $f$  is the tensile force,  $A_0$  is the cross-sectional area of the test strip in the unstrained state,  $\lambda$  is the elongation ratio, i.e., the ratio of the stretched length to the unstretched length, and  $C_1$  and  $C_2$  are elastic constants. The tensile measurements were found to give reasonably linear relations when plotted in accordance with equation (1) and values of  $C_1$  and  $C_2$  obtained from the intercept at  $1/\lambda = 0$  and the slope are given in Table 1.

According to the kinetic theory of rubber elasticity, the coefficient  $C_1$  is related to the effective number  $\nu$  of molecular network strands per unit volume ( 5 ) :

$$C_1 = \frac{1}{2} \nu kT, \quad (2)$$

where  $k$  is Boltzmann's constant and  $T$  is absolute temperature. Although the magnitude of the numerical term in this relation is somewhat debatable, and  $\nu$  may include physically-entangled molecular strands as well as chemically crosslinked ones, the  $C_1$  term has been found to be approximately proportional to the number of chemical crosslinks, at least for one particular crosslinking system ( 6 ). A similar proportionality is assumed to hold for the present crosslinking systems also.

The second method employed for studying the development of crosslinking was by measuring the equilibrium degree of swelling of the samples in n-heptane or benzene. Values of the volume fraction  $c$  of rubber in the swollen gel are given in Table 1, together with values of the number  $\nu$  of molecular network strands per unit volume, calculated from  $c$  by means of the Flory-Huggins relationship ( 7 ) :

$$\nu = -A[\ln(1-c) + c + \chi_1 c^2] / V_1 (c^{1/3} - c/2) \quad (3)$$

where  $A$  is Avogadro's number,  $V_1$  is the molar volume of the

swelling liquid and  $\chi_1$  is the rubber-liquid interaction parameter. Values of  $\chi_1$  were obtained from published data; the values used are listed in Table 1.

A series of samples was made with varying amounts of interfacial interlinking by varying the time  $t_1$ , and hence the amount of crosslinking of the elastomer sheets before they were brought into contact and the crosslinking process taken to completion. The final degree of crosslinking of all the samples in the series was identical, because the total cure time  $t_1 + t_2$  was held constant. It corresponded to the fully-cured state. Only the amount of interfacial bonding was varied, decreasing as the time  $t_1$  increased. The extent of interfacial bonding for each specimen was characterized by the increase  $\Delta C_1$  in the elastic constant  $C_1$ , and by the increase  $\Delta \nu$  in the number  $\nu$  of network strands per unit volume, as the time of cure was increased from  $t_1$  to  $t_1 + t_2$ .

A peeling test, shown in Figure 2, was used to determine the work  $G_a$  of detachment per unit area of interface. Various rates of peel were used, ranging from 0.4 to 170  $\mu\text{m/s}$ , and the tests were carried out either at room temperature, about 23°C, or at 90-100°C. Also, some specimens were swollen uniformly

by a light paraffin oil before being peeled apart.

The work of detachment was calculated from the measured peel force as follows:

$$G_a = 2\lambda_s^2 F/w \quad (4)$$

where  $\lambda_s$  is the linear swelling ratio, ranging from 1.0 for unswollen specimens up to a maximum value of 1.75, and  $w$  is the width of the bonded interface. The factor  $\lambda_s^2$  takes into account the reduced number of molecular chains crossing unit area of interface in a swollen elastomer<sup>(11)</sup>. As will be shown later, values of  $G_a$  for both swollen and unswollen samples were found to agree closely when calculated in this way, provided that the measurements on unswollen samples were made under certain conditions, namely, at low rates of peel and at high temperatures. Contributions to the strength of adhesion from viscous or dissipative processes in the bulk material are minimized under these test conditions and the measured work of detachment may be regarded as an inherent property of the interface. It is termed here the threshold detachment energy, to distinguish it from the (larger) values obtained under other test conditions, i.e., at lower temperatures and at higher rates of peel.

Measurements of tear strength, or cohesive fracture energy, were made for each fully-cured material, using a somewhat similar test method, Figure 3. Again, threshold values of the tear energy  $\underline{G_c}$  per unit area of the fracture plane were determined by employing low rates of tearing, high test temperatures, or samples swollen with paraffin oil (11, 12). Equation (4) was adopted for calculating  $\underline{G_c}$  from the measured tear force, the width  $\underline{w}$  of the tear path being measured subsequently, by microscopy of the torn surfaces.

Experimental results and discussion(a) Polybutadiene, crosslinked with dicumyl peroxide

Measurements of the work of detachment  $G_a$  are shown in Figures 4 and 5 plotted against the rate  $R$  of peeling. These measurements were carried out at a temperature of  $100^\circ\text{C}$  to minimize viscoelastic contributions to the observed peel strength. At the lowest rates of peeling the results do, indeed, approach asymptotically towards threshold values,  $G_o$ , which range from 5 to  $60 \text{ J/m}^2$ , depending upon the degree of chemical interlinking.

Further increase of the test temperature is neither an effective nor a practical way to reduce viscoelastic contributions to peel strength still further, since the internal viscosity of polybutadiene is rather insensitive to temperature at temperatures greater than  $100^\circ\text{C}$  or so, and the elastomer itself becomes liable to thermal or oxidative decomposition. Measurements were therefore made instead on selected samples swollen with light paraffin oil. As shown in Figure 6, the dependence of the work of detachment upon rate of peeling was greatly reduced for the swollen samples, but the extrapolated threshold values at zero peel rate were approximately the same as before.

It should be noted that the measured work of detachment for swollen samples has been corrected by the factor  $\lambda_s^2$ , where  $\lambda_s$  is the linear swelling ratio (1.38 in the present experiments). Thus, the numerical agreement obtained between the results for dry and swollen samples confirms the extrapolation procedure for determining the threshold work of detachment.

The time  $t_1$  of crosslinking the two sheets separately before they were brought together for subsequent reaction for a further time  $t_2$  was varied from 0 to 90 minutes. As the sheets were fully crosslinked after 90 minutes, the lowest curve,  $t_1 = 90$  min, in Figure 4 represents adhesion with little or no chemical interlinking and the uppermost curve,  $t_1 = 0$  min, represents zero time of crosslinking of the sheets separately, and full crosslinking together. In the second case the peeling experiment consists of tearing through a single sheet. As the energy required for tear propagation is formally equivalent to a detachment energy, although larger in value, it can be compared directly with the detachment energy for partially-interlinked sheets.

In Figures 7 and 8, values of the detachment energy  $G_0$  under threshold conditions, obtained by extrapolating

experimental values over a wide range of peel velocities to a zero-velocity condition, are plotted against the two measures of the degree of chemical interlinking. In Figure 7, the increase  $\Delta C_1$  in the Mooney-Rivlin elastic coefficient  $C_1$  has been employed as a measure of the amount of interlinking. As can be seen, the threshold strength of adhesion was found to increase in direct proportion to the degree of interfacial bonding, from very low values up to the measured tear energy, denoted by an open circle and square for the two levels of crosslinking employed in these experiments.

The second method of measuring the degree of crosslinking of the sheets and hence the degree of interlinking, was by means of the equilibrium degree of swelling. Again, the threshold strength of adhesion was found to be accurately proportional to the increase  $\Delta v$  in the degree of crosslinking of the two elastomer sheets whilst they were in contact, Figure 8.

Thus, there appears to be a direct proportionality between the mechanical strength obtained under threshold conditions and the density of chemical bonding between the two elastomer layers. This proportionality extended over the entire range of interlinking, from zero, when only dispersion forces are assumed to



apply at the interface, up to the fully crosslinked state, when cohesive rupture took place by tearing.

It is noteworthy that the sheets prepared with 0.2 percent of dicumyl peroxide crosslinking agent were weaker under all circumstances than the sheets prepared with a smaller amount of dicumyl peroxide. They were weaker in adhesion and weaker in tear strength, in the fully reacted state. This change in tear strength has been attributed by Lake and Thomas to the polymeric nature of elastomers (13). In order to rupture a molecular network strand, all <sup>of</sup> the bonds in that strand must be stretched equally. Thus, more energy is expended in breaking longer strands than shorter ones. Materials that are more highly crosslinked and contain shorter network strands will therefore be weaker than less highly crosslinked materials, as is observed experimentally (12, 14).

It now appears that the same factor is present in the detachment energy of partially interlinked layers. Although the threshold energy is directly proportional to the number of interlinking strands, it is also dependent upon their length, being uniformly lower when the strand length is shorter.

(b) Poly(ethylene-co-propylene) (EPR), crosslinked with dicumyl peroxide

Similar experiments were carried out for EPR layers. Typical peeling and tearing results for both unswollen and swollen samples are shown in Figure 9. Again, good agreement was obtained between the extrapolated results for unswollen samples at low rates of peel or tear and those for samples swollen in paraffin oil. These values have been taken as the threshold energy of detachment or tear energy.

As the initial period  $t_1$  of crosslinking decreased and the  $t_2$  of interlinking increased, the threshold work of detachment increased continuously. In Figures 10 and 11  $G_0$  is plotted against the two measures of the amount of interfacial bonding, the increase  $\Delta C_1$  in the elastic coefficient  $C_1$  and the increase  $\Delta v$  in the density  $v$  of molecular strands calculated from equilibrium swelling measurements. Again, a direct proportionality is obtained between the threshold strength and the inferred density of chemical interlinking. However, on extrapolating the peel strength results to the fully-interlinked state the value deduced for the threshold fracture energy, about  $40 \text{ J/m}^2$ , is much smaller than the experimentally-determined value, about  $80 \text{ J/m}^2$ . This discrepancy is much larger than errors associated with either the peeling or tearing experiments. Moreover, it is in marked contrast to the good agreement found for BR layers,

as described in the preceding section. It is attributed to microscopic roughness of the tear plane in EPR, and in other samples (see later), in contrast to the relatively smooth torn surfaces of peroxide-crosslinked BR(15), and the smooth plane of separation of flat adhering layers. Apart from the anomalously-high threshold tear strength, however, the effects of chemical interlinking for EPR layers are closely similar to those observed for BR layers, raising the strength of adhesion from a low value, about  $1 \text{ J/m}^2$ , when no chemical interlinking is present, up to a value of about  $40 \text{ J/m}^2$  in the fully-interlinked state.

(c) Polybutadiene, crosslinked with sulfur

Two vulcanization recipes were used; a conventional one, giving polysulfide crosslinks, and an efficient one giving a higher proportion of monosulfidic crosslinks. Two levels of crosslinking were achieved with each recipe by changing the amounts of accelerator and sulfur. Details are given in the Appendix.

A series of interlinked sheets was prepared as before, with varying amounts of interlinking. The degree of interlinking was determined as before, from measurements of the equilibrium degree of swelling in n-heptane. The work of separation was then measured at various rates of peel and at a temperature of 120°C. By extrapolation to zero rate of peel, values of the threshold detachment energy  $G_0$  were deduced. They are plotted in Figures 12 and 13 for the two vulcanization systems.

Reasonably linear relations were obtained between  $G_0$  and the inferred degree of interlinking  $\Delta v$  between the two layers. Again, the extrapolated value of the detachment energy for fully-interlinked sheets was found to be considerably below the directly-measured value of tear energy for the fully-crosslinked sheets, especially for sheets made using a conventional sulfur recipe, (Table 2). This discrepancy is again attributed to a marked roughness of the tear plane on a microscopic scale, even at high temperatures and low rates of tear.

A further anomaly was noted in the present experimental results. The threshold energy of detachment for fully-cured sheets pressed together, when the degree of chemical interlinking should be zero, was found to be relatively large, 15 - 25 J/m<sup>2</sup> for the conventional sulfur recipes and 5 - 15 J/m<sup>2</sup> for the EV recipes, in contrast to the small values obtained previously for peroxide-cured sheets, of only 1 - 2 J/m<sup>2</sup>. Continued crosslinking of the contacting sheets is known not to take place. However, rearrangement of existing crosslinks, without much change in the total amount, has been reported for networks containing polysulfidic crosslinks (16). It is noteworthy that the level of adhesion obtained with fully-crosslinked sheets is higher for the conventional recipe, containing a greater proportion of labile polysulfide crosslinks, than for the EV system. It is, therefore, suggested that the abnormally high values of the energy of detachment for fully-cured sheets pressed together arises from interchange reactions of polysulfidic crosslinks, leading to chemical interlinking of the two sheets.

(d) Poly(ethylene-co-propylene) (EPDM), crosslinked with sulfur.

Similar experiments were carried out with an ethylene-propylene-diene terpolymer, containing about 3.2 per cent of the diene comonomer, crosslinked with a sulfur vulcanization system. The results are given in Figure 14, where the threshold energy of detachment  $G_0$  for two interlinked sheets

is plotted against the degree  $\Delta v$  of interlinking, inferred from swelling measurements on the sheets before and after they were joined together. In this case a markedly nonlinear dependence of  $G_0$  upon  $\Delta v$  was found. Substantially the same general results were obtained using the increases in the elastic coefficient  $C_1$  as a measure of interlinking, so that the nonlinearity cannot be attributed solely to errors in measuring  $v$  by swelling.

It appears to be a feature of the particular cross-linking system employed. The present recipe gives an extremely large threshold tear strength, of about 200 J/m<sup>2</sup> (Table 2), so that the rapid rise in the detachment energy at high degrees of interlinking may reflect the onset of gross roughening of the plane of separation. However, the low initial rate of increase of the energy of detachment with the degree of interlinking requires further examination. It suggests the presence of a surface contaminant preventing intimate contact of fully-cured or nearly fully-cured sheets. Such a contaminant could well be produced during this sulfur-accelerator crosslinking reaction, in the form of a relatively insoluble by-product.

### Conclusions

1. With the single exception noted above, of a sulfur-cured EPDM system, the threshold mechanical strength of adhesion between two elastomer layers has been shown to be directly proportional to the degree of chemical interlinking.
2. At any degree of interlinking, the threshold strength has been found to be lower for networks composed of shorter molecular strands, which are thus interlinked by shorter strands. This is in accord with the Lake-Thomas theory for the threshold strength of elastomer networks.
3. The extrapolated value of the strength of adhesion for fully-interlinked layers agreed well with the measured tear strength for BR layers crosslinked with peroxide, but in all other cases the measured tear strength was higher than the extrapolated value, Table 2. This discrepancy is attributed to a marked roughness of the tear plane during tearing experiments in contrast to the smooth plane of separation for two adhering layers. It is noteworthy that the peroxide-cured BR materials gave relatively smooth torn surfaces. They were also the weakest elastomers studied. Observations of torn surfaces of elastomers are described elsewhere (15).
4. Unusually high levels of adhesion were noted between fully-crosslinked sheets of sulfur-cured BR. They are provisionally attributed to an interchange of labile polysulfidic crosslinks across the interface.

References

1. A. Ahagon and A. N. Gent, J. Polymer Sci. Polymer Phys. Ed. 13, 1285-1300 (1975).
2. P. Dreyfuss, Y. Eckstein, Q. S. Lien and H. H. Dollwet, submitted to J. Polymer Sci. Polymer letters Ed.
3. W. S. Bahary, D. I. Sapper and J. H. Lane, Rubber Chem. Technol. 40, 1529-1543 (1967).
4. L. R. G. Treloar, "The Physics of Rubberlike Elasticity," 2nd. ed., Oxford University Press, London, 1968, p. 156, eq. (8.12).
5. Ibid, pp. 71 and 193.
6. C. G. Moore and W. F. Watson, J. Polymer Sci. 19, 237-254 (1956).
7. Ref. 4, p. 136, eq. (7.22a).
8. G. Kraus, J. Appl. Polymer Sci. 7, 1257-1263 (1963).
9. U. Flisi and G. Crespi, J. Appl. Polymer Sci. 12, 1947-1957 (1968).
10. T. J. Dudek and F. Bueche, Rubber Chem. Technol. 37, 894-903 (1964).
11. H. K. Mueller and W. G. Knauss, Trans. Soc. Rheol. 15, 217-233 (1971).
12. A. Ahagon and A. N. Gent, J. Polymer Sci. Polymer Phys. Ed. 13, 1903-1911 (1975).
13. G. J. Lake and A. G. Thomas, Proc. Roy. Soc. (Lond.)



A300, 108-119 (1967).

14. A. N. Gent and R. H. Tobias, in preparation.
15. A. N. Gent and C. T. R. Pulford, in preparation.
16. L. Bateman, C. G. Moore, M. Porter and B. Saville,  
Chap. 15 in "The Chemistry and Physics of Rubberlike  
Substances," John Wiley & Sons, New York, 1963.

Appendix

The following mix formulations in parts by weight were employed to prepare test specimens. Crosslinking was effected by heating at 150° C (140° C for recipe VIII).

Polybutadiene (BR), Peroxide Crosslinking

- I. Diene 35 NFA (Firestone Rubber And Latex Company), 100; dicumyl peroxide, 0.08.
- II. Diene 35 NFA, 100; dicumyl peroxide, 0.20.

Poly(ethylene-co-propylene) (EPR), Peroxide Crosslinking

- III. Vistalon 404 (EXXON Chemical Company) 100; dicumyl peroxide, 2.7; sulfur, 0.32.

Polybutadiene (BR), Conventional Crosslinking

- IV. Diene 35 NFA, 100; zinc oxide, 5; stearic acid, 2; phenyl-2-naphthylamine 1, benzothiazyl disulfide, 1.5; sulfur, 2.
- V. As for recipe IV, except: benzothiazyl disulfide, 3; sulfur, 4.

Polybutadiene (BR), EV Sulfur Crosslinking

- VI. Diene 35 NFA, 100; zinc oxide, 5; zinc 2-ethylhexanoate, 2; Agerite Resin D (Vanderbilt Chemical Company), 1; 2-morpholiniothio benzothiazole, 0.72; tetrabutylthiuram disulfide, 0.3; sulfur, 0.3.
- VII. As for recipe VI, except: 2-morpholiniothio benzothiazole, 1.44; tetrabutylthiuram disulfide, 0.6; sulfur, 0.6.

Poly(ethylene-co-propylene) (EPDM), Sulfur Crosslinking

- VIII. Vistalon 4608 (EXXON Chemical Company), 100; zinc oxide, 4; stearic acid, 1; 2-mercaptobenzothiazole, 0.6; 50/50

mixture of tetramethylthiuram disulfide and tetraethylthiuram disulfide, 1.5; sulfur, 1.5.

Table 1. Kinetics of crosslinking for BR (recipes I and II), EPR (recipe III), and EPDM (recipe VIII).

<u>Cure time</u> (Min at 150°C)	$\frac{C_1}{(k Pa)}$	$\frac{C_2}{(k Pa)}$	$c^a$	$\frac{M_c^b}{(kg/mole)}$	$\frac{v^b \times 10^{-26}}{(m^{-3})}$
<u>BR, 0.08 per cent DCP (Recipe I)</u>					
15	0	93	0.090	56.5	0.10
20	17	143	-	-	-
25	20.5	162	0.201	14.9	0.36
30	-	-	0.220	12.8	0.42
35	52	176	0.239	11.1	0.49
50	87	208	0.259	9.6	0.58
90	107	212	0.308	6.9	0.81
140	114	240	0.335	5.8	0.92
<u>BR, 0.2 per cent DCP (Recipe II)</u>					
11	14	167	-	-	-
15	53.5	201	0.262	9.1	0.59
20	70	229	0.316	6.55	0.82
25	118	235	0.336	5.8	0.93
40	176	243	0.392	4.05	1.34
60	228	211	0.427	3.2	1.67
80	247	308	0.438	3.0	1.79

EPR, 2.7 per cent DCP, 0.32 per cent S (Recipe III)

10	5.5	162	0.193	40.0	0.13
20	32.5	193	0.271	8.8	0.59
30	58	189	0.324	5.0	1.04
40	68	191	0.338	4.3	1.20
60	79	201	0.362	3.5	1.47
90	85	206	0.360	3.5	1.49

EPDM, sulfur-cured (Recipe VIII)

15	0	350	0.081	84.1	0.06
17.5	-	-	0.094	62.5	0.08
20	1,820	401	0.166	17.3	0.30
25	8,010	405	0.246	6.5	0.80
30	10,000	410	0.280	4.6	1.12
35	-	-	0.292	4.1	1.25
70	13,800	385	0.312	3.45	1.51
100	14,700	395	0.324	3.1	1.67

-----  
and EPDM

<sup>a</sup> BR swollen in n-heptane, EPR swollen in benzene.

<sup>b</sup> Calculated from  $\underline{c}$  by means of equation (3) using the following values for  $\chi_1$ .

$$\chi_1 = 0.37 + 0.52c \text{ for BR/n-heptane system (9).}$$

$$\chi_1 = 0.485 + 0.256c \text{ for EPR/benzene system (10).}$$

$$\chi_1 = 0.44 \text{ for EPDM/n-heptane system (11).}$$

Table 2. Comparison of the extrapolated threshold work of separation  $G_{od}$  for fully-interlinked sheets with the measured threshold tear energy  $G_{ot}$ .

<u>Polymer</u>	<u>Recipe</u>	<u>Cure time</u> (min at 150 °C)	$\frac{v \times 10^{-26}}{(m^{-3})}$	$\frac{G_{od}}{(J/m^2)}$	$\frac{G_{ot}}{(J/m^2)}$
<u>Peroxide crosslinking systems</u>					
BR	I	90	0.85	62	58 ± 4
BR	II	80	1.75	41	45 ± 4
EPR	III	70	1.45	41	76 ± 4
<u>Sulfur crosslinking systems</u>					
BR	IV	80	0.70	56	140 ± 15
BR	V	80	1.10	42	115 ± 10
BR	VI	60	0.95	45	76 ± 5
BR	VII	80	1.35	38	62 ± 12
EPDM	VIII	80 (140°C)	1.55	-	215 ± 15

Figure Legends

- Figure 1. Sketch of crosslinking reaction.
- Figure 2. Peel test.
- Figure 3. Tear test.
- Figure 4. Detachment energy  $G_a$  at  $100^\circ \text{C}$  vs. rate  $R$  of peel for partially-interlinked BR sheets (recipe I, 0.08 per cent dicumyl peroxide).
- Figure 5. Detachment energy  $G_a$  at  $100^\circ \text{C}$  vs. rate  $R$  of peel for partially-interlinked BR sheets (recipe II, 0.2 per cent dicumyl peroxide).
- Figure 6. Detachment energy  $G_a$  or fracture energy  $G_c$  at  $100^\circ \text{C}$  vs. rate  $R$  of crack propagation for partially-interlinked BR sheets, recipe I, dry ( $\bullet$ ) and swollen with paraffin oil ( $\circ$ ),  $\lambda_s = 1.38$ .
- Figure 7. Threshold detachment energy  $G_o$  vs. increase  $\Delta C_1$  in the elastic coefficient  $C_1$  while two BR sheets were crosslinked in contact. Recipes I and II.
- Figure 8. Threshold detachment energy  $G_o$  vs. increase  $\Delta v$  in the density  $v$  of network chains while two BR sheets were crosslinked in contact. Recipes I and II.
- Figure 9. Detachment energy  $G_a$  or fracture energy  $G_c$  at  $90^\circ \text{C}$  vs. rate  $R$  of crack propagation for partially-interlinked EPR sheets, recipe III, dry ( $\bullet$ ) and swollen with paraffin oil ( $\circ$ ),  $\lambda_s = 1.50$ .
- Figure 10. Threshold detachment energy  $G_o$  vs. increase  $\Delta C_1$  in the elastic coefficient  $C_1$  while two EPR sheets

were crosslinked in contact. Recipe III.  $G_o(\bullet), G_c(O)$ .

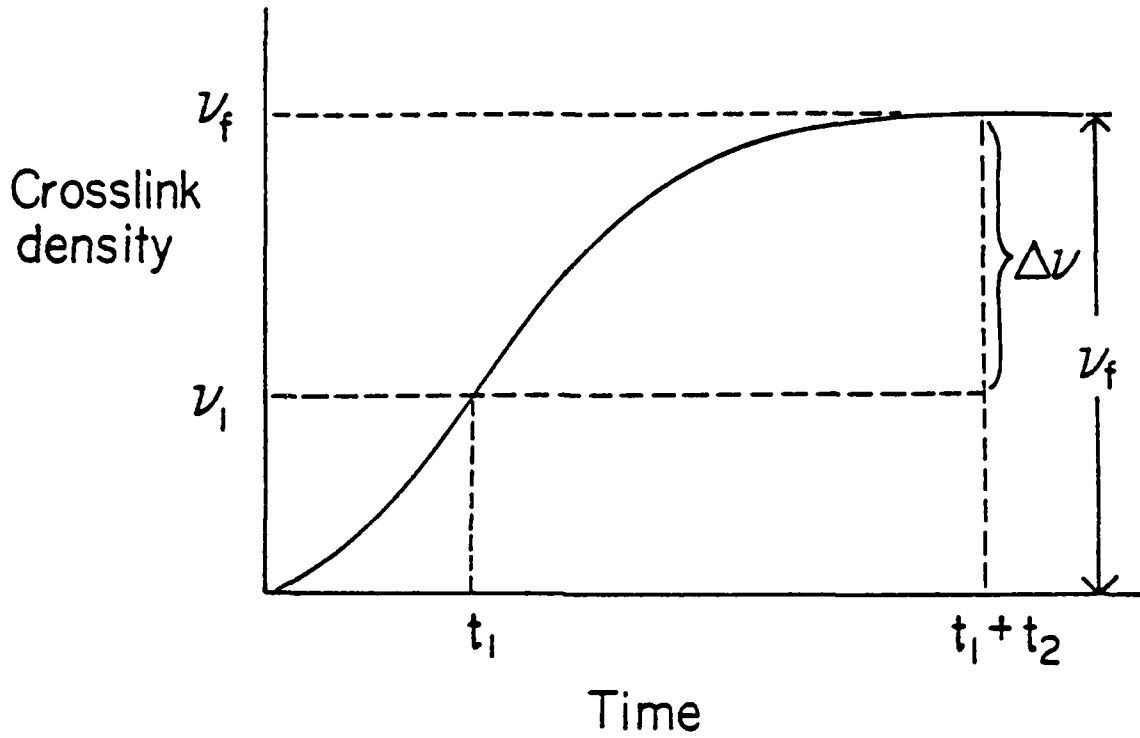
Figure 11. Threshold detachment energy  $G_o$  vs. increase  $\Delta v$  in the density  $v$  of network chains while two EPR sheets were crosslinked in contact. Recipe III.

Figure 12. Threshold detachment energy  $G_o$  vs. increase  $\Delta v$  in the density of network chains while two BR sheets were crosslinked in contact, using conventional sulfur recipes (IV and V).

Figure 13. Threshold detachment energy  $G_o$  vs. increase  $\Delta v$  in the density of network chains while two BR sheets were crosslinked in contact using EV sulfur recipes (VI and VII).

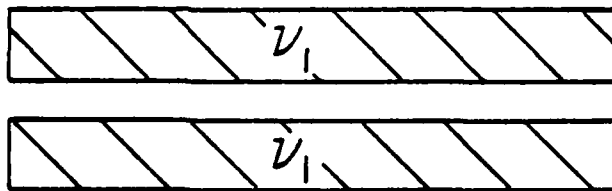
Figure 14. Threshold detachment energy  $G_o$  vs. increase  $\Delta v$  in the density of network chains while two EPDM sheets were crosslinked in contact using a sulfur recipe (VIII).





Step 1

Partially crosslinked for time  $t_1$



Step 2

Crosslinked in contact for a further time  $t_2$

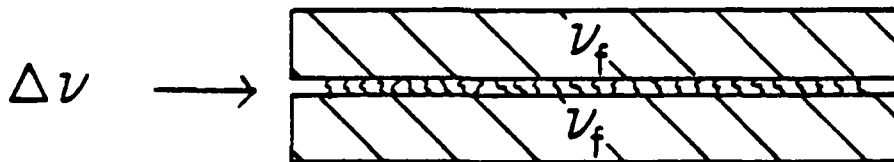


FIGURE 1

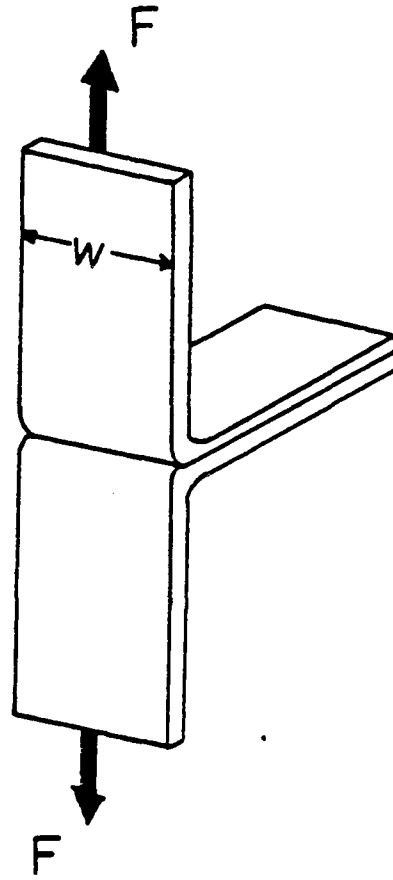


FIGURE 2

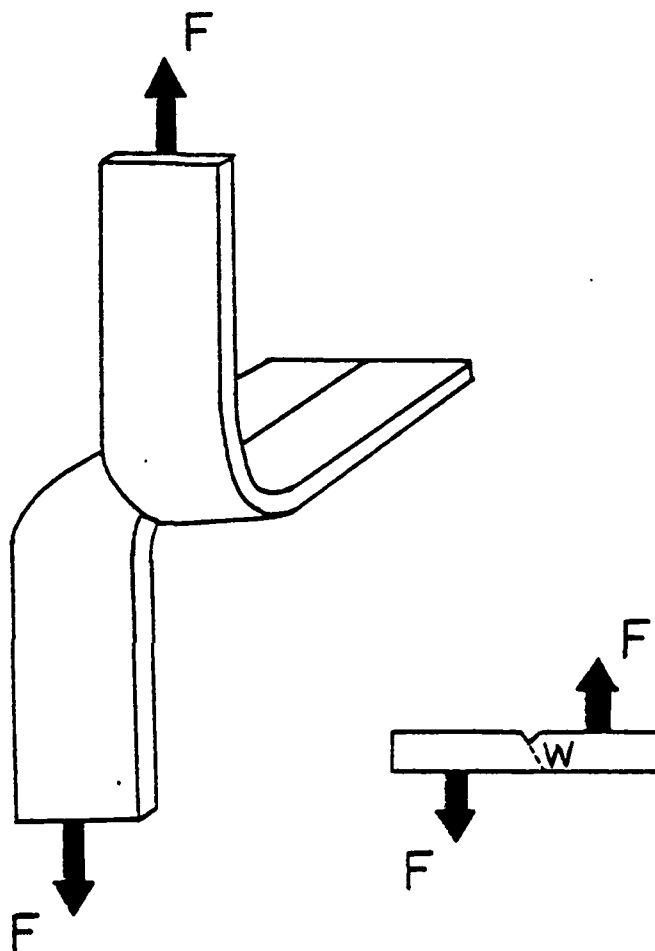


FIGURE 3

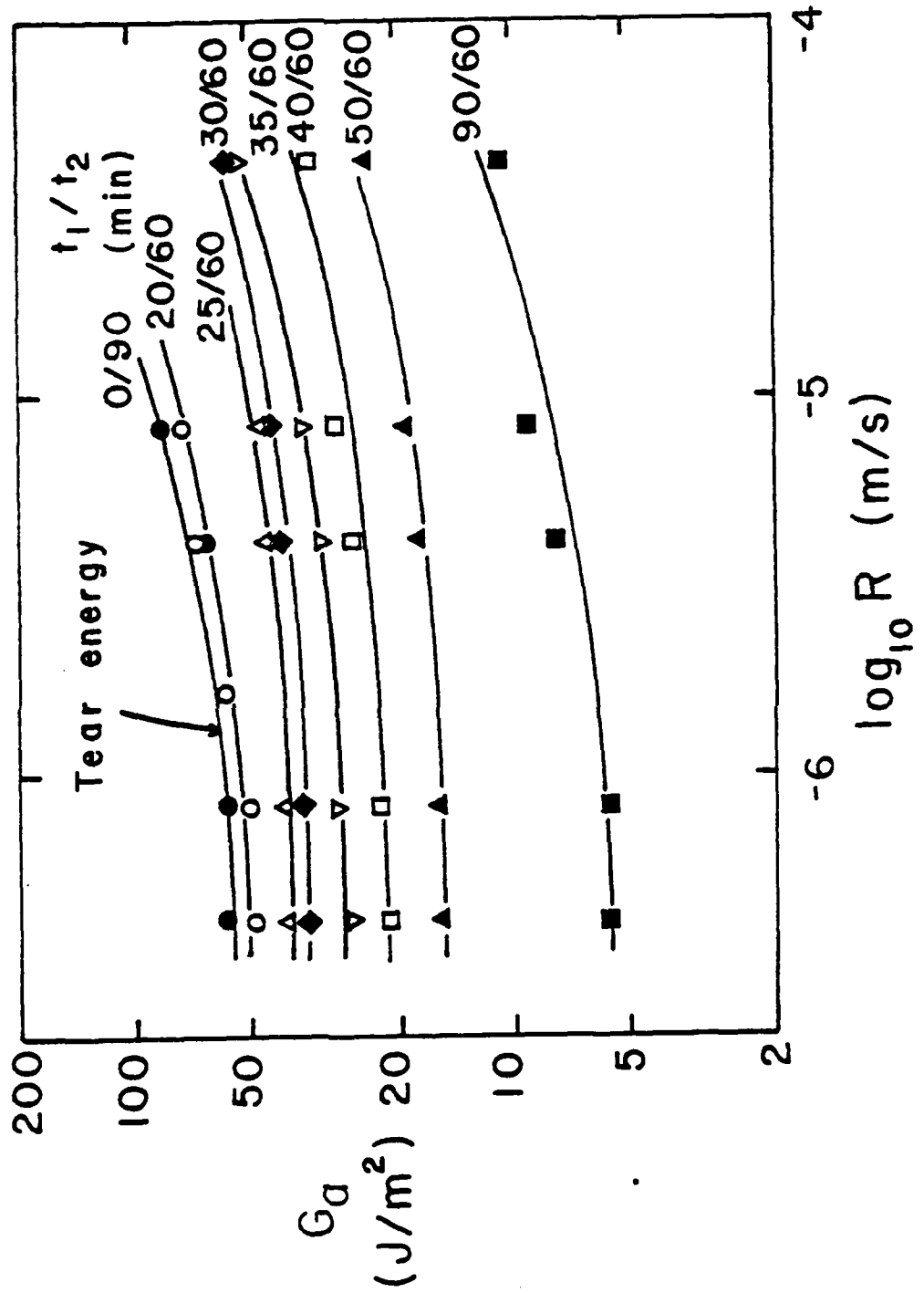


FIGURE 4

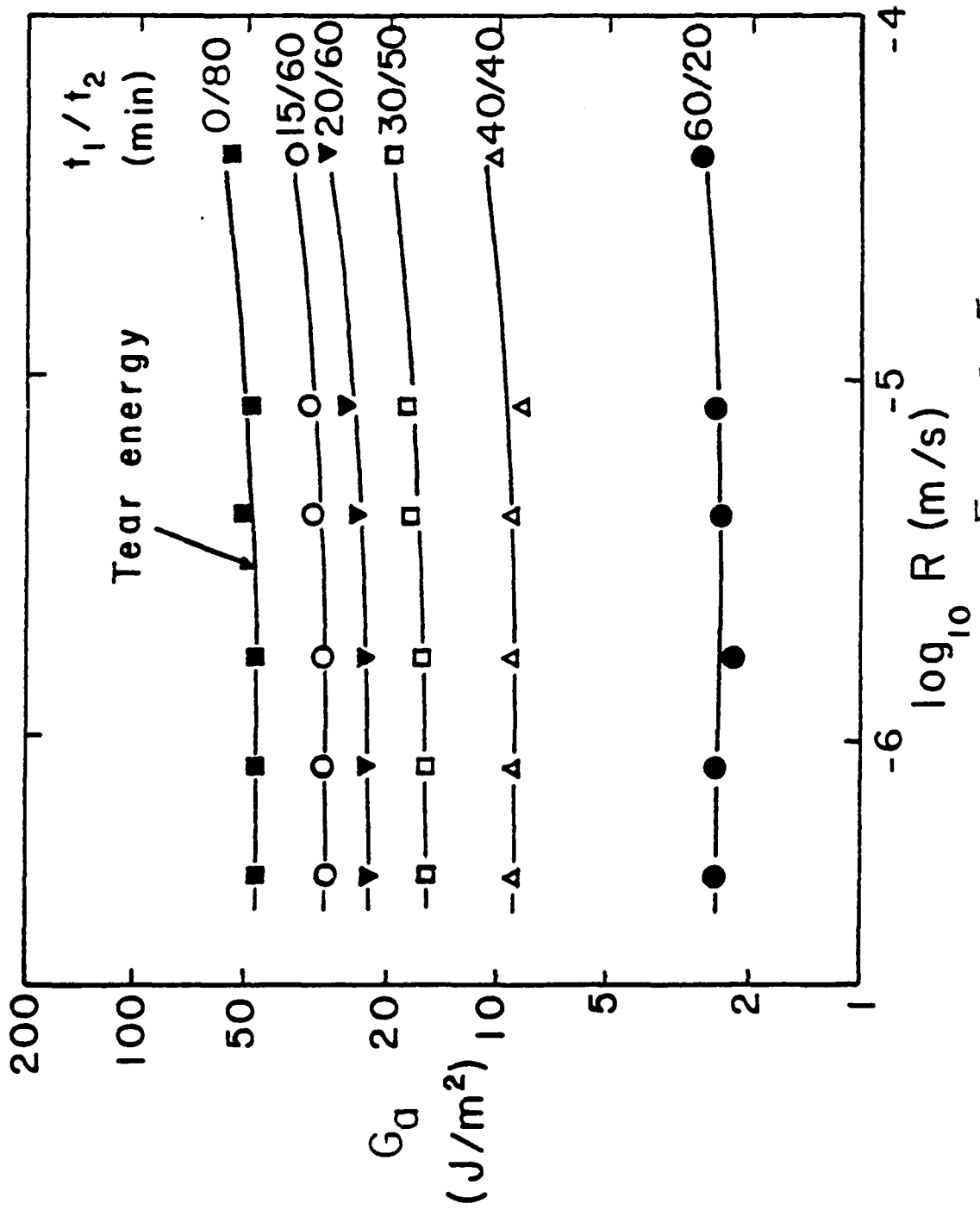


FIGURE 5

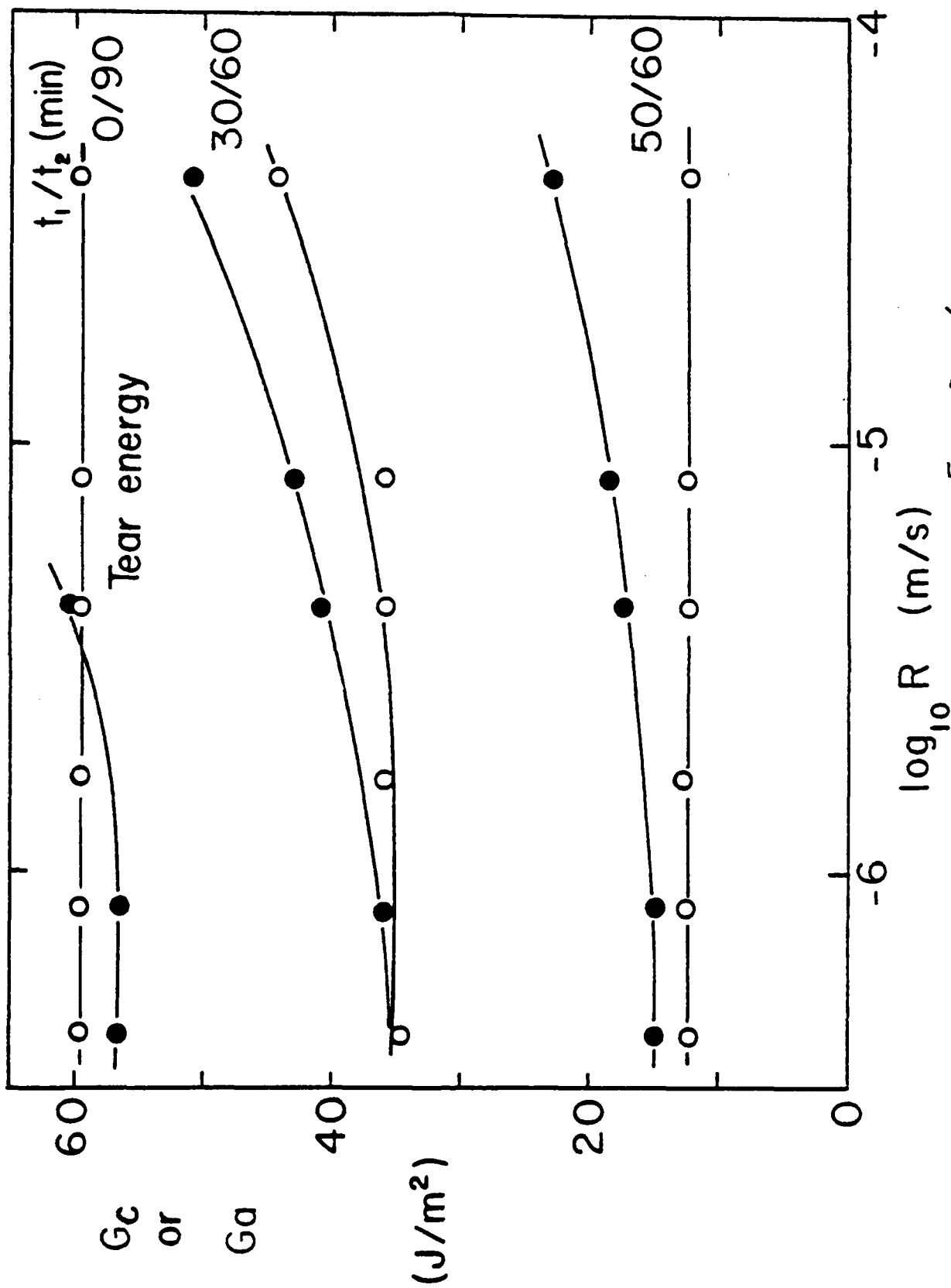


FIGURE 6

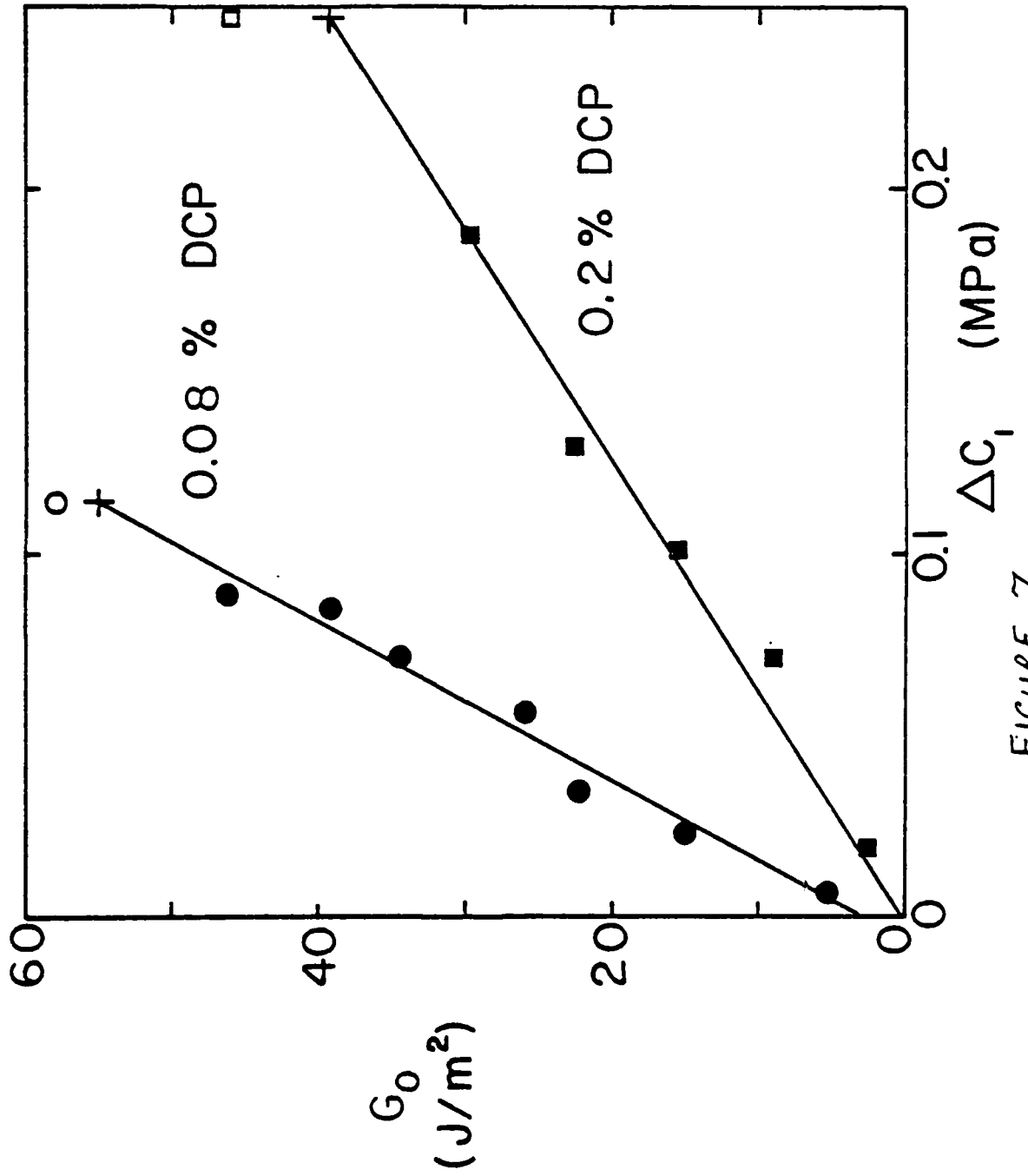
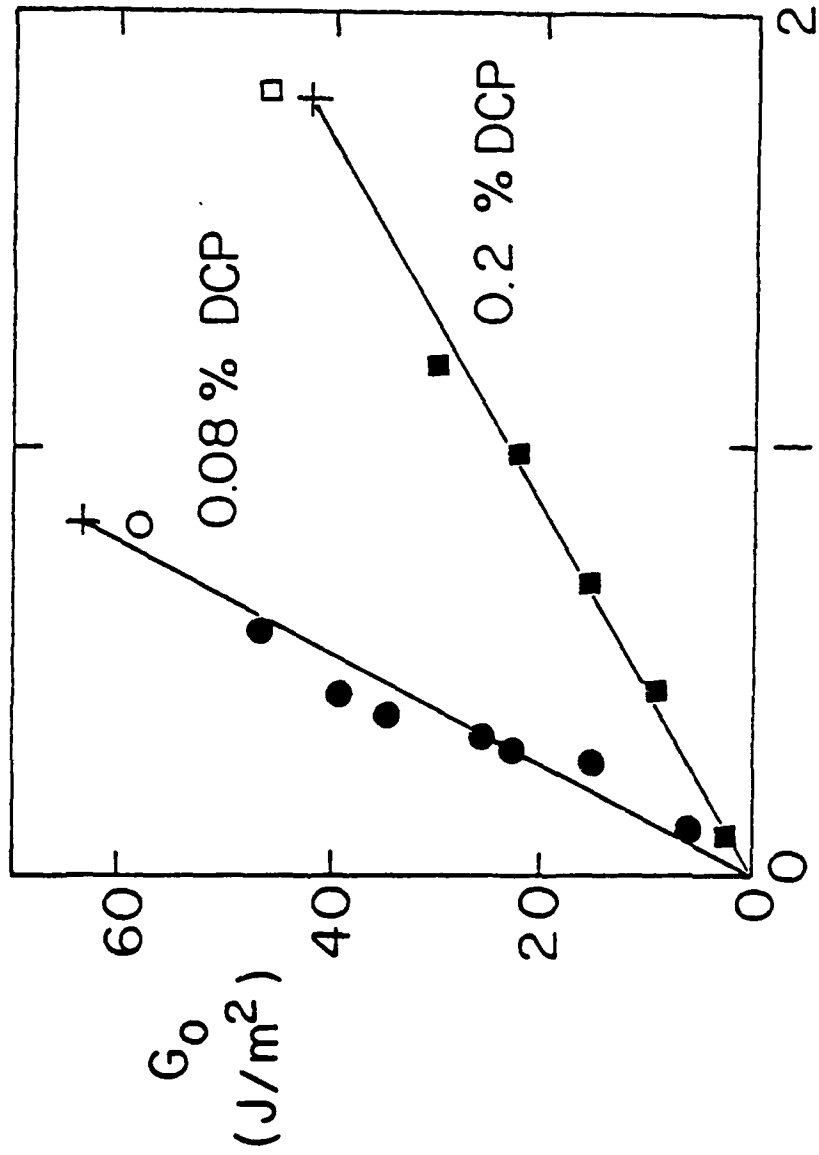


FIGURE 7



$\Delta\nu \times 10^{-26}$  ( $m^{-3}$ )

FIGURE 8



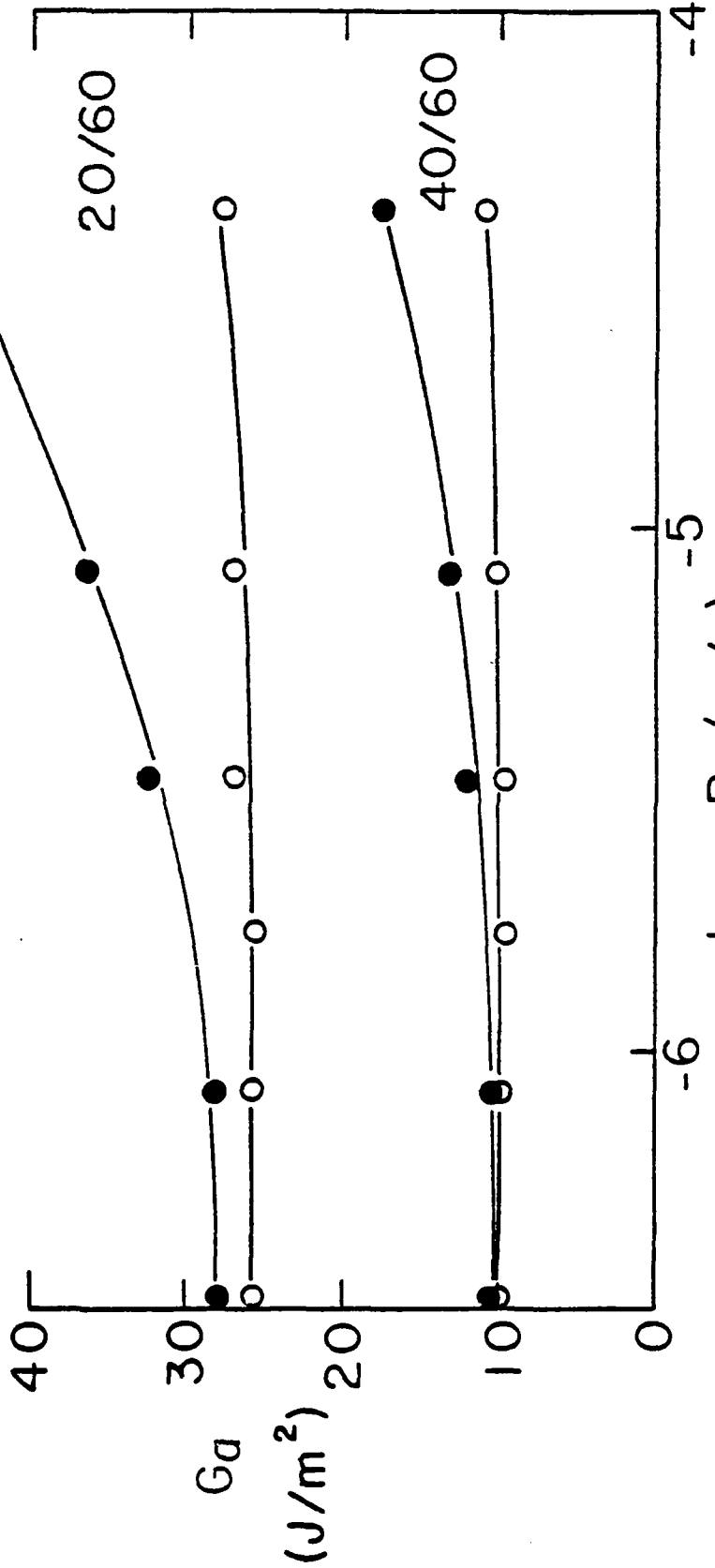
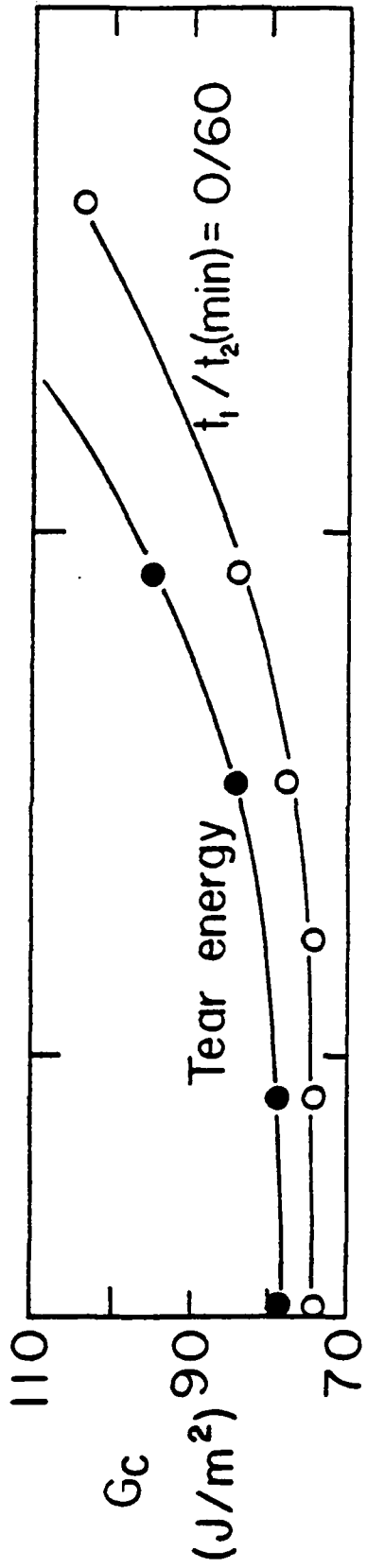


FIGURE 9

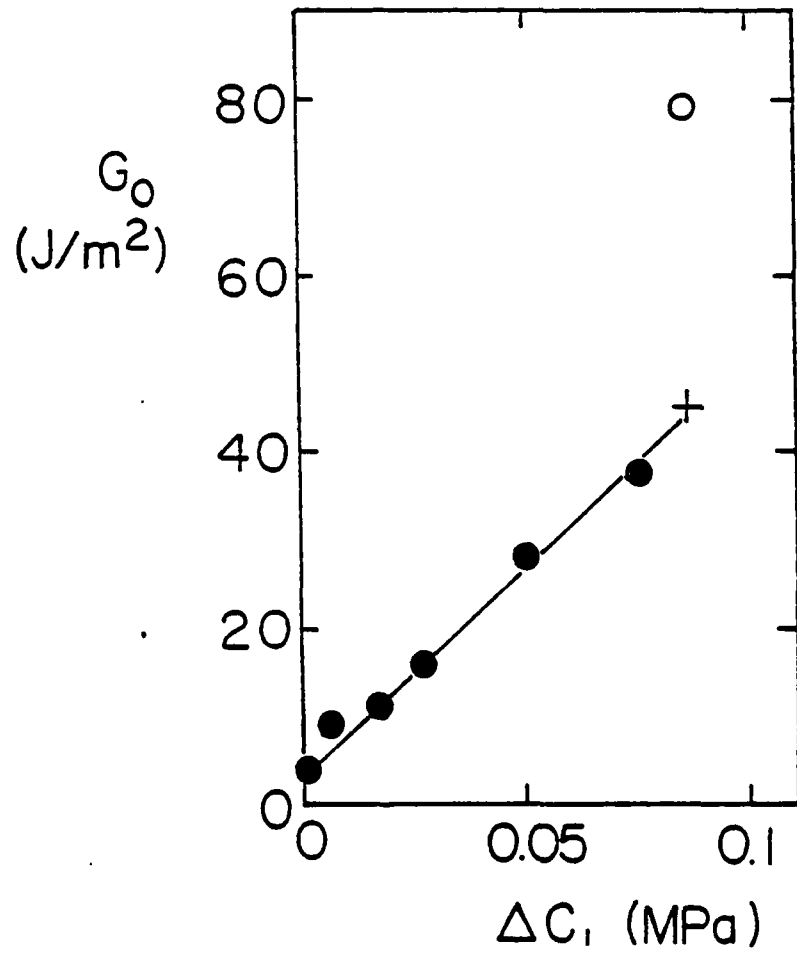


FIGURE 10

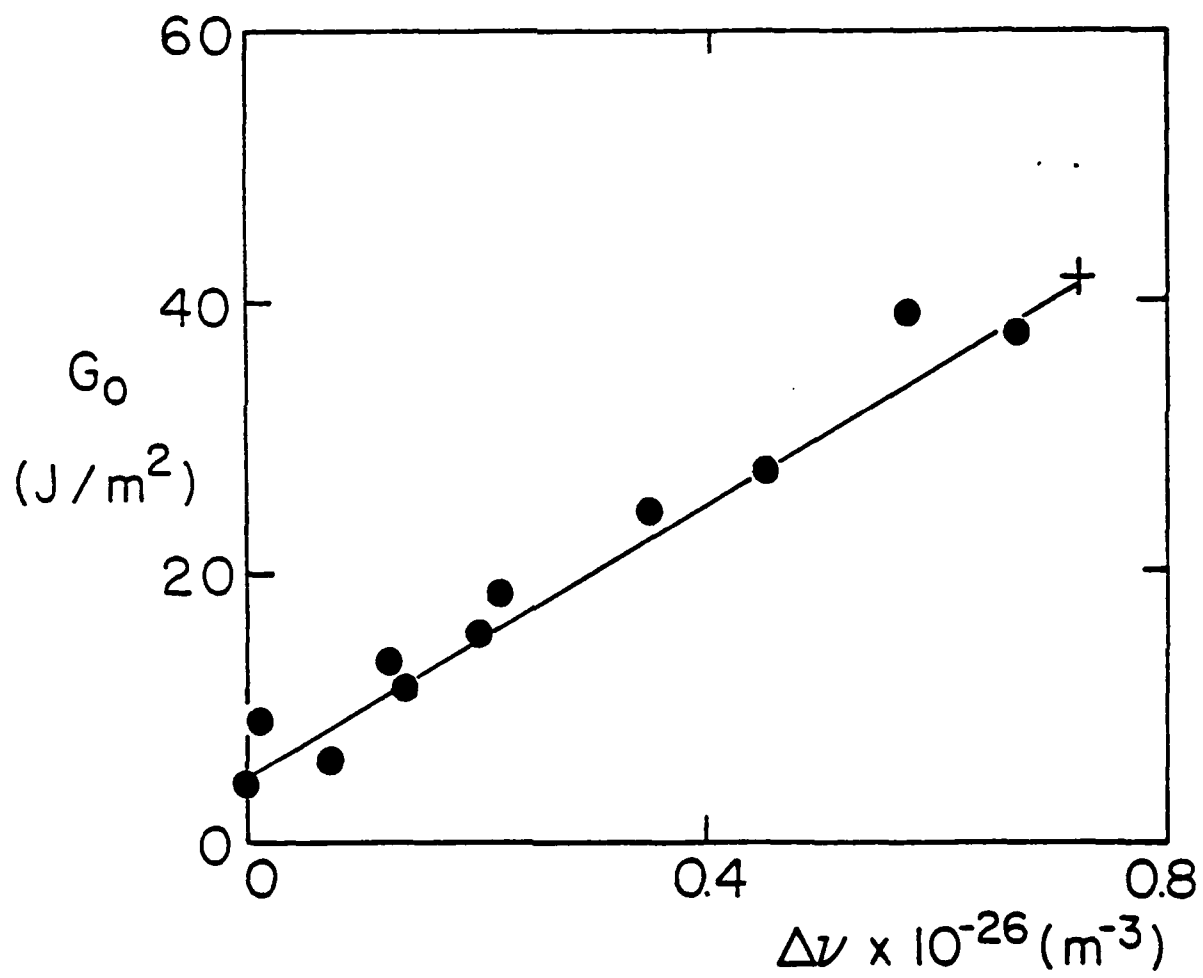


FIGURE 11

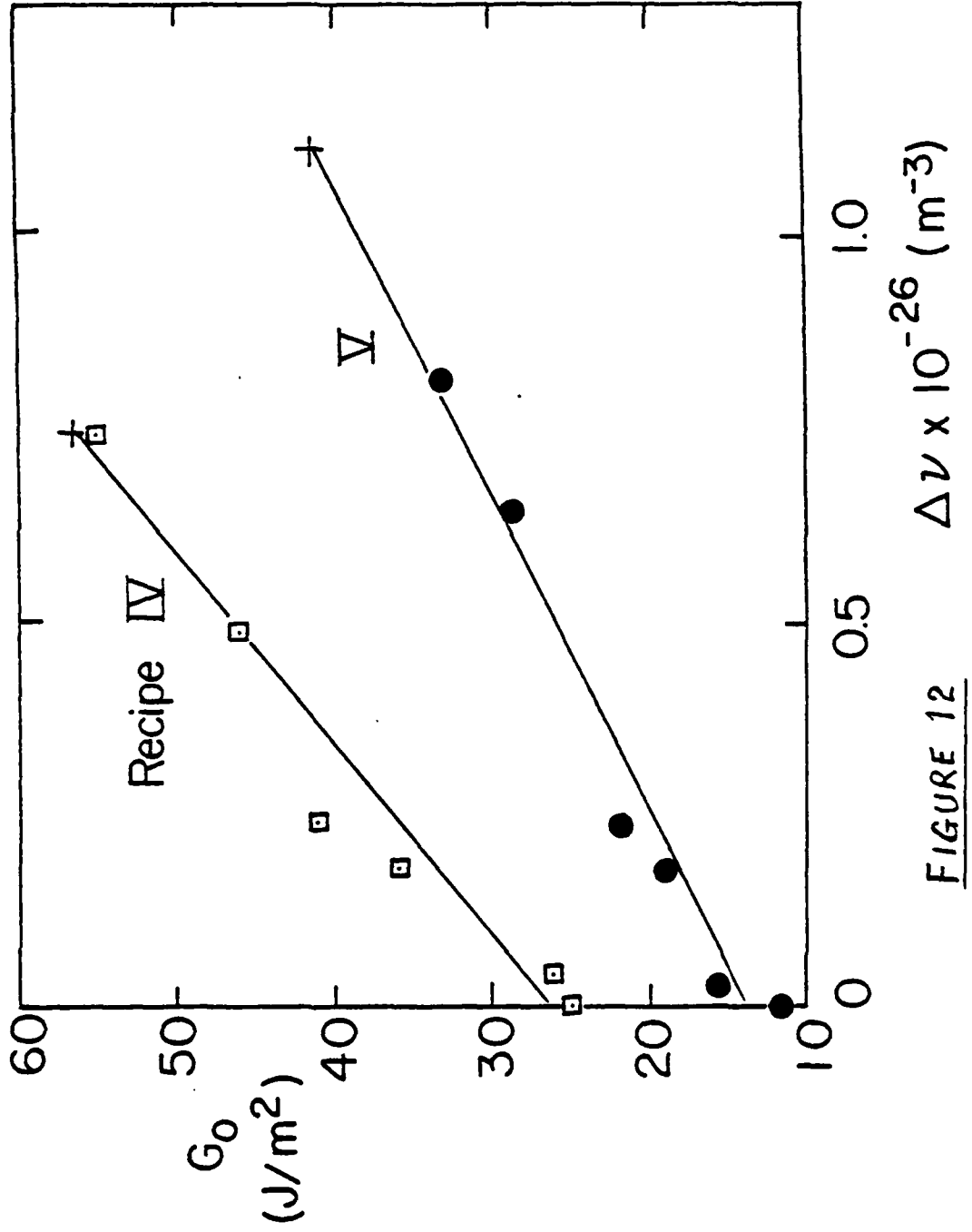


FIGURE 12

$\Delta\nu \times 10^{-26}$  ( $m^{-3}$ )

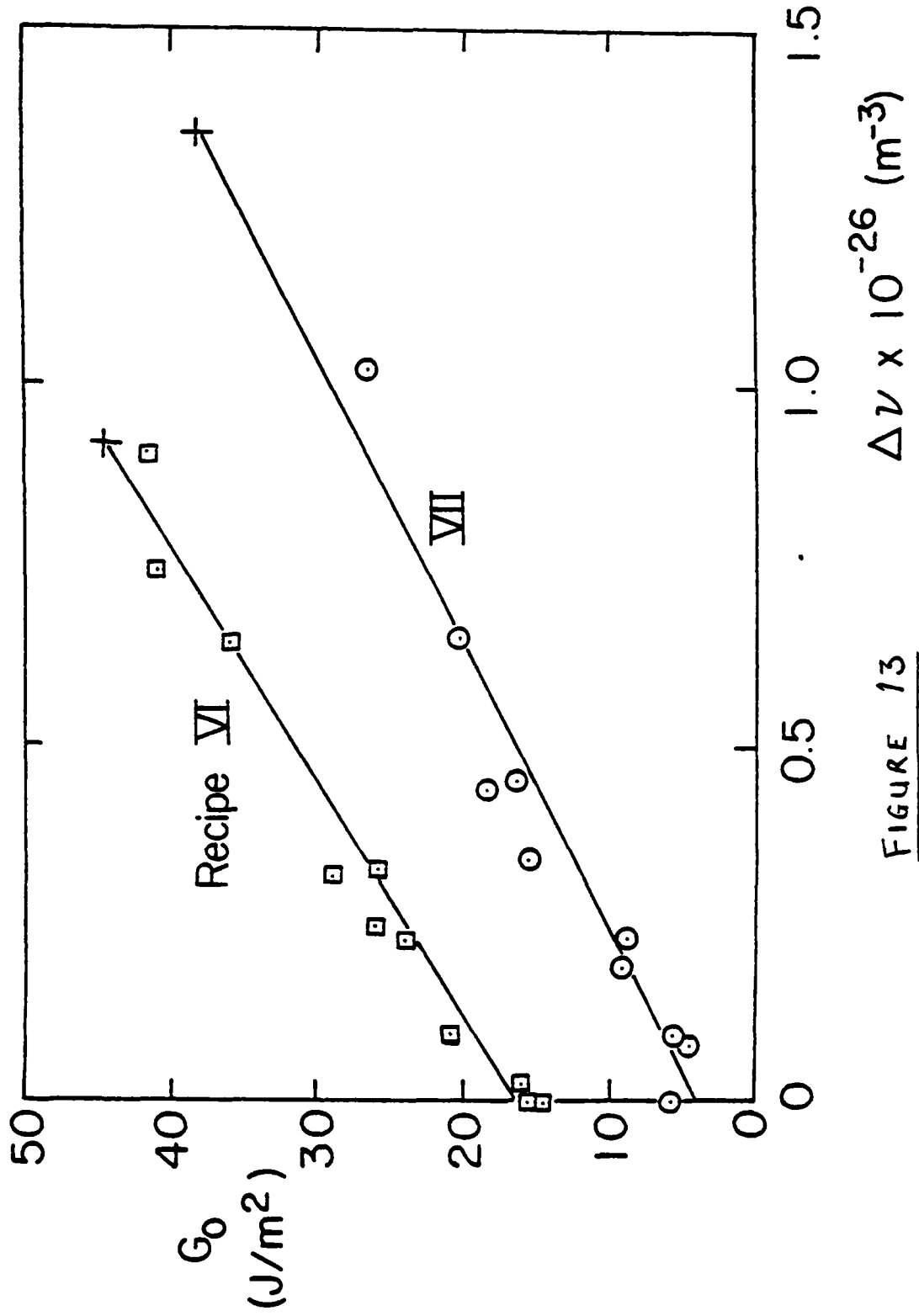


FIGURE 13

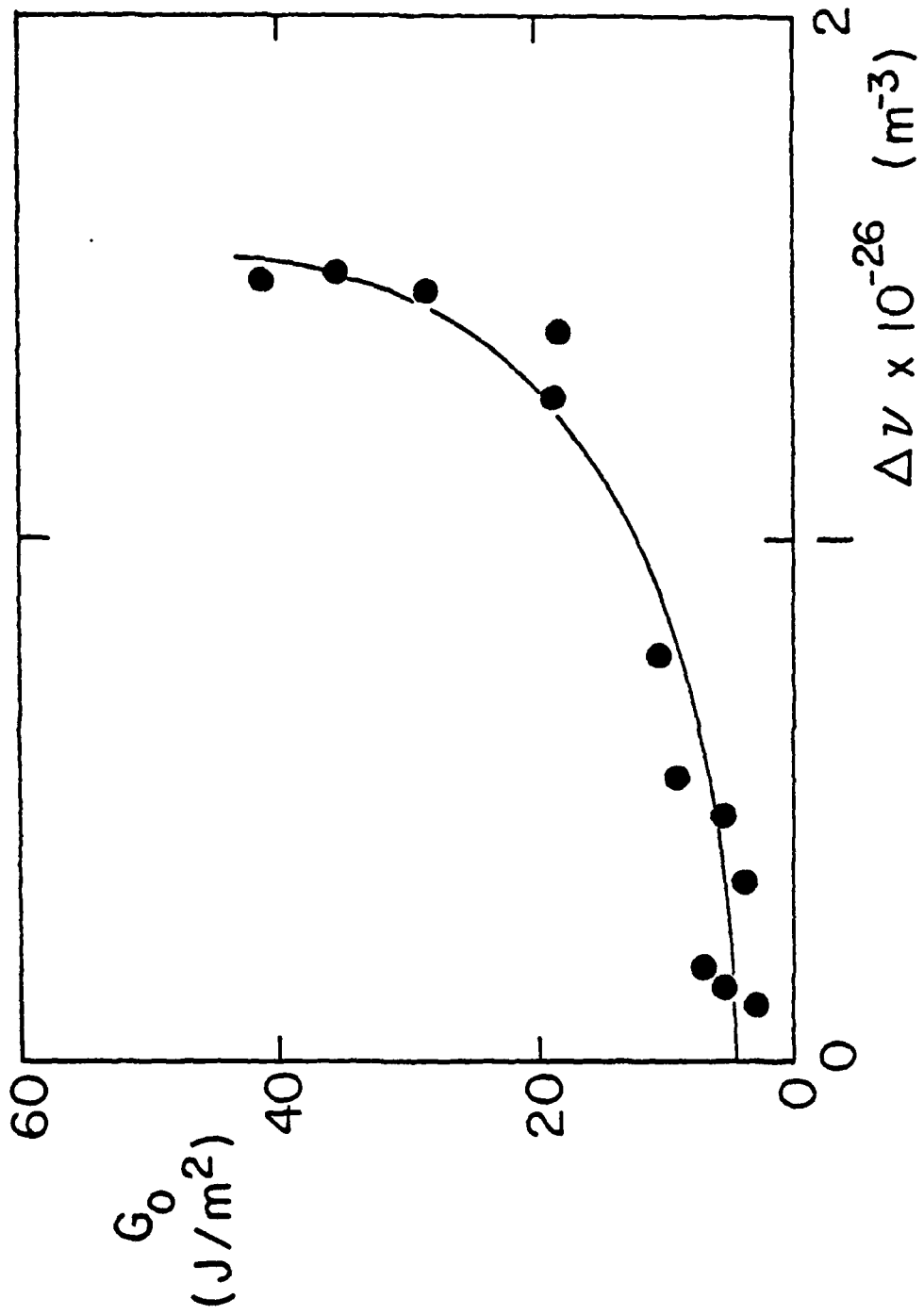


FIGURE 14

ENERGETIC MATERIALS RESEARCHDISTRIBUTION LIST

	<u>No. Copies</u>		<u>No. Copies</u>
Assistant Secretary of the Navy (R, E, and S) Attn: Dr. R.E. Reichenbach Room 5E787 Pentagon Washington, DC 20350	1	AFATL Eglin AFB, FL 32542 Attn: Dr. Otto K. Heiney	1
Office of Naval Research Code 473 Arlington, VA 22217 Attn: Dr. R. Miller	10	AFRPL Code PACC Edwards AFB, CA 93523 Attn: Mr. W. C. Andrepont	1
Office of Naval Research Code 2008 Arlington, VA 22217 Attn: Dr. J. Enig	1	AFRPL Code CA Edwards AFB, CA 93523 Attn: Dr. R. R. Weiss	1
Office of Naval Research Code 260 Arlington, VA 22217 Attn: Mr. D. Siegel	1	Code AFRPL MKPA Edwards AFB, CA 93523 Attn: Mr. R. Geisler	1
Office of Naval Research Western Office 1030 East Green Street Pasadena, CA 91106 Attn: Dr. T. Hall	1	Code AFRPL MKPA Edwards AFB, CA 93523 Attn: Dr. F. Roberto	1
Office of Naval Research Eastern Central Regional Office 495 Summer Street Boston, MA 02210 Attn: Dr. L. Peebles Dr. A. Wood	2	AFSC Andrews AFB, Code DLFP Washington, DC 20334 Attn: Mr. Richard Smith	1
Office of Naval Research San Francisco Area Office One Hallidie Plaza Suite 601 San Francisco, CA 94102 Attn: Dr. P. A. Miller	1	Air Force Office of Scientific Research Directorate of Chemical & Atmospheric Sciences Bolling Air Force Base Washington, DC 20332	1
Defense Technical Information Center DTIC-DDA-2 Cameron Station Alexandria, VA 22314	12	Air Force Office of Scientific Research Directorate of Aero- space Sciences Bolling Air Force Base Washington, DC 20332 Attn: Dr. L. H. Caveny	1
		Anal-Syn Lab Inc. P.O. Box 547 Paoli, PA 19301 Attn: Dr. V. J. Keenan	1

DEF.

	<u>No. Copies</u>		<u>No. Copies</u>
Army Ballistic Research Labs Code DRDAR-BLP Aberdeen Proving Ground, MD 21005 Attn: Mr. L. A. Watermeier	1	Hercules Inc. Eglin AFATL/DLDL Eglin AFB, FL 32542 Attn: Dr. Ronald L. Simmons	1
Army Ballistic Research Labs ARRADCOM Code DRDAR-BLP Aberdeen Proving Ground, MD 21005 Attn: Dr. Ingo W. May	1	Hercules Inc. Magna Bacchus Works P.O. Box 98 Magna, UT 84044 Attn: Mr. E. H. DeButts	1
Army Ballistic Research Labs ARRADCOM Code DRDAR-BLT Aberdeen Proving Ground, MD 21005 Attn: Dr. Philip Howe	1	Hercules Inc. Magna Bacchus Works P.O. Box 98 Magna, UT 84044 Attn: Dr. James H. Thacher	1
Army Missile Command Code DRSME-RK Redstone Arsenal, AL 35809 Attn: Dr. R. G. Rhoades Dr. W. W. Wharton	2	HQ US Army Material Development Readiness Command Code DRCDE-DW 5011 Eisenhower Avenue Room 8N42 Alexandria, VA 22333 Attn: Mr. S. R. Matos	1
Atlantic Research Corp. 5390 Cherokee Avenue Alexandria, VA 22314 Attn: Dr. C. B. Henderson	1	Johns Hopkins University APL Chemical Propulsion Information Agency Johns Hopkins Road Laurel, MD 20810 Attn: Mr Theodore M. Gilliland	1
Ballistic Missile Defense Advanced Technology Center P.O. Box 1500 Huntsville, AL 35807 Attn: Dr. David C. Sayles	1	Lawrence Livermore Laboratory University of California Livermore, CA 94550 Attn: Dr. M. Finger	1
Ballistic Research Laboratory USA ARRADCOM DRDAR-BLP Aberdeen Proving Ground, MD 21005 Attn: Dr. A. W. Barrows	1	Lawrence Livermore Laboratory University of California Livermore, CA 94550 Attn: Dr. R. McGuire	1
Hercules Inc. Cumberland Aerospace Division Allegany Ballistics Lab P.O. Box 210 Cumberland, MD 21502 Attn: Dr. Rocco Musso	2	Lockheed Missiles and Space Co. P.O. Box 504 Sunnyvale, CA 94088 Attn: Dr. Jack Linsk Org. 83-10 Bldg. 154	1



DEF.

	<u>No. Copies</u>		<u>No. Copies</u>
Lockheed Missile & Space Co. 3251 Hanover Street Palo Alto, CA 94304 Attn: Dr. H. P. Marshall Dept. 52-35	1	Naval Research Lab Code 6100 Washington, DC 20375	1
Los Alamos Scientific Lab P.O. Box 1663 Los Alamos, NM 87545 Attn: Dr. R. Rogers, WX-2	1	Naval Sea Systems Command Washington, DC 20362 Attn: Mr. G. Edwards, Code 62R3 Mr. J. Murrin, Code 62R2 Mr. W. Blaine, Code 62R	1
Los Alamos Scientific Lab P.O. Box 1663 Los Alamos, NM 87545 Attn: Dr. B. Craig, M Division	1	Naval Sea Systems Command Washington, DC 20362 Attn: Mr. R. Beauregard SEA 64E	1
Naval Air Systems Command Code 330 Washington, DC 20360 Attn: Mr. R. Heitkotter Mr. R. Brown	1	Naval Surface Weapons Center Code R11 White Oak, Silver Spring, MD 20910 Attn: Dr. H. G. Adolph	1
Naval Air Systems Command Code 310 Washington, DC 20360 Attn: Dr. H. Mueller Dr. H. Rosenwasser	1	Naval Surface Weapons Center Code R13 White Oak, Silver Spring, MD 20910 Attn: Dr. R. Bernecker	1
Naval Explosive Ordnance Disposal Facility Indian Head, MD 20640 Attn: Lionel Dickinson Code D	1	Naval Surface Weapons Center Code R10 White Oak, Silver Spring, MD 20910 Attn: Dr. S. J. Jacobs	1
Naval Ordnance Station Code 5034 Indian Head, MD 20640 Attn: Mr. S. Mitchell	1	Naval Surface Weapons Center Code R11 White Oak, Silver Spring, MD 20910 Attn: Dr. M. J. Kamlet	1
Naval Ordnance Station Code PM4 Indian Head, MD 20640 Attn: Mr. C. L. Adams	1	Naval Surface Weapons Center Code R04 White Oak, Silver Spring, MD 20910 Attn: Dr. D. J. Pastine	1
Dean of Research Naval Postgraduate School Monterey, CA 93940 Attn: Dr. William Tolles	1	Naval Surface Weapons Center Code R13 White Oak, Silver Spring, MD 20910 Attn: Dr. E. Zimet	1
Naval Research Lab Code 6510 Washington, DC 20375 Attn: Dr. J. Schnur	1		

DEF.

	<u>No. Copies</u>		<u>No. Copies</u>
Naval Surface Weapons Center Code R101 Indian Head, MD 20640 Attn: Mr. G. L. MacKenzie	1	Naval Weapons Center Code 388 China Lake, CA 93555 Attn: D. R. Derr	1
Naval Surface Weapons Center Code R17 Indian Head, MD 20640 Attn: Dr. H. Haiss	1	Naval Weapons Center Code 388 China Lake, CA 93555 Attn: Dr. R. Reed Jr.	1
Naval Surface Weapons Center Code R11 White Oak, Silver Spring, MD 20910 Attn: Dr. K. F. Mueller	1	Naval Weapons Center Code 385 China Lake, CA 93555 Attn: Dr. A. Nielsen	1
Naval Surface Weapons Center Code R16 Indian Head, MD 20640 Attn: Dr. T. D. Austin	1	Naval Weapons Center Code 3858 China Lake, CA 93555 Attn: Mr. E. Martin	1
Naval Surface Weapons Center Code R122 White Oak, Silver Spring, MD 20910 Attn: Mr. L. Roslund	1	Naval Weapons Center China Lake, CA 93555 Attn: Mr. R. McCarten	1
Naval Surface Weapons Center Code R121 White Oak, Silver Spring, MD 20910 Attn: Mr. M. Stosz	1	Naval Weapons Support Center Code 5042 Crane, Indiana 47522 Attn: Dr. B. Douda	1
Naval Weapons Center Code 3853 China Lake, CA 93555 Attn: Dr. R. Atkins	1	Rohm and Haas Company 723-A Arcadia Circle Huntsville, Alabama 35801 Attn: Dr. H. Shuey	1
Naval Weapons Center Code 3205 China Lake, CA 93555 Attn: Dr. L. Smith	1	Strategic Systems Project Office Dept. of the Navy Room 901 Washington, DC 20376 Attn: Dr. J. F. Kincaid	1
Naval Weapons Center Code 3205 China Lake, CA 93555 Attn: Dr. C. Thelen	1	Strategic Systems Project Office Dept. of the Navy Room 1048 Washington, DC 20376 Attn: Mr. E. L. Throckmorton Mr. R. Kinert	2
Naval Weapons Center Code 385 China Lake, CA 93555 Attn: Dr. A. Amster	1	Thiokol Chemical Corp. Brigham City Wasatch Division Brigham City, UT 84302 Attn: Dr. G. Thompson	1

DEF.

	<u>No. Copies</u>		<u>No. Copies</u>
USA ARRADCOM DRDAR-LCE Dover, NJ 07801 Attn: Dr. R. F. Walker	1	Georgia Institute of Technology Office of Research Administration Atlanta, Georgia 30332 Attn: Professor Edward Price	1
USA ARRADCOM DRDAR-LCE Dover, NJ 07801 Attn: Dr. N. Slagg	1	Univ. of Utah Dept. of Mech. & Industrial Engineering MEB 3008 Salt Lake City, Utah 84112 Attn: Dr. Stephen Swanson	1
U.S. Army Research Office Chemistry Division P.O. Box 12211 Research Triangle Park, NC 27709	1	Space Sciences, Inc. 135 Maple Avenue Monrovia, CA 91016 Attn: Dr. M. Farber	1
Institute of Polymer Science University of Akron Akron, OH 44325 Attn: Professor Alan N. Gent	1	Washington State University Dept. of Physics Pullman, WA 99163 Attn: Professor G.D. Duvall	1
SRI International 333 Ravenswood Avenue Menlo Park, CA 94025 Attn: Dr. Y.M. Gupta	1	Univ. of Maryland Department of Mechanical Eng. College Park, MD 20742 Attn: Professor R.W. Armstrong	1
Graduate Aeronautical Lab. California Institute of Technology Pasadena, CA 91125 Attn: Professor W.G. Knauss	1	The Catholic University of America Physics Department 520 Michigan Ave., N.E. Washington, D.C. 20017 Attn: Professor T. Litovitz	1
Pennsylvania State University Dept. of Mechanical Engineering University Park, PA 16802 Attn: Professor Kenneth Kuo	1	Sandia Laboratories Division 2513 P.O. Box 5800 Albuquerque, N.M. 87185 Attn: Dr. S. Sheffield	1
Office of Naval Research 800 N. Quincy St. Arlington, VA 22217 Attn: Dr. G. Neece Code 472	1	IBM Research Lab. K42.282 San Jose, CA 95193 Attn: Dr. Thor L. Smith	1
Thiokol Corp. Huntsville Huntsville Div. Huntsville, AL 35807 Attn: Mr. J.D. Byrd	1	California Institute of Tech. Dept. of Chemical Engineering Pasadena, CA 91125 Attn: Professor N.W. Tschoegl	1
Washington State University Dept. of Physics Pullman, WA 99163 Attn: Prof. T. Dickinson	1	Northwestern University Dept. of Civil Engineering Evanston, IL 60201 Attn: Professor J.D. Achenbach	1
University of California Dept. of Chemistry 405 Hilgard Avenue Los Angeles, CA 90024 Attn: Prof. M.F. Nicol	1	Office of Naval Research Structural Mechanics Program Arlington, VA 22217 Attn: Dr. N.L. Basdekas, Code 474	1

DEF.

No. Copies

University of California Berkeley, CA 94720 Attn: Prof. A.G. Evans	1
Texas A&M Univ. Dept. of Civil Engineering College Station, TX 77843 Attn: Professor Richard A. Schapery	1
SRI International 333 Ravenswood Ave. Menlo Park, CA 94025 Attn: Mr. M. Hill	1
Los Alamos Scientific Laboratory Los Alamos, NM 87545 Attn: Dr. J.M. Walsh	1
Rockwell International 12214 Lakewood Blvd. Downey, California 90241 Attn: H. M. Clancy, Mail Stop AB70	1

DATE  
FILMED  
— 8