NASA CR 65734

# *Aerospace Research Center*

## HIGH TEMPERATURE STABLE CARBORANE ADHESIVES

CONTRACT NAS 9-5527

FINAL REPORT

**Prepared for:**

National Aeronautics and Space Administration
Manned Spacecraft Center
2101 Webster-Seabrook Road
Houston, Texas.

FACILITY FORM 602

| | |
|---|---|
| N67-39393 | |
| (ACCESSION NUMBER) | (THRU) |
| 52 | 1 |
| (PAGES) | (CODE) |
| CR#65734 | 18 |
| (NASA CR OR TMX OR AD NUMBER) | (CATEGORY) |

January 15, 1967

GENERAL PRECISION AEROSPACE
Little Falls, New Jersey

Rg/47611

# HIGH TEMPERATURE STABLE CARBORANE ADHESIVES

Contract NAS 9-5527

FINAL REPORT

Prepared for:

National Aeronautics and Space Administration
Manned Spacecraft Center
2101 Webster-Seabrook Road
Houston, Texas.

Approved: Daniel Grafstein
Dr. Daniel Grafstein
Principal Staff Scientist
Manager, Materials Department

January 15, 1967

**RESEARCH CENTER**
**AEROSPACE GROUP**
GENERAL PRECISION, INC.
LITTLE FALLS, NEW JERSEY

## ABSTRACT

The terminal diolefins, bis(butenyl)carborane and bis(hexenyl)carborane, were prepared and converted to the corresponding diepoxide monomers, bis(epoxybutyl)carborane and bis(epoxyhexyl)carborane. Polymerization was demonstrated with several different catalytic reagents. Both epoxy derivatives were easily cured to hard solids at 175°C in the presence of boron trifluoride monoethylamine. Evaluation of the cured systems for adhesive applications was initiated based on this catalyst. Lap-shear test specimens were assembled from type 17-7 stainless steel strips. Bond strength values increased markedly during the program as curing conditions were optimized and lay-up conditions were improved. Room temperature bond-strengths up to 2810 p.s.i. were achieved with the bis(epoxyhexyl)carborane system. The corresponding epoxybutyl system gave values up to 1840 p.s.i. Post cure at 250°C for one hour in the former resulted in a decrease of 15 - 25% in the room temperature bond strengths. Failure was cohesive in all instances where glass cloth was used as a binder in the joint area. The results are sufficiently encouraging to suggest that further work will lead to a practical high temperature adhesive system.

# ADMINISTRATIVE INFORMATION

This twelve-month program was sponsored by the NASA-Manned Spacecraft Center, Houston, Texas under Contract NAS 9-5527, Control No. P.R.No. 5320022. The NASA Technical Representative was Mr. Ivan K. Spiker/ES4. The Project Supervisor at the General Precision Inc., Aerospace Research Center, 1225 McBride Avenue, Little Falls, New Jersey was Dr. Daniel Grafstein. The principal contributing personnel were Dr. Robert Barnes and Dr. Edward J. Hughes. Mr. William Benko assisted in the preparation of monomers and the assembly of lap-shear specimens. Results of the Instron testing program were obtained with the assistance of Mr. Fred Bossler and Mr. Charles Maccia. Infrared spectra were obtained with the assistance of Mrs. Elizabeth Sevean, Mr. Lawrence Flint and Mr. Clifford Whitmore.

# TABLE OF CONTENTS

## TABLE OF CONTENTS

Page

## TABLE OF CONTENTS

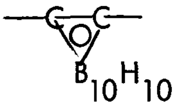
## LIST OF ILLUSTRATIONS

# I. INTRODUCTION

The object of this program was the synthesis of adhesives that are stable above 600°F, and as high as 1000°F for aerospace applications. To achieve this objective, we undertook to prepare and study certain epoxy adhesives containing carborane units in the polymer structure.

Aside from the problem of thermal stability, conventional epoxies offer an unlimited scope of modification and application possibilities. However, the best epoxy systems, such as those derived from bis-phenol A, are not serviceable above 350°F. Modified epoxy phenolics are very versatile adhesives and are serviceable to 350°F continuously. They retain satisfactory strength for short exposures up to 500°F. Our approach to the design of a high temperature adhesive was to incorporate a group into the simple epoxide system which serves to increase thermal stability without detracting from the favorable characteristics of epoxies, particularly their ready cure without by-product evolution. Since the carborane polyhedron appears to impart excellent thermal and physical properties to certain polymer structures in which it is incorporated, it seemed appropriate to construct a polymer system which combined a carborane moiety with an epoxy function.

The carboranes, first reported in 1963, are noted for their inherent thermal and chemical stability, their non-polar character and their high solubility in organic solvents. In the series $RR'C_2B_{10}H_{10}$, carborane is the trivial name given to the compound where R and R' are hydrogens attached to the adjacent carbon atoms. The fundamental $C_2B_{10}H_{10}$ structure is nearly icosahedral and can be represented by the following flat projection.

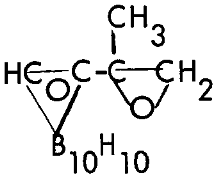


The electronic distribution in the polyhedron is highly delocalized over the entire structure. A strong electron-withdrawing character, attributed to the polyhedron, affects the chemistry of various groups bonded to the icosahedral carbon atoms. The polyhedron is remarkedly stable to oxidizing and reducing agents. This permits selective oxidation and reduction reactions to be performed on the organic substituents.(1)

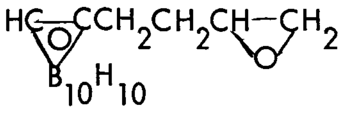
The thermal stability of carboranes is remarkable when compared to that of other boron-hydrogen containing materials. A slow isomerization occurs when carborane is heated at 465 - 500°C in an inert atmosphere(2), forming meta carborane. Para carborane is formed at 630°C(3).

Several research teams have concentrated recently on the synthesis of high temperature stable polymers by the incorporation of carborane and metacarborane units into polymer structures with other groups(4 - 5). The increased thermal stability of these polymers over conventional systems is due in part to the electron defiency of the carborane group and its influence on the thermal stability of adjacent chemical bonds. The bulky, three-dimensional ring system also induces a degree of internal plasticization in the polymer, presumably because it prevents close-packing of the polymer chains.

A few monofunctional epoxyalkylcarboranes have previously been described(2), including epoxy propylcarborane and epoxybutylcarborane. The ease of ring-opening is apparently dependent on the proximitry of the electron withdrawing carborane cage to the epoxy linkage. For example, the isopropyl derivative,

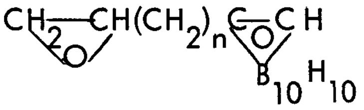


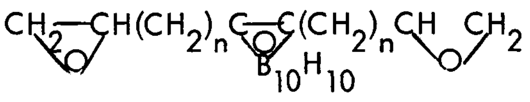
is stable to attack by acids whereas, under identical conditions, the epoxy linkage in the butyl derivative



is readily cleaved.

In order to investigate the potential usefulness of carboranes as high temperature adhesives, this program has been designed to synthesize epoxyalkylcarborane monomers of the following type





where n = 2, 4

and to investigate their adhesive qualities in the presence of several conventional catalytic curing agents. Progress on the program is presented under the following headings.

1. Synthesis of Carborane Intermediates
2. Synthesis of Epoxycarborane Monomers
3. Curing and Polymerization Studies
4. Adhesive Bond Property Evaluation

# II. DISCUSSION

## A. SYNTHESIS OF CARBORANE INTERMEDIATES

The synthesis of several epoxyalkylcarborane monomers required the initial preparation of the corresponding alkenyl and dialkenyl carboranes. Although the particular dialkenyl carboranes of interest have not been described before, methods for the synthesis of substituted carboranes had been well established by previous workers in the field. The compounds were prepared in a stepwise fashion starting from decaborane. First carborane was synthesized in four steps according to a published reaction sequence(2, 3). The pertinent reaction sequences, and the amounts of materials prepared, are summarized below.

### 1. 6,9-Bis(acetonitrilo)decaborane (BAND)

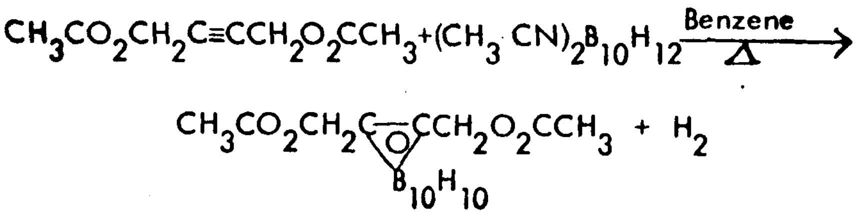
A total of 2600 grams of BAND was prepared from 2100 grams of decaborane in six batches. The following equation describes the synthetic route.

$$B_{10}H_{14} + 2CH_3CN \longrightarrow (CH_3CN)_2B_{10}H_{12} + H_2$$

The overall conversion of decaborane to BAND was 77 percent.

### 2. 1,2-Bis(acetoxymethyl)carborane (BAMC)

A total of 1195 grams of BAMC was prepared in eleven batches, according to the following reaction scheme

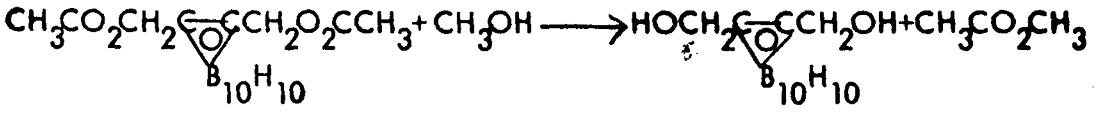


$$CH_3CO_2CH_2C{\equiv}CCH_2O_2CCH_3+(CH_3CN)_2B_{10}H_{12}\xrightarrow[\Delta]{Benzene}$$
$$CH_3CO_2CH_2\underset{\substack{O\\B_{10}H_{10}}}{C-C}CH_2O_2CCH_3 + H_2$$

The overall conversion of BAND to product was 45 percent.

3. 1,2-Bis(hydroxymethyl)carborane (BHMC)

A total of 495 grams of BHMC was prepared in three batches using an acid-catalyzed methanol transesterification reaction:

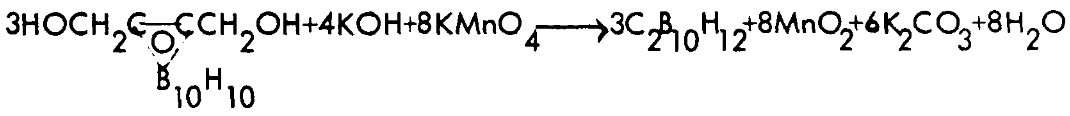


$$CH_3CO_2CH_2\underset{\substack{O\\B_{10}H_{10}}}{C-C}CH_2O_2CCH_3+CH_3OH\longrightarrow HOCH_2\underset{\substack{O\\B_{10}H_{10}}}{C-C}CH_2OH+CH_3CO_2CH_3$$

The overall conversion of BAMC to product was 42 percent.

4. Carborane

Carborane was prepared by the oxidation of 1,2-bis(hydroxymethyl)-carborane with alkaline potassium permanganate.

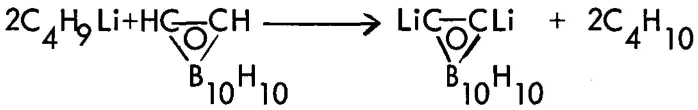


$$3HOCH_2\underset{\substack{O\\B_{10}H_{10}}}{C-C}CH_2OH+4KOH+8KMnO_4\longrightarrow 3C_2B_{10}H_{12}+8MnO_2+6K_2CO_3+8H_2O$$

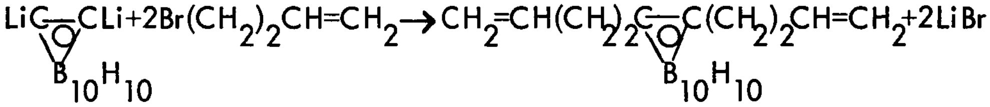
A total of 183 grams of carborane was prepared in 15 batches. The overall conversion of BHMC to desired product was 60 percent.

### 5. 1,2-Bis(3-butenyl)carborane

The dibutenylcarborane, previously unreported, was prepared by the following reaction sequence.



$$2C_4H_9Li + \underset{B_{10}H_{10}}{HC{-}CH} \longrightarrow \underset{B_{10}H_{10}}{LiC{-}CLi} + 2C_4H_{10}$$



$$\underset{B_{10}H_{10}}{LiC{-}CLi} + 2Br(CH_2)_2CH{=}CH_2 \rightarrow CH_2{=}CH(CH_2)_2\underset{B_{10}H_{10}}{C{-}C}(CH_2)_2CH{=}CH_2 + 2LiBr$$

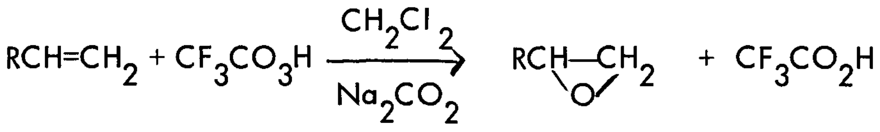
The infrared spectrum of the compound is shown in Figure 1. A total of 78 grams of crude material was obtained in 4 batches.

### 6. 1,2-Bis(5-hexenyl)carborane

Dihexenylcarborane was prepared in a similar sequence by the reaction of dilithiocarborane with 6-bromo-1-hexene. The infrared spectrum of the product is shown in Figure II. A total of 117.2 grams of material was prepared in three batches.

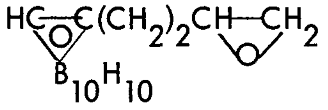
## B. SYNTHESIS OF EPOXYALKYLCARBORANE MONOMERS

Alkenylcarboranes were converted to the corresponding epoxides using the well known trifluoroperacetic acid reagent. The reaction route is represented by the following equation:

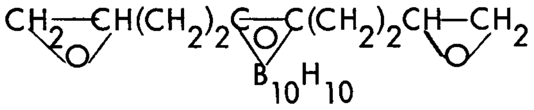


In the presence of trifluoroacetic acid, the epoxy ring could open to give the hydroxy-trifluoroacetate derivative. However, epoxy ring-opening is avoided in this system since sodium carbonate is used as a base and neutralizes free acids . It also destroys excess peracid. There was no evidence for the formation of the glycol derivatives in this work.

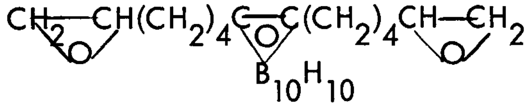
The following epoxy derivatives were prepared.



m.p. 60 - 63°C



m.p. 68 - 71°C



Both butyl derivatives are solids whereas the hexyl derivative is a liquid at room temperature. To our knowledge, this is the first preparation of the bis(epoxyalkyl)carboranes.

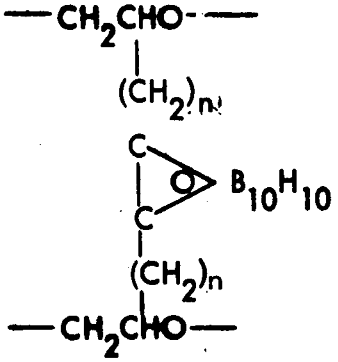
## C. CURING AND POLYMERIZATION STUDIES

Several catalytic agents were investigated for the polymerization of the epoxyalkylcarborane systems. Catalytic agents were chosen in preference to reactive hardeners because the latter usually requires a larger amount of reagent per given amount of resin. The introduction of any amount of a foreign species into the system would also result in a decrease in the inherent thermal stability provided by the carborane nucleus. The catalytic type system would introduce the least amount of reagent and still give an effective cure.

Precapio et al(7) state that olefin oxides with no ether linkage between the epoxide group and the rest of the molecule generally react faster with acidic reagents than with basic reagents. Accordingly, the complex boron trifluoride-monethylamine was chosen for an investigation of curing characteristics prior to the assembly of specimens for lap-shear tests. Lee and Neville(8) state that this complex is effective in amounts as small as one phr (parts per 100 parts resin) but that optimum properties are obtained when a higher percentage (three to five phr) is used. A drawback to this catalyst is that it is moisture sensitive.

Most reports on the curing of epoxy resins with boron trifluoride-monoethylamine state that the complex undergoes dissociation at elevated temperatures, and that curing is actually accomplished by the acid species, boron trifluoride. However, Harris and Temin (9) have recently concluded that curing is initiated by reaction of the complex with the epoxy groups rather than by decomposition to a reactive group. They found that the complex itself slowly decomposed at 190-200°C to products containing the $BF_4^-$ ion. Lee and Neville report that colored castings have been obtained at curing temperatures greater than 105°C.(8)

We have found that both bis(epoxybutyl)carborane and bis(epoxyhexyl)-carborane readily cure at elevated temperatures in the presence of boron trifluoride monoethylamine. Hard thin discs were formed when mixtures containing 3 phr catalyst were heated at 175°C for one hour. These discs were tan in color and resistant to moderate flexure. A cross-linked polyether results since two functional groups are present per molecule.

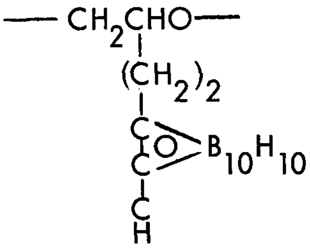


Both epoxyalkylcarboranes can be conveniently "B-staged" at 100°C to give materials which are non-flowing plastics having string-forming characteristics at room temperature. The epoxyhexyl system appears to react faster than the epoxybutyl system. After a two hour period, an initial cloudiness vanishes in the hexyl system whereas a cloudy suspension remains in the butyl system. At 100°C, both systems are free-flowing liquids and can thus be easily applied to specimens for lap-shear tests.

The apparent greater ease of reactivity of the hexyl system compared to the butyl system toward the curing agent is not unexpected. Grafstein and co-workers(1) previously reported that the carborane nucleus inhibited acid catalyzed epoxy ring openings on a side chain. For example, a stable epoxide was obtained from the reaction of isopropenyl carborane with trifluoroperacetic acid whereas with this same reagent, monobutenyl-carborane gave a glycol trifluoroacetic adduct. Presumably the epoxybutyl intermediate is further attacked by excess reagent to give the adduct. The same reaction, conducted under alkaline conditions to remove the ring-opening species, gave the expected mono(epoxybutyl)carborane.

A preliminary investigation was made of the effect of two basic-type curing agents, N, N-dimethylbenzylamine and 2,4,6-tris(dimethylaminomethyl)phenol (DMP-30) on bis(epoxybutyl)carborane. In both cases, room temperature brittle solids were obtained.

Some basic reagents are known to degrade the carborane cage to $B_9$ species. However, studies made with the above basic catalysts and with boron trifluoride-monoethylamine on the mono(epoxybutyl) system showed that epoxy ring opening, and not degradation, had occurred. With a curing temperature of 175°C and a concentration of 3 phr, only a slight increase in solution viscosity was noted at 175°C but viscous plastics having string-forming characteristics formed when the samples were cooled to room temperature. Opening of the epoxy ring was confirmed by an examination of the infrared spectra. Since only one reactive epoxy ring is present per molecule, a linear structure will result.



Control experiments were run under identical conditions using the mono-(epoxybutyl)carborane itself to rule out a spontaneous thermal curing mechanism. The behavior of butenylcarborane was also studied in the presence of DMP-30 catalyst. There was no visual or infrared evidence of reaction or degradation in either system.

It was anticipated that curing a mixture of mono and bis(epoxybutyl)-carborane might result in a hard polymer. Long chains would be formed by linkage of monofunctional species. These chains would then be cross-linked into a large network by the difunctional species. Preliminary experiments were conducted by heating equal weight mixtures of the two species with a catalyst at 180°C. However, all three catalyst systems resulted in the formation of room temperature brittle solids.

Based on these results, the adhesive characteristics of bis(epoxybutyl)-carborane and bis(epoxyhexyl)carborane were evaluated in the testing program described in the following section. The catalyst boron trifluoride-monoethylamine was chosen as the curing agent since this species gave the hardest solids on polymerization.

## D. ADHESIVE BOND PROPERTY EVALUATION

The adhesive properties of both bis(epoxybutyl)carborane and bis(epoxy-hexyl)carborane cured with boron trifluoride-monoethylamine were evaluated by lap-shear tests. Specimens were assembled from type 17/7 stainless steel strips to give an overlap area of 0.5 in$^2$. All testing was conducted at room temperature with an Instron Tensile Machine. A substantial improvement was made in lay-up techniques during the course of this evaluation. The best results were obtained by the application of 15 p.s.i. to the overlap area and the use of a glass cloth binder (Volan A-181) to hold the epoxy in the joint during cure. Curing time, curing temperature, degree of "B-staging" and the effect of post-cure at elevated temperatures were varied in this evaluation. Failure was mainly cohesive in all systems where glass cloth was used as a binder. The data are shown in tabular form in Tables I and II. Glue line thicknesses were difficult to measure precisely , but were about 6 mils for the best samples.

It is worth noting that the highest bond strength value obtained in the bis-(epoxyhexyl)carborane system was 2810 p.s.i. (HEC-74).* The resin contained three percent catalyst and had been "B-staged" at 100°C for two hours and an additional seven minutes at 125°C. The resulting liquid was very viscous at this temperature and was gummy at 25°C. Glass cloth to be used as the binder was impregnated with the resin from an acetone solution. The curing cycle was 175°C for 45 minutes. These results were obtained on a sample of bis(epoxyhexyl)carborane that had been vacuum distilled before use. This bond strength represented an improvement over very early studies using undistilled epoxy. It is also better by about ten percent over average values obtained on other specimens reported below. This increase in bond strength using the same distilled epoxy is probably due to the fact that, in this lay-up technique, a maximum amount of the epoxy is retained in the bond area.

Lower bond strength values were obtained when the glass cloth filler was not impregnated with the resin-catalyst system prior to specimen assembly. With curing and "B-staging" conditions similar to those reported above, the average bond-strengths of seven specimens obtained in the series HEC-63 to 69 was 2219 p.s.i. with a range of 1710 to 2590 p.s.i. This range of values reflects the difficulty that is encountered in assembling identical specimens.

---

* HEC-74 in the notebook identification of lap-shear specimen; sample # -74 using bis(epoxyhexyl)carborane (HEC).

Since a suitable apparatus was not yet available to conduct lap-shear tests at elevated temperatures, the effect of post-cure on bond strengths was investigated first. Four specimens were assembled simultaneously (cure cycle of 175°C for one hour) from a mixture containing 3 phr catalyst that had been "B-staged" at 100°C for two hours. Two specimens were tested immediately and gave bond strengths of 2410 p.s.i. (HEC-70) and 2060 p.s.i. (HEC-71). The remaining two specimens were post-cured at 250°C for one hour and gave room temperature bond strengths of 1470 p.s.i. (HEC-72) and 1727 p.s.i. (HEC-73). This represents an average decrease of about 25 percent in bond strength.

Curing at 150°C did not give values significantly different from those at 175°C. An average value of 2287 p.s.i. was obtained on two specimens (2074 p.s.i. - HEC-59 and 2500 p.s.i. HEC-60). Two additional specimens were post-cured at 250°C for one hour and gave values of 2070 p.s.i. (HEC-61) and 1780 p.s.i. (HEC-62) (average of 1925 p.s.i.).

The above results of post-curing at 250°C for one hour, although limited, show that a decrease of 15 to 25 percent occurs in room temperature lap-shear strengths. On all the specimens that were post-cured, the epoxy in the glue line retained its water-white color, but the portion outside the joint had turned light-brown.

The best bond strength value obtained in the bis(epoxybutyl)system was 1840 p.s.i. (BEC-39). The resin contained ten percent catalyst and was not "B-staged" before application. In this series (BEC 36-39), values ranged from 1000 p.s.i. to 1840 p.s.i. for an average of 1440 p.s.i. Another set of seven specimens was assembled using three percent catalyst and a one hour "B-stage" period at 100°C. Three specimens, BEC-40, 41, and 42, were tested without post-cure and gave bond strengths of 1280 p.s.i., 1490 p.s.i., and 1700 p.s.i. (average value of 1490 p.s.i.). Two specimens were post-cured at 190°C for one hour (1400 and 1280 p.s.i.) and two specimens for two hours at 190°C (1210 and 1290 p.s.i.). This limited series of results suggests that this system retains most of its bond-strength under these post-cure conditions. No significant improvement was noted when vacuum distilled bis(epoxybutyl)carborane was used for lap-shear testing.

A comparison of the bis(epoxybutyl) system with the bis(epoxyhexyl) system shows that consistently higher bonding strengths are obtained in the latter epoxy. It is impossible, at this stage of the work, to decide if this is a real phenomenon or reflects the proportionately greater effort on the improvement in lay-up procedures devoted to the epoxyhexyl system. It might be argued that the epoxyhexyl system should give higher bond-strength values in lap-shear tests because the additional two $CH_2$ groups in the polyether chain (as compared to the epoxybutyl system) remove the ether linkages further from the large carborane moiety.

However, this advantage of increased strength must be balanced by a possible increase in thermal stability (proceeding from the hexyl to the butyl derivatives). The electron-deficient carborane polyhedron exerts a stabilizing influence (to thermal degradation) on adjacent chemical groupings. The closer the carborane nucleus is to these groupings, the greater should be the overall thermal stability of the species. On this basis, bis(epoxybutyl)carborane should be the most thermally stable of the two species. Since adhesive failure at elevated temperatures is due, in part, to the thermal degradation of the structure, the epoxybutyl system should give the adhesive having the best performance at elevated temperature. A complete analysis of bond strength values in both systems at elevated temperatures will have to be made to test the hypothesis.

## TABLE I

### Lap-Shear Bond Strengths Using Bis(epoxyhexyl)carborane

| Specimen Number | Cure Time | Cure Temp. | Post-Cure Time | Post-Cure Temp. | Glue Line Thickness | Nature of Failure | Bond Strength (p.s.i.) |
|---|---|---|---|---|---|---|---|
| 25 | 2 1/2hrs. | 150°C | | | | adhesive | 2030 |
| 26 | 2 1/2hrs. | 150°C | | | | adhesive | 1808 |
| 47 | 1 hr. | 175°C | | | .011-.012 in. | cohesive | 2320 |
| 48 | 1 hr. | 175°C | 1 hr. | 190°C | .011-.012 in. | cohesive | 1530 |
| 49 | 1 hr. | 175°C | | | | cohesive | 2230 |
| 50 | 1 hr. | 175°C | | | | cohesive | 2180 |
| 51 | 1 hr. | 175°C | | | .022 in. | cohesive | 2125 |
| 52 | 1 hr. | 175°C | | | .024 in. | cohesive | 2160 |
| 59 | 1 hr. | 150°C | | | .010 in. | cohesive | 2074 |
| 60 | 1 hr. | 150°C | | | .012 in. | cohesive | 2500 |
| 61 | 1 hr. | 150°C | 1 hr. | 250°C | .013 in. | cohesive | 2070 |
| 62 | 1 hr. | 150°C | 1 hr. | 250°C | .013 in. | cohesive | 1780 |
| 63 | 1 hr. | 175°C | | | .004 in. | cohesive | 2150 |
| 64 | 1 hr. | 175°C | | | .006 in. | cohesive | 2540 |
| 65 | 1 hr. | 175°C | | | .015 in. | cohesive | 1710 |
| 66 | 1 hr. | 175°C | | | .013 in. | cohesive | 2177 |
| 67 | 1 hr. | 175°C | | | .008 in. | cohesive | 2277 |
| 68 | 1 hr. | 175°C | | | .009 in. | cohesive | 2590 |
| 69 | 1 hr. | 175°C | | | .014 in. | cohesive | 2090 |
| 70 | 1 hr. | 175°C | | | .005 in. | cohesive | 2410 |
| 71 | 1 hr. | 175°C | | | .007 in. | cohesive | 2060 |
| 72 | 1 hr. | 175°C | 1 hr. | 250°C | .009 in. | cohesive | 1740 |
| 73 | 1 hr. | 175°C | 1 hr. | 250°C | .009 in. | cohesive | 1737 |
| 74 | 3/4 hr. | 175°C | | | | cohesive | 2810 |
| 75 | 3/4 hr. | 175°C | 1/2 hr. | 175°C | | cohesive | 2740 |

## TABLE II

### Lap-Shear Bond Strengths Using Bis(epoxybutyl)carborane

| Specimen Number | Cure Time | Cure Temp. | Post-Cure Time | Post-Cure Temp. | Glue Line Thickness | Nature of Failure | Bond Strength (p.s.i.) |
|---|---|---|---|---|---|---|---|
| 6 | 2 1/2 hrs. | 150°C | | | .017 in. | adhesive | 1229 |
| 7 | 2 1/2 hrs. | 150°C | | | .017 in. | adhesive | 1250 |
| 8 | 2 1/2 hrs. | 150°C | | | .021 in. | adhesive | 1192 |
| 15 | 2 1/2 hrs. | 150°C | | | | mixed | 1330 |
| 17 | 16 hrs. | 120°C | | | | adhesive | 1240 |
| 18 | 16 hrs. | 120°C | | | | adhesive | 1670 |
| 20 | 16 hrs. | 120°C | | | | adhesive | 1621 |
| 24 | 2 1/2 hrs. | 150°C | | | | adhesive | 1324 |
| 36 | 1 hr. | 175°C | | | | cohesive | 1580 |
| 37 | 1 hr. | 175°C | | | | cohesive | 1000 |
| 38 | 1 hr. | 175°C | | | | cohesive | 1390 |
| 39 | 1 hr. | 175°C | | | | cohesive | 1840 |
| 40 | 2 hrs. | 170°C | | | .006 in. | cohesive | 1280 |
| 41 | 2 hrs. | 170°C | | | .006 in. | cohesive | 1490 |
| 42 | 2 hrs. | 170°C | | | .006 in. | cohesive | 1700 |
| 43 | 2 hrs. | 170°C | 1 hr. | 190°C | | cohesive | 1400 |
| 44 | 2 hrs. | 170°C | 1 hr. | 190°C | | cohesive | 1280 |
| 45 | 2 hrs. | 170°C | 2 hrs. | 190°C | | cohesive | 1210 |
| 46 | 2 hrs. | 170°C | 2 hrs. | 190°C | | cohesive | 1290 |
| 53 | 2 hrs. | 170°C | | | .009 in. | cohesive | 1280 |
| 54 | 2 hrs. | 170°C | | | .015 in. | cohesive | 1640 |
| 55 | 2 hrs. | 170°C | | | .007 in. | cohesive | 1350 |

# III. EXPERIMENTAL

## A. SYNTHESIS OF CARBORANE INTERMEDIATES

### 1. 6,9-Bis(acetonitrilo)decaborane (BAND)

In a typical preparation, 300 g of crude decaborane was added with stirring to 1500 ml of chromatoquality acetonitrile. The resulting suspension was filtered, and the residue was discarded. The decaborane-acetonitrile solution was transferred to a three liter flask equipped with a mechanical stirrer, thermometer and reflux condensor. The flask was heated at 80 - 84 °C for 4 1/2 hours, during which time a yellow solid formed. The mixture was cooled and the solid product was collected on a Büchner funnel using No. 42 filter paper. The product was washed with several 100 ml portions of fresh acetonitrile and air-dried. A light-yellow product (BAND) was obtained. The filtrate, containing unreacted decaborane and BAND was used in place of fresh acetonitrile for a subsequent run. This reuse of filtrate is reflected in the percent conversion of decaborane to BAND.

### 2. 1,2-Bis(acetoxymethyl)carborane (BAMC)

In a typical preparation, a mixture of 175 g BAND (.870 moles), 151 g of 1,4-bis(acetoxy)butyne -2 (.887 moles) and one liter of benzene was heated in a three liter flask equipped with a mechanical stirrer, thermometer and reflux condensor. The mixture was refluxed at 82 -85°C for 20 to 24 hours. The resulting suspension was cooled and Büchner - filtered using Number 42 filter paper. Benzene-insoluble "B-solids" retained on the filter paper were destroyed by reaction with methanol. The benzene solvent was removed from the brown filtrate on a vacuum rotary evaporator at 40 - 45°C. The dark brown semi-solid remaining in the flask was agitated with one liter of pentane.

The suspension was allowed to settle, and the supernatant liquid was gravity-filtered to give a light yellow solution. The solution was cooled to -80°C, and the resulting solid (crude BAMC) was suction filtered. The residual brown solids were treated with fresh 500 ml portions of pentane until no appreciable amount of solid appeared when the filtered liquid was cooled to -80°C. The brown pentane-insoluble "B-solids" were destroyed by reaction with methanol. The combined off-white product was usually a semi-solid at room temperature. (The reported melting point of BAMC is 42 - 43°C (6)). Possible impurities are "B-solids" and unreacted butyne. BAND is relatively insoluble in pentane. After standing for several days, a small portion of the crude solid would not redissolve in fresh pentane. The purest product was obtained by adding enough fresh pentane to the crude material to dissolve all but the most insoluble material, filtering, cooling to -80°C, filtering, washing the precipitate with cold fresh pentane and suction drying. The product obtained was white and melted at 38 - 42 °C.

### 3. 1,2-Bis(hydroxymethyl)carborane (BHMC)

Gaseous hydrogen chloride was passed into a solution of 550 g. of BHMC in 3.0 liters of methanol. The solution was refluxed for four hours with a continuous stream of hydrogen chloride bubbling through the solution. During this time, the solution turned light brown in color. About two-thirds of the methanol-methylacetate mixture was boiled away, and distilled water was added to the hot solution until a cloud formed. The solution was cooled to room temperature to precipitate the crude BHMC which was collected, washed with water and air-dried. Recrystallization from water gave 162 g. of white product (for an overall conversion of BAMC to product of 42 percent).

## 4. Carborane

In a typical preparation, a suspension of 40.6 g. (0.200 moles) of 1,2-bis(hydroxymethyl)carborane in 400 ml of 20 percent aqueous potassium hydroxide was stirred at 20°C. Potassium permanganate (96.4 g. - 0.610 moles) was slowly added over a 3 - 3.5 hour period. An initial deep green color ($MnO_4^{2-}$) was observed which gave way to a brown suspension ($MnO_2$ and carborane). The suspension was stirred for an additional hour, cooled to 0°C, and acidified with excess concentrated hydrochloric acid. Several ml of ethyl ether were added to break the resulting foam. In order to convert $MnO_2$ to $Mn^{2+}$, a solution of 63.5 g. of $NaHSO_3$ (0.61 mole) in 300 ml of water was slowly added to the acidified mixture. The resulting white suspension was filtered, and the solid was washed with water and vacuum dried at room temperature. Recrystallization from a 1-butanol-heptane mixture gave 16.4 g. of product (representing a 57.0 percent conversion of BHMC to carborane). The infrared spectrum of the product was identical to that of carborane.

## 5. 1,2-Bis(3-butenyl)carborane

A slight excess of 1.6 M butyllithium solution (135 ml or 0.216 moles of BuLi) was transferred to a dropping funnel in a nitrogen-filled glove bag. The solution was added over a 15 minute period, with stirring, to 11.5 g. (0.0800moles) of carborane dissolved in 75 ml of anhydrous ethyl ether contained in a round bottom reaction flask. During the addition, a nitrogen flow was maintained over the system, and the flask was cooled with an ice-water bath. After the addition was complete, the suspension of heavy white solid was stirred at room temperature for about one hour. The suspension was allowed to settle, and the bulk of the supernatant liquid was removed with a syringe. About 75 ml of anhydrous ethyl ether was added to the system with stirring to wash the solid. The bulk of the solution was removed, and the procedure was repeated. About 100 ml of anhydrous ethyl ether was added, and the system was heated to reflux. A weighed quantity of 4- bromo-1-butene (27.0 g. - 0.200moles) was added to the system over a 10 minute period. After a two hour reflux period, the white solid had completely disappeared leaving a light brown solution. The reaction mixture was poured into 200 ml of water and thoroughly mixed. The ether layer was separated and dried with magnesium sulphate. The crude product, obtained from the removal of ether solvent on a rotary evaporator, was fractionally crystallized from methanol-water. The final solution was evaporated on a rotary evaporator at room temperature and gave a brown oil.

| Fraction | $H_2O$ added (ml) | Product (g.) | M.P. °C |
|---|---|---|---|
| II-1 | 3 | 0.6 | 71-73 |
| II-2 | 5 | 5.2 | 70-72 |
| II-3 | 20 | 3.3 | 69-71 |
| II-4 | 20 | 0.4 | 58-64 |
| II-5 | Rinco off solvent | oil brown | |

An elemental analysis of fraction II-2, representing 50 percent of the total product, was in excellent agreement with the theoretical values.

| | |
|---|---|
| Calcd. for $B_{10}C_{10}H_{24}$: | B, 42.8; C, 47.7; H, 9.5 |
| Found: | B, 42.4; C, 48.2; H, 9.5 |

The infrared spectrum of the product is shown in Figure 1. Characteristic peaks are as follows: 3085cm$^{-1}$ (C-H stretch of the methylene of the

$-CH = CH_2$ group), 2580 and 2600 $cm^{-1}$ doublet (B-H stretch), 1640 $cm^{-1}$ (C=C stretch), 910 $cm^{-1}$ ($CH_2$ out-of-plane deformation of the methylene of the $-CH=CH_2$ group), and 720 $cm^{-1}$ (carborane cage vibration).

## 6. 1,2-Bis(5-hexenyl)carborane

The procedure for the preparation of this material is the same as that used for the preparation of the corresponding butenyl compound. The amounts of materials used are as follows: carborane, 14.4 g. (0.100 moles); butyllithium in 1.6 M hexane solution, 150 ml (0.240 moles); 6-bromo-1-hexene, 32 g (0.20 moles). Only a small amount of solid, presumably unreacted dilithiocarborane, remained after a ten hour reflux period. The reaction mixture was poured into 200 ml of water and thoroughly mixed. The ether layer was separated and dried with magnesium sulphate. The crude product (26.8 g. representing a conversion of 87 percent) obtained from the removal of ether solvent on a rotary evaporator, was a yellow oil. Vacuum distillation gave a colorless mobile liquid whose infrared spectrum is shown in Figure 11. The spectrum was compared to those of carborane and 6-bromo-1-hexene. The only significant feature to be expected in the spectrum of the product would be the lack of carborane C-H stretch at 3075 $cm^{-1}$. However, the bromohexene also absorbs in this region (3080 $cm^{-1}$). Spectral analysis of the product was therefore made by a ratio method. The product appears to be of high purity since the ratio of the C-H stretch at 3080 $cm^{-1}$ to the C=C absorption at 1640 $cm^{-1}$ is identical to that in 6-bromo-1-hexene.

## 7. Purification of 1-(3-butenyl)carborane

Attempts to remove a liquid impurity from a "wet"shelf sample of 1-(3-butenyl)carborane by vacuum sublimation and by recrystallization from cyclohexane and heptane were unsuccessful. Crystallization of a 5.0 gm sample from methanol-water followed by vacuum drying at room temperature gave 4.1 g. of a white solid. The melting point of 42 - 44°C compared favorably with the reported melting point for 1-(3-butenyl)carborane of 45 - 46°C(1). However, on standing on the shelf for several months in a closed container, the product reverted to a "wet" solid.

## B. SYNTHESIS OF EPOXYALKYLCARBORANE MONOMERS

### 1. Mono(epoxybutyl)carborane

Trifluoroperacetic acid was prepared in the following manner. Twenty ml of methylene chloride was added to 1.1 ml (0.040 moles) of 90 percent hydrogen peroxide in an open beaker cooled by ice water. A total of 5.65 ml (0.405 moles ) of trifluoroacetic anhydride was added to the above solution with stirring over a ten minute period. The beaker was covered with a watch glass, and stirring was continued for another ten minutes. A mixture of 30 ml of methylene chloride, 12.0 g. of sodium carbonate and 5.0 g. (0.25 moles) of 1-(3-butenyl)carborane was placed in a 3-necked round bottom flask. The flask was equipped with a mechanical stirrer, reflux condensor and a dropping funnel. The solution of trifluoroperacetic acid was added dropwise over a 90 minute period. During this time, the temperature of the reaction was maintained below reflux by the use of an ice-water bath. After the addition was completed, the mixture was refluxed for 30 minutes. Following the reflux period, reaction of a drop of the supernatant liquid to starch-iodide paper was negative, indicating the absence of peroxides. Gravity filtration of the reaction mixture followed by removal of solvent from the filtrate on a rotary evaporator gave 4.1 g. of a white solid. The melting point of the solid was 60 - 63°C (lit 60 - 62°C (1)). The infrared spectrum of the product contained peaks characteristic of the epoxy linkage at 840 $cm^{-1}$, 855 $cm^{-1}$, and 3000 $cm^{-1}$.

## 2. Bis(epoxybutyl)carborane

The procedure used for the preparation of mono(epoxybutyl)carborane was followed. In a typical preparation, the amounts of reagents were 4.4 ml of 90 percent hydrogen peroxide (0.16 moles) 22.8 ml of trifluoroacetic anhydride (0.160 moles) and 13.2 g. of dibutenylcarborane (0.0520 moles). A total of 13.0 g. of a white solid (m.p. 68 - 71°C) was isolated. Vacuum distillation of the solid yielded a middle fraction whose infrared spectrum (Figure III) and melting point were identical to that of the crude material. Absorption bands characteristic of the epoxy linkage were present at 840cm$^{-1}$, 855 cm$^{-1}$, and 1250 cm$^{-1}$. A band at 1640 cm$^{-1}$ characteristic of the C=C group was not present.

In one preparation, the infrared spectrum of the product contained a band at 1640 cm$^{-1}$ characteristic of dibutenylcarborane. An additional treatment with trifluoroperacetic acid removed this band.

## 3. Bis(epoxyhexyl)carborane

The procedure used for the preparation of mono(epoxybutyl)carborane was followed. In a typical preparation, the amounts of reagents were 4.4 ml of 90 percent hydrogen peroxide (0.16 moles), 22.8 ml. of trifluoroacetic anhydride (0.160 moles) and 13.6 g. of dihexenylcarborane (0.0432 moles). A total of 13.6 g. of a cloudy yellow liquid was isolated. Vacuum distillation gave a water-white viscous liquid whose infrared spectrum (Figure IV) was essentially identical to that of the crude product. As compared to the spectrum of dihexenylcarborane, the band at 1640 cm$^{-1}$ characteristic of the C=C group had vanished. Bands characteristic of the epoxy linkage appeared at 830 cm$^{-1}$, 845 cm$^{-1}$, and 1250 cm$^{-1}$.

## C. CURING AND POLYMERIZATION STUDIES

### 1. Mono(epoxybutyl)carborane

The catalyst used for the preliminary investigation was DMP-30; tris-(dimethylaminomethyl)phenol. One gram samples of the epoxy were heated in test tubes in a water bath held at 85 - 90°C. With 20 drops of catalyst, the epoxy turned to a non-flowing viscous liquid in 30 minutes. With 5 drops of catalyst, the same consistency was obtained within a one hour period.

The thermal stability of the uncatalyzed epoxy was then investigated. Also, the stability of the carborane cage was tested in the presence of DMP-30. One gram quantities of the following compounds were heated in closed test tubes to prevent contact of the enclosed materials with water vapor.

a. epoxybutylcarborane + 5 drops DMP-30
b. epoxybutylcarborane
c. monobutenylcarborane + 5 drops catalyst

The samples were heated for one hour in a water bath held at 85 - 90°C. As expected, system #1 set to a non-flowing viscous liquid. Systems #2 and # 3 (monobutenylcarborane melts at 42 - 44°C) remained free-flowing liquids. On cooling, all three systems solidified, #1 and #2 to brittle solids and #3 to a "wet" solid. There was no visual or infrared evidence of reaction or degradation in either system.

To continue the work initiated with the DMP-30 catalyst, one gram samples of mono(epoxybutyl)carborane were heated in corked test tubes for one hour at 175°C with the following catalysts.

d. DMP-30 - one drop
e. N, N-dimethylbenzylamine - one drop
f. boron trifluoride-monoethylamine 0.1 gm

In each case, only a slight increase in solution viscosity was noted at 175°C but viscous plastics having string-forming characteristics formed when the samples were cooled to room temperature. Infrared spectra on all three samples showed broad absorption in the 1060- 1150 $cm^{-1}$ region. This is characteristic of the ether linkage in cured epoxies. The infrared spectra also showed the expected decrease in the epoxy absorption at 855 $cm^{-1}$ relative to the carborane cage absorption at 728 $cm^{-1}$.

A one gram sample of the carborane epoxy with the boron trifluoride-ethylamine catalyst was heated at 85 - 90°C for one hour. Little, if any, polymerization had taken place under these conditions. This is not unexpected since the literature specifies that curing takes place in this catalytic system only at temperatures greater than 90°C (9).

## 2. Bis(epoxybutyl)carborane

Exploratory curing studies on bis(epoxybutyl)carborane were conducted in a manner similar to those described in the mono(epoxybutyl)carborane system. With the $BF_3$:$EtNH_2$ catalyst (10 phr) a solid formed almost immediately at 180°C from the initial melt. The solid was hard at room temperature and not easily fractured by impact with a sharp instrument. However, it did not appear homogeneous, probably the result of too rapid a cure.

With N,N-dimethylbenzylamine as catalyst, the bis(epoxybutyl)carborane system remained a free flowing liquid at 180°C. A solid, that was brittle and easily fractured, formed when the sample cooled to room temperature.

DMP-30 catalyst cured the diepoxy system to a spongy mass which turned to a brittle solid when cooled to room temperature.

Since our initial studies above had indicated that the $BF_3$:$EtNH_2$ system appeared to be the most promising, an investigation was made of curing at lower temperatures. After curing a mixture of 1.0 g. epoxy and 0.1 g. catalyst for 1/2 hour at 80 - 90°C, very little change in solution viscosity at temperature was noted. An additional two hours of heating gave a viscous liquid at 90°C, and a viscous plastic formed when the sample was cooled to room temperature. An additional treatment at 120°C for three hours gave a soft solid at this temperature, but a hard solid, not easily fractured, formed on cooling to room temperature.

An identical sample was then heated at 150°C. After 15 minutes, a non-flowing viscous liquid had formed at this temperature. After one hour, the sample was a hard solid at 150°C which, at room temperature, was not easily fractured. This encouraging result suggested that lap-shear specimens be assembled in this system.

One gram mixtures (equal weight amounts of mono and bisepoxybutylcarborane) were heated with 0.1 g. quantities of DMP-30, N,N-dimethylbenzylamine, and $BF_3$:$EtNH_2$ at 180°C for one hour. Under these conditions, curing resulted in room temperature brittle solids.

A mixture containing 0.5 g. amounts of mono(epoxybutyl)carborane, bis(epoxybutyl)carborane and bis(hydroxymethyl)carborane was heated with 0.15 g. of DMP-30 for one hour at 180°C. A room temperature brittle solid was obtained. The same result was observed when N,N-dimethylbenzylamine catalyst was used.

### 3. Bis(epoxyhexyl)carborane

Several mixtures of crude epoxy and $BF_3$:$EtNH_2$ were placed in corked test tubes and heated for one hour. The solid catalyst did not appear to be miscible with the epoxy at room temperature. Results of several experiments are described below.

| Percent Catalyst | Curing Temperature °C | Observation |
|---|---|---|
| 10 | 150 | Hard solid |
| 20 | 150 | Hard solid |
| 10 | 100 | Viscous liquid |
| 20 | 100 | Very viscous liquid |

These results show that the epoxyhexyl derivative cures in a manner similar to the epoxybutyl derivative. The same results were obtained when the catalyst concentration was decreased to 3 phr.

## D. ADHESIVE BOND PROPERTY EVALUATION

### 1. Preparation of Lap-Shear Specimens and Testing Procedures

Type 17/7 stainless steel strips were machined according to Mil Spec MIL-A-00509E. The final strip dimensions were 5.094 in x 1.000 in x 0.050 in. Each lap-shear specimen consisted of two of the above strips overlapped by 0.5 in.

The following clean-etch procedure was followed on all specimens. After step 1, white gloves were used to handle the specimens.

a. Degrease by thoroughly wiping with methylethyl ketone.

b. Etch for 10 minutes at room temperature in the following solution.

| | |
|---|---|
| Nitric Acid (70%) | 10% by volume |
| HF Acid (50%) | 2% by volume |
| $H_2O$ | 88% by volume |

c. Rinse in tap water

d. Passivate for 10 minutes at 71°C in the following solution which had been aged with aluminum metal.

| | |
|---|---|
| Sodium dichromate | 28.5 g. |
| Sulphuric acid | 285.0 g. |
| Tap water | To make one liter. |

e. Rinse with tap water.

f. Rinse with distilled water

g. Observe the panels to make sure they hold a continuous film of water on the areas to be bonded.

h. Dry for 30 minutes in an air oven at 71°C.

Several different methods were utilized for specimen assembly. The most successful involved the use of a special jig with guides for the alignment of the steel strips. Seven specimens could be assembled simultaneously on this jig. Strip supports were used under the top strips for leveling purposes. The overlap area was covered by a strip of silicone rubber and a strip of aluminum metal. The stainless steel specimens were taped to the alignment jig, and a piece of heavy glass cloth was placed over the complete assembly. The apparatus was placed in a specially designed vacuum bag constructed of Tedlar film and Prestite 587. A near vacuum (about 15 p.s.i. differential) was maintained on the system during cure with the weight on the overlap joint distributed by the pressure of the glass cloth. In all work involving the vacuum bag, Volan A-181 glass cloth, washed with MEK, was placed in the joint to aid in holding the resin in place.

Other specimens were assembled, without the use of an alignment jig, in a Carver press at elevated pressure. Some assemblies were also made under self supporting pressure. However, in most cases, the best-looking samples were obtained using the alignment jig and the specially designed vacuum bag.

Glue line thickness was difficult to determine on the assembled specimens. Excess epoxy leaked out of the joint area and cured on the outside of the strips. The presence of this solid prevented any direct measurement of the glue line. The values reported were determined microscopically. They are higher than the true values because rounded edges were formed from the filing procedure described below. It is felt that a glue line thickness of about 6 mils was obtained on the best specimens.

All specimens were tested in an Instron tensile machine at a constant strain rate of 0.01 in/in/min. This strain rate gave a test time which ranged between 1.9 mins. and 2.4 mins. The specimens were filed to remove epoxy from the outside of the joint on the sides. After testing, the overlap areas were examined to determine the mode of failure, adhesive or cohesive.

## 2. Assembly of Lap-Shear Specimens Using Bis(epoxyhexyl)carborane and $BF_3$:$EtNH_2$ Catalyst

Series a.)

The mixture contained 10 percent by weight of catalyst and had been "B-staged" at 100°C for one hour. The sample was warmed and stirred to give a mobile liquid. This warm liquid was applied to strips which were assembled into two specimens. The specimens were cured at 150°C under self-supporting pressure for 2 1/2 hours using the alignment jig.

| Specimen Number | Bond Strength | Glue Line Thickness | Type of Failure |
|---|---|---|---|
| HEC #25 | 2030 p.s.i. | N.M.* | adhesive |
| HEC #26 | 1808 p.s.i. | N.M.* | adhesive |

* Not Measured

Series b.)

The mixture contained three percent by weight of catalyst and had been "B-staged" at 100°C for one hour. The specimens were cured at 175°C for one hour in the vacuum bag (about 15 p.s.i.) on the alignment jig with glass cloth filler. Specimen Number 48 was given a one hour post-cure at 190°C.

| Specimen Number | Bond Strength | Glue Line Thickness | Type of Failure |
|---|---|---|---|
| HEC #47 | 2320 p.s.i. | .011-.012 in. | cohesive |
| HEC #48 | 1530 p.s.i. | .011-.012 in. | cohesive |

Series c.)

The mixture contained three percent by weight of catalyst and had been "B-staged" at 100°C for two hours. The specimens were cured at 175°C for one hour in the vacuum bag (about 15 p.s.i.) using the alignment jig and glass cloth filler. These specimens were cured in the same assembly as Specimens Numbered BEC 53, 54, 55 in the butyl system.

| Specimen Number | Bond Strength | Glue Line Thickness | Type of Failure |
|---|---|---|---|
| HEC #49 | 2230 p.s.i. | N.M.* | cohesive |
| HEC #50 | 2180 p.s.i. | N.M.* | cohesive |
| HEC #51 | 2125 p.s.i. | .022 in. | cohesive |
| HEC #52 | 2160 p.s.i. | .024 in. | cohesive |

* Not Measured

Series d.)

The mixture was from the batch used for the specimen prepared above. Specimens were cured at 150°C for one hour, in the vacuum bag (15 p.s.i.) using the alignment jig and glass cloth filler. Specimen Numbers 61 and 62 were given an additional post-cure at 250°C for one hour.

| Specimen Number | Bond Strength | Glue Line Thickness | Type of Failure |
|---|---|---|---|
| HEC #59 | 2074 p.s.i. | .010 in. | cohesive |
| HEC #60 | 2500 p.s.i. | .012 in. | cohesive |
| HEC #61 | 2070 p.s.i. | .013 in. | cohesive |
| HEC #62 | 1780 p.s.i. | .013 in. | cohesive |

As a result of the 250°C post-cure, the resin spill-over on Specimen HEC #61 and #62 was tan in color but the cured resin in the joint remained colorless.

Series e.)

The mixture was from the batch used for the specimens prepared above. Specimens were cured at 175°C for one hour in the vacuum bag (15 p.s.i.) using the alignment jig and glass cloth filler.

| Specimen Number | Bond Strength | Glue Line Thickness | Type of Failure |
|---|---|---|---|
| HEC #63 | 2150 p.s.i. | .004 in. | cohesive |
| HEC #64 | 2540 p.s.i. | .006 in. | cohesive |
| HEC #65 | 1710 p.s.i. | .015 in. | cohesive |
| HEC #66 | 2177 p.s.i. | .013 in. | cohesive |
| HEC #67 | 2277 p.s.i. | .008 in. | cohesive |
| HEC #68 | 2590 p.s.i. | .009 in. | cohesive |
| HEC #69 | 2090 p.s.i. | .014 in. | cohesive |

Series f.)

The mixture was from the batch used for the specimens prepared above. Specimens were cured at 175°C for one hour in the vacuum bag (15 p.s.i.) using the alignment jig. Specimen Numbers #72 and #73 were given an additional post-cure at 250°C for one hour.

| Specimen Number | Bond Strength | Glue Line Thickness | Type of Failure |
|---|---|---|---|
| HEC #71 | 2410 p.s.i. | .005 in. | cohesive |
| HEC #71 | 2060 p.s.i. | .007 in. | cohesive |
| HEC #72 | 1740 p.s.i. | .009 in. | cohesive |
| HEC #73 | 1737 p.s.i. | .009 in. | cohesive |

Series g.)

The mixture was the residue from the batch used for the specimens reported above. However, a special treatment was used to apply the epoxy. The "B-staging" was continued at 125°C for seven minutes to give a very viscous liquid at this temperature. The material was a gummy mass at 25°C. It was dissolved in acetone and the resulting solution was transferred to a small beaker. The solution was concentrated.by evaporation for ease of impregnation of the glass cloth. Squares of glass cloth were soaked in the solution and air dried to remove solvent. The solution was concentrated further, and the viscous solution was applied to the metal strips. Residual solvent was removed by gentle warming with an air gun. Two specimens were assembled using the alignment jig and the vacuum bag. The cure cycle was 175°C for 45 minutes. One specimen was tested immediately (HEC #74). The second specimen (HEC #75) was post-cured at 175°C for an additional half hour.

| Specimen Number | Bond Strength | Glue Line Thickness | Type of Failure |
|---|---|---|---|
| HEC #74 | 2810 p.s.i. | N.M.* | cohesive |
| HEC #75 | 2740 p.s.i. | N.M.* | cohesive |

* N.M. - Not Measured

### 3. Assembly of Lap-Shear Specimens Using Bis(epoxybutyl)carborane and $BF_3$:$EtNH_2$ Catalyst

Series a.)

A mixture of 2.0 gram of epoxy and 0.19 gram of $BF_3$:$EtNH_2$ catalyst was warmed to 90°C to give a homogeneous milky liquid. When this liquid was applied to the stainless steel strips, it solidified almost immediately. Five specimens were assembled without glass cloth binder and placed in an air oven at 150°C for 2 1/2 hours. No external pressure was applied during this treatment.

| Speciment Number | Bond Strength | Glue Line Thickness | Type of Failure |
|---|---|---|---|
| BEC #6 | 1229 p.s.i. | 0.017 in. | mainly adhesive |
| BEC #7 | 1250 p.s.i. | 0.017 in. | entirely adhesive |
| BEC #8 | 1192 p.s.i. | 0.021 in. | mainly adhesive |
| BEC #15 | 1330 p.s.i. | N. M. * | cohesive and adhesive |

* N.M. - Not Measured

Series b.)

Special vacuum treatments were applied to observe the effect of outgassing on lap-shear strength. A mixture containing the bis-epoxy and $BF_3$:$EtNH_2$ (10 percent by weight) was melted and applied to the strips. Three specimens (BEC 17, 18, and 20) were assembled and heated at 120°C for 16 hours in vacuo. Two other coated strips were vacuum treated at 70°C for 30 minutes. One specimen (BEC 24) was assembled and heated at 150°C in air for 2 1/2 hours.

| Specimen Number | Bond Strength | Glue Line Thickness | Type of Failure |
|---|---|---|---|
| BEC #17 | 1240 p.s.i. | N. M. * | adhesive |
| BEC #18 | 1670 p.s.i. | N.M. * | adhesive |
| BEC #20 | 1621 p.s.i. | N. M. * | adhesive |
| BEC #24 | 1324 p.s.i. | N.M. * | adhesive |

* N.M. - Not Measured

The specimens listed above were poorly aligned. No evaluation could therefore be given to the vacuum techniques used for sample preparation.

Series c.)

The mixture contained ten percent by weight catalyst and was not "B-staged" before application. The specimens were cured at 175°C for one hour in the vacuum bag (about 15 p.s.i.) in the alignment jig with glass cloth filler.

| Specimen Number | Bond Strength | Glue Line Thickness | Type of Failure |
|---|---|---|---|
| BEC #36 | 1580 p.s.i. | N.M.* | cohesive |
| BEC #37 | 1000 p.s.i. | N.M.* | cohesive |
| BEC #38 | 1340 p.s.i. | N.M.* | cohesive |
| BEC #39 | 1840 p.s.i. | N.M.* | cohesive |

* N.M. - Not Measured

Series d.)

The mixture contained three percent by weight of catalyst and was "B-staged" at 100°C for one hour. Specimens were cured at 170°C for two hours using the procedure described above.

Specimens BEC #43 and #44 were post-cured at 190°C for one hour whereas BEC #45 and #46 were post-cured for two hours at 190°C.

| Specimen Number | Bond Strength | Glue Line Thickness | Type of Failure |
|---|---|---|---|
| BEC #40 | 1280 p.s.i. | .006 in. | cohesive |
| BEC #41 | 1490 p.s.i. | .006 in. | cohesive |
| BEC #42 | 1700 p.s.i. | .006 in. | cohesive |
| BEC #43 | 1400 p.s.i. | N.M.* | cohesive |
| BEC #44 | 1280 p.s.i. | N.M.* | cohesive |
| BEC #45 | 1210 p.s.i. | N.M.* | cohesive |
| BEC #46 | 1290 p.s.i. | N.M. | cohesive |

* N.M. - Not Measured

Series e.)

A vacuum distilled sample of epoxy was "B-staged" with three percent catalyst at 100°C for one hour. The specimens were assembled as described above.

| Specimen Number | Bond Strength | Glue Line Thickness | Type of Failure |
|---|---|---|---|
| BEC #53 | 1280 p.s.i. | .009 in. | cohesive |
| BEC #54 | 1640 p.s.i. | .015 in. | cohesive |
| BEC #55 | 1350 p.s.i. | .007 in. | cohesive |

## 4. Attempted Assembly of Lap-Shear Specimens Using Mono(epoxybutyl)carborane

DMP-30 catalyst (18 drops) was added to 3.7 g. of liquid epoxybutylcarborane at about 80°C. The resulting liquid, which contained some bubbles, was applied to the preheated specimens. The specimens were assembled and placed in an air oven at 110°C for 20 hours. The only pressure at the joints was that of the top specimen itself. Little or no cohesion was observed after the samples had cooled to room temperature. The solid that did adhere to the steel surface was brittle and easily removed by scratching. The remainder of the resin, after having stood for several days at room temperature, was reheated to about 80°C. The sticky solid was applied to specimens along with Volan A-181 glass cloth to aid in holding the resin in place. The specimens were assembled in a Carver Press and treated at 175°C and 100 p.s.i. for one hour. Again, no cohesion was observed and the assemblies easily separated. However, the cured epoxy did appear to "wet" the metal surface.

# IV. FUTURE WORK

Bond strength values obtained on lap-shear tests in the present program show that both bis(epoxybutyl)carborane and bis(epoxyhexyl)carborane, cured with boron trifluoride-ethylamine catalyst, exhibit good adhesive properties. Follow-on work is required in several areas in order to satisfy the ultimate goal of determining adhesive capability of the epoxyalkylcarborane systems at elevated temperatures. First of all, bond strengths at temperature must be obtained.

The program on evaluation of various curing agents should be continued using several different amine-type catalysts. Combinations of the several monomers might be formulated in order to develop staged compositions possessing optimum physical properties for adhesive applications. Curing conditions for the use of boron trifluoride-monoethylamine catalyst might well be optimized.

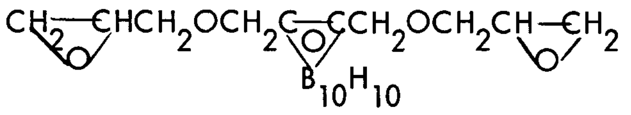
Polymers which are to be applied to steel substrates should be viscous liquids. Studies should be continued to determine the optimum amount of "B-staging" for substrate application. In conjunction with this work, a program should be conducted to determine the pot-life of the monomers in the presence of the catalyst.

Based on an analysis of the data generated in the testing program, modifications of the formulation of the adhesive can be made in regards to:

1. Additives
2. Plasticizers
3. Curing Cycle

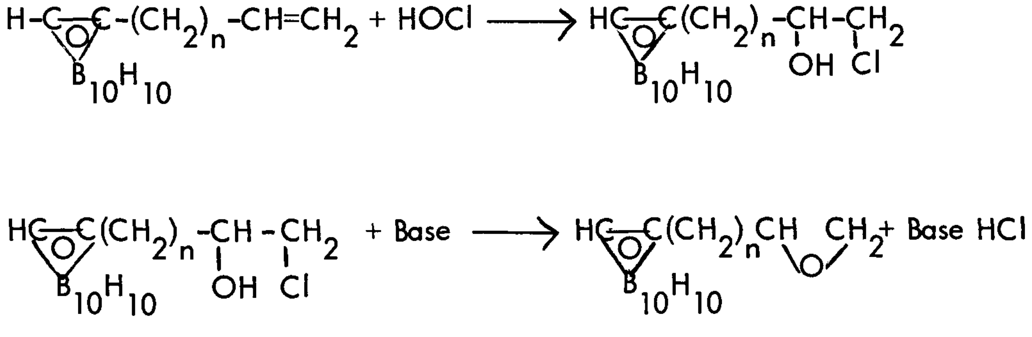
It is suggested that dipentenylcarborane will give an epoxy which, when cured, should have properties intermediate between the epoxybutyl and the epoxyhexyl derivatives.

The synthesis of two neocarborane (m) epoxide monomers, bis(epoxybutyl)-m-carborane and bis(epoxyhexyl)-m-carborane is recommended. In the meta system the carbon atoms are non-adjacent whereas they are adjacent in the ortho isomer. An additional step, the isomerization reaction, is required for their synthesis. It is expected that the m-carborane polymers will display better physical and perhaps better thermal properties than their ortho carborane analogs. Also, the following diepoxy compound could be prepared from the reaction of epichlorohydrin with bis-(hydroxymethyl)carborane.



This compound, when cured, might give a greater bond strength than the corresponding bis(epoxyalkyl)carborane system because of the additional polar ether linkages present in the backbone.

Alternative routes for the conversion of alkenylcarboranes to epoxycarboranes should be sought in order to develop a method of synthesis which is more readily adaptable to large scale manufacturing. This should include, but not be limited to, a study of other peracid reagents and the hypochlorous acid route outlined below.



## REFERENCES

1. D. Grafstein, J. Bobinski, J. Dvorak, H. Smith, N. Schwartz, M. Cohen and M. Fein, Inorg. Chem., 2, 1120 (1963).

2. D. Grafstein and J. Dvorak, Inorg. Chem., 2, 1128 (1963).

3. S. Papetti and T. Heying, J. Am. Chem. Soc., 86 , 2295 (1964).

4. Olin Mathieson Chemical Corp., Final Report on SiB. Polymer Development, Contract NOBS 92143, February 28, 1966.

5. Thiokol Chemical Corp., RMD 5040 - SR - 2, Contract NOBS 900 65, Task 1000, April 1964.

6. M. Fein, J. Bobinski, N. Mayes, N. Schwartz and M. Cohen, Inorg. Chem., 2, 1111 (1963).

7. F. Precapio et al in Modern Materials, Henry H. Hause, Ed., 3, p. 55, Academic Press, New York, 1962.

8. H. Lee and K. Neville, Epoxy Resins, McGraw-Hill, New York, 1957.

9. J. Harris and S. Temin, J. Appl. Polymer Sci., 10, 523 (1966).

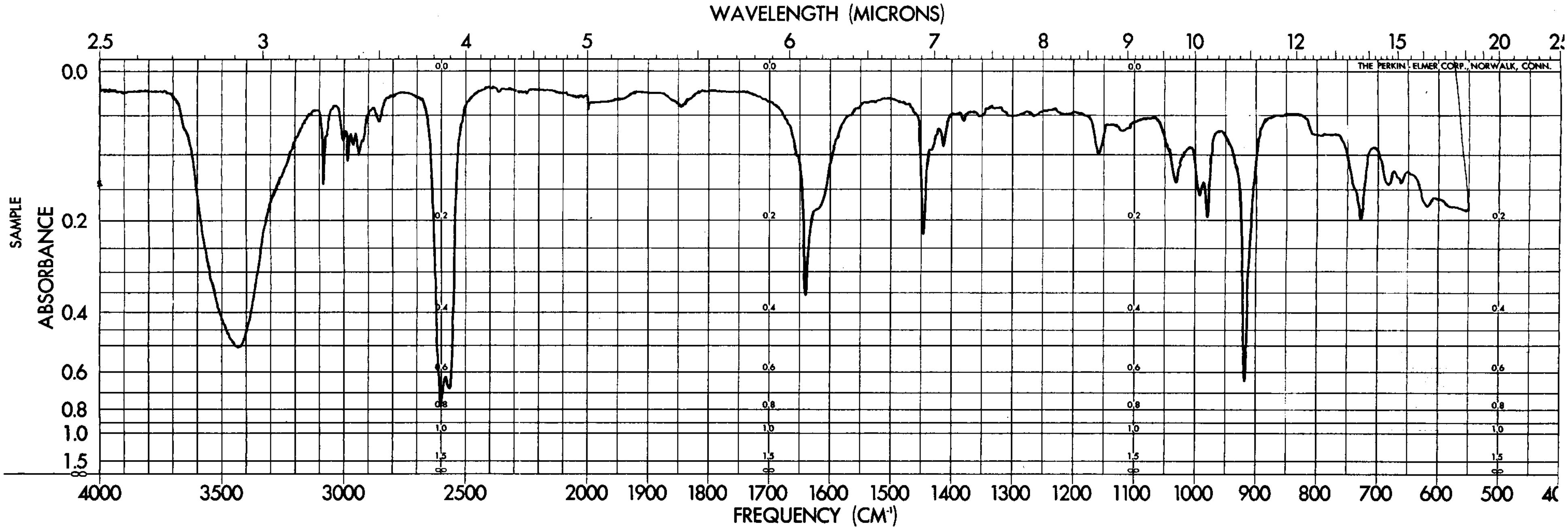


FIGURE I

INFRARED SPECTRUM OF DIBUTENYLCARBORANE

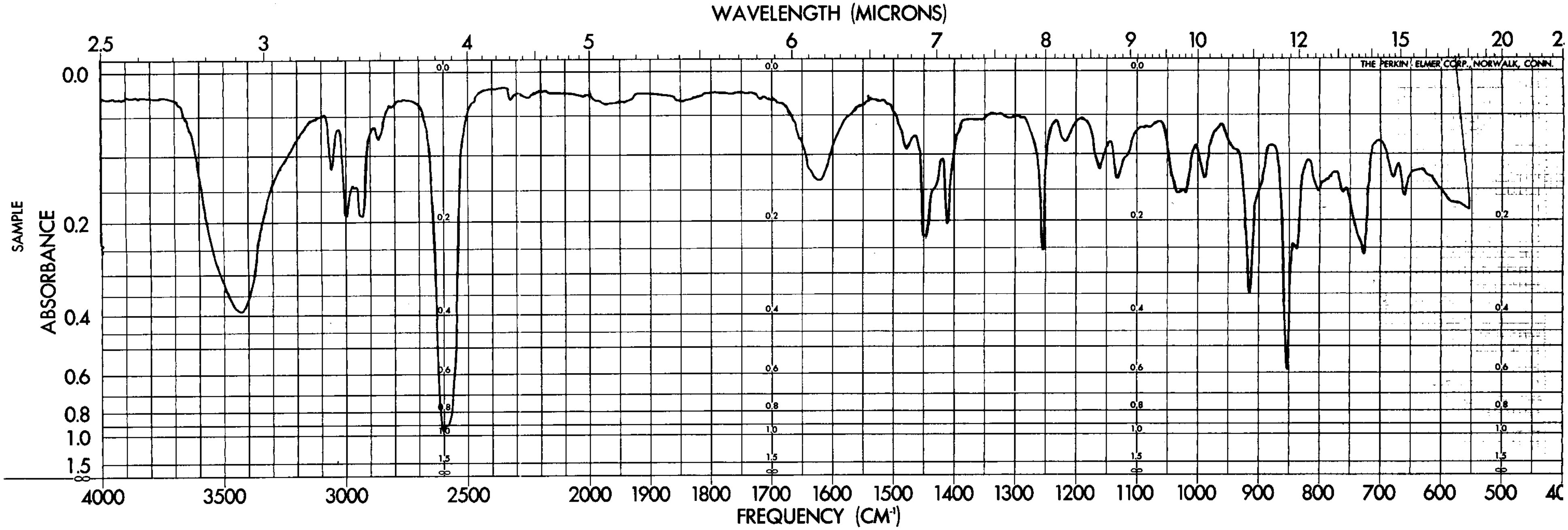


FIGURE III

INFRARED SPECTRUM OF BIS(EPOXYBUTYL)CARBORANE

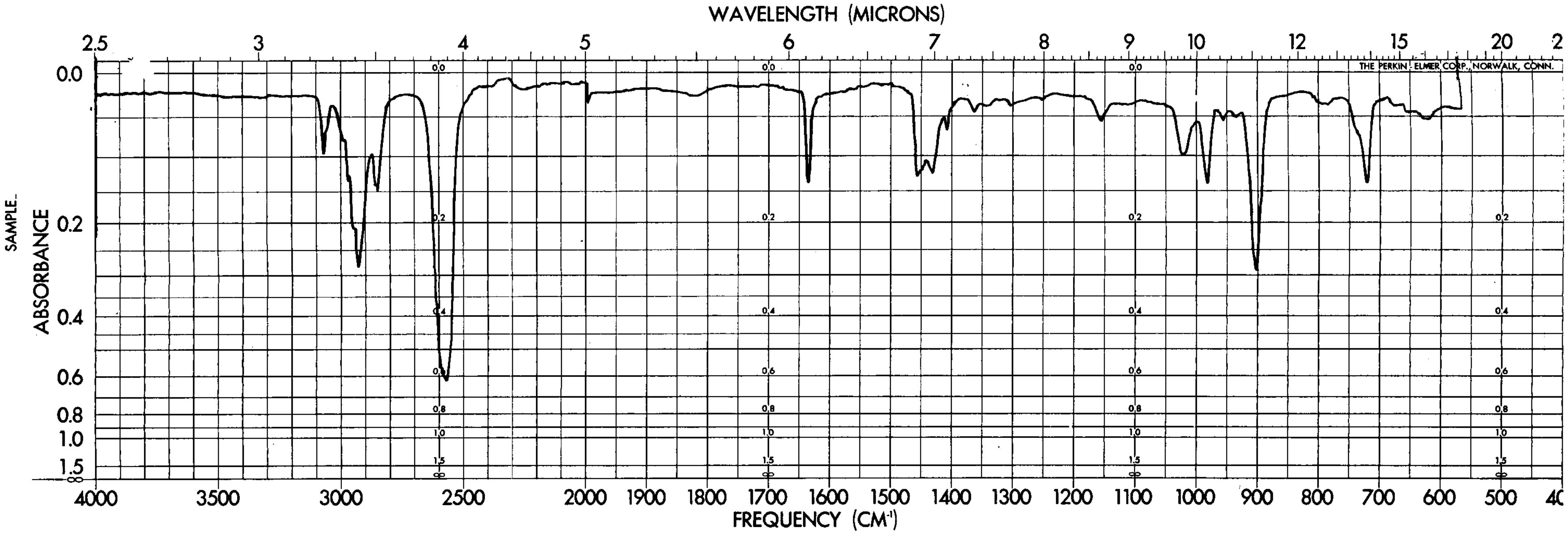


FIGURE II

INFRARED SPECTRUM OF DIHEXENYLCARBORANE

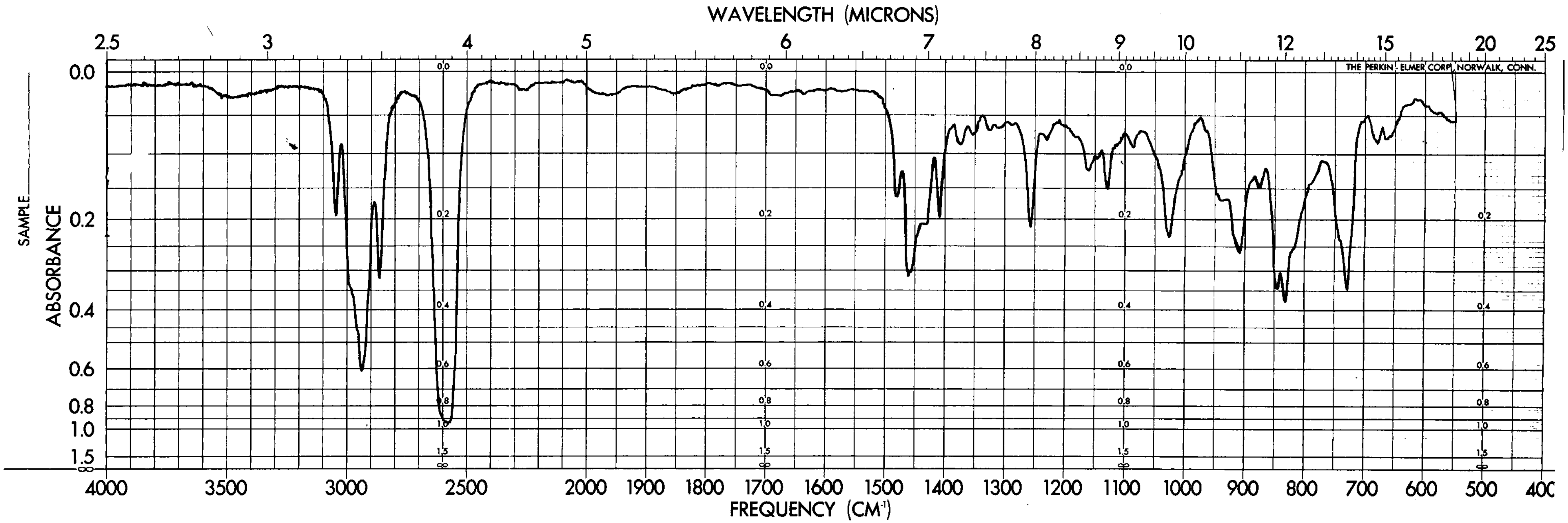


FIGURE IV

INFRARED SPECTRUM OF BIS(EPOXYHEXYL)CARBORANE