2 of 3

Report RMD 5038-F
Contract No. NObs 90065
Index No SR-007-03-03
Task No. 1000

31 pg - $1.00

DIELECTRIC MATERIALS FOR HIGH TEMPERATURE EVALUATION

Report Period: 16 December 1963 to 30 April 1964

Thiokol
CHEMICAL CORPORATION
REACTION MOTORS DIVISION
DENVILLE, NEW JERSEY

Thiokol
REACTION MOTORS DIVISION

DIELECTRIC MATERIALS FOR HIGH TEMPERATURE EVALUATION

Nathan Mayes

Report Period: 16 December 1963 to
30 April 1964

Contract No. NObs 90065
Report RMD 5038-F

Index No. SR-007-03-03

Task No. 1000

Submitted by: Joseph Green
JOSEPH GREEN
Supervisor,
Applied Chemical
Research Section

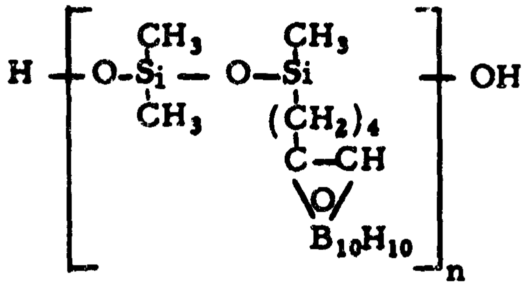
Approved by: MSCohen
MURRAY S. COHEN
Manager,
Chemistry Department

DJ Mann
DAVID J. MANN
Director of Research

CONTENTS

ABSTRACT

Carborane siloxane polymers of the general structure



were studied as thermally stable materials.

Methods of polymerization to obtain high molecular weight linear polymers were investigated. Cohydrolysis of dimethyldichlorosilane and (4-carboranylbutyl)-methyldichlorosilane and solvent fractionation of the products yielded linear polymers of 7000-14,000 molecular weight. This preparation was scaled up to produce 21 lb of polymer which upon fractionation yielded approximately 10.5 lb of high molecular weight product. A higher molecular weight carborane siloxane elastomer was prepared by addition of butenylcarborane to a silicone gum that contained silyl hydrogens. Addition occurred readily when the reaction sites were uniformly separated but was sterically hindered when the sites were randomly located.

Carborane siloxane polymers were cured, using ethoxysilane curatives and metal octoate catalysts, to investigate potential applications in varnishes, laminates, elastomers and plastics.

The thermal properties of uncured and cured carborane siloxane polymer were investigated in an application study. Tests in simulated sealed electric motors at 185°C showed no corrosion of the carbon brushes due to the carborane siloxane polymer.

ADMINISTRATIVE INFORMATION

Research efforts to prepare thermally stable dielectric materials and elastomers were originally authorized by Bureau of Ships Contract NObs 84774, 15 June 1961. The Navy Index Number was SR-007-03-03, Task 1000. That contract expired 15 December 1962. Technical work was resumed 15 February 1963 under Bureau of Ships Contract NObs 88318, Index Number SF-007-03-03, Tasks 1000 and 1003 and continued through 1 September 1963. Technical work was again resumed 15 September 1963 under Contract NObs 90065, Index No. SR-007-03-03, Task 1000, RMD Project 5038.

The Bureau of Ships Project Engineer is Mr. William Shetterly. The Project Supervisor at Thiokol Chemical Corporation, Reaction Motors Division is Mr. Joseph Green. Other contributing personnel include Mr. A. Jackson, Mr. A. Lum, Mr. N. Mayes, Mr. R. Michaels and Mr. J. Paustian.

SUMMARY

THE PROBLEM

The program objective was the preparation of carborane based compounds useful as dielectric materials and elastomers for application over the range of 25-500°C. Carborane siloxane polymer has been selected for intensive study toward meeting this objective.

FINDINGS

Investigation of methods to prepare carborane siloxane polymers determined that cohydrolysis of dimethyldichlorosilane and (4-carboranylbutyl)methyldichlorosilane yielded products that could be solvent fractionated to approximately 50 percent cyclosiloxanes and low molecular weight polymer and 50 percent linear, hydroxy terminated polymer of molecular weight 7000-14,000. The crude cyclosiloxanes could not be polymerized by acid or base catalysts.

A rubbery polymer was prepared by addition of butenylcarborane to a high molecular weight copolymer of methyl hydrogen siloxane and dimethyl siloxane. The addition reaction went to near completion only when an oriented copolymer containing hydrogens on every fourth silicon was used. Steric hindrance to addition was encountered when reaction sites were randomly located on 50 percent of the silicon atoms.

A program to produce 20-30 lb of carborane siloxane polymer was completed with the preparation of 21 lb of unfractionated polymer and 10.5 lb of fractionated, high molecular weight linear polymer.

The curing behavior of carborane siloxanes was studied to determine their potential for use in varnishes, laminates, elastomers, and plastics. Multifunctional polymers cured with (4-carboranylbutyl)methyldiethoxysilane and lead octoate were shown to be brittle or flexible products depending on the degree of crosslinking. Difunctional polymers cured with (4-carboranylbutyl)-triethoxysilane and lead octoate [illegible] flexible plastics. The rubber produced by post-carboranylation could be cured with benzoyl peroxide.

High temperature application studies conducted at USNASL showed the carborane siloxane polymer to be noncorrosive to carbon brushes in a simulated sealed electric motor operating at 185°C.

I. BACKGROUND

Several years ago, Thiokol-RMD demonstrated the outstanding thermal stability of the carborane nucleus (Ref 1). On the basis of this work, a contract was awarded by the Bureau of Ships to Thiokol Chemical Corporation, Reaction Motors Division, for the preparation and evaluation of prototype carboranes as model compounds for ultrahigh temperature dielectric materials (Ref 2). The thermal stability and dielectric results obtained on the initial contract (Ref 3) were sufficiently promising so that a continuation contract was awarded in which the goals were:

1. To study and develop thermally stable carborane-based dielectric embedding materials.
2. To study and develop carborane-based elastomers for high temperature application.

The target thermal stability for these materials was continuous operation at 350°C and 3000 hours at 500°C.

Under the continuation contract (NObs 84774), a number of carborane-based materials were synthesized and evaluated for thermal stability and electrical properties. They included carborane-fluorocarbon polyesters, carborane-epoxies, carborane-phenylenes and carborane-silicones. Of these, the polyesters did not demonstrate the required thermal stability, and the epoxies and phenylene derivatives, although promising on the basis of thermal properties, presented difficulties in synthesis that removed them from consideration except as a long range research effort. The silicone derivatives showed excellent promise with electrical properties that met the program specifications and thermal stability at temperatures greater than 400°C. Work was therefore concentrated in this area, and the program was reoriented into three phases: (1) improvement of the process for monomer and polymer synthesis to allow for early scaleup, (2) studies leading to higher molecular weight polymers for elastomer and embedding compound applications and (3) curing studies.

By the end of the contract period, significant progress had been made in each phase. Process development studies resulted in greatly improved yields and shorter reaction times. For example, starting with bromomethylcarborane, the overall yield of the monomer, (4-carboranylbutyl)methyldichlorosilane, was increased from 8 to 52 percent, and the preparative time was substantially reduced. Changing the method of polymer preparation from catalyzed condensation to cohydrolysis reduced polymerization time from five days to two hours. In the second area, polymer molecular weights of ca. 2,000 obtained initially were increased to ca. 13,000, and progress was made in isolating cyclosiloxanes through which polymers of much higher molecular weight may ultimately be prepared. Initial curing studies indicated that the liquid polymer could be cured through reactive end groups and showed that the carborane silicones could be cured in the several ways common in silicone polymer technology.

A continuation contract (NObs 88318) was awarded on the basis of the previous results and the potential ability of carborane siloxanes to meet the goals of the program. The goals and target requirements have not changed. Greater emphasis has been placed on the development and fabrication of end items. Thus, the preparation of carborane cyclosiloxanes as intermediates for high molecular weight siloxanes, the preparation and curing of multifunctional carborane silicones, the preparation of carborane siloxane liquid plasticizers, the preparation of fiber glass cloth laminates, and studies of the adhesion of carborane siloxanes to metals were investigated.

The present contract (NObs 90065) continues the investigation and development of carborane siloxanes for high temperature service. The immediate objectives are:

- Prepare 20 to 30 pounds of carborane silicone.
- Conduct curing studies.
- Prepare glass-resin laminates for physical, thermal and electrical testing.
- Prepare experimental varnishes for evaluation of high temperature resistant electrical wire coatings.

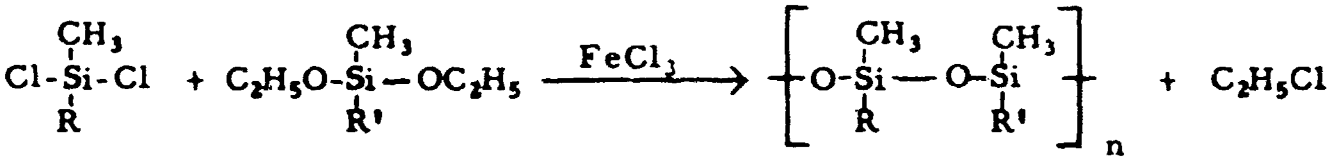
II. RESULTS

PHASE I. PREPARATION OF CARBORANE SILOXANE POLYMERS

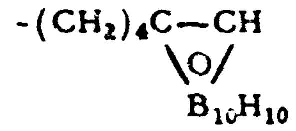
A. Selection of Scaleup Method

1. Polymerization of Silanes

The original preparation of dimethylsiloxane /(4-carboranylbutyl)methylsiloxane copolymer was a ferric chloride catalyzed condensation of the appropriate dichloro and diethoxy silanes.

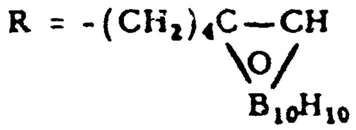


$$Cl\text{-}\overset{CH_3}{\underset{R}{Si}}\text{-}Cl + C_2H_5O\text{-}\overset{CH_3}{\underset{R'}{Si}}-OC_2H_5 \xrightarrow{FeCl_3} \left[O\text{-}\overset{CH_3}{\underset{R}{Si}}-O\text{-}\overset{CH_3}{\underset{R'}{Si}} \right]_n + C_2H_5Cl$$



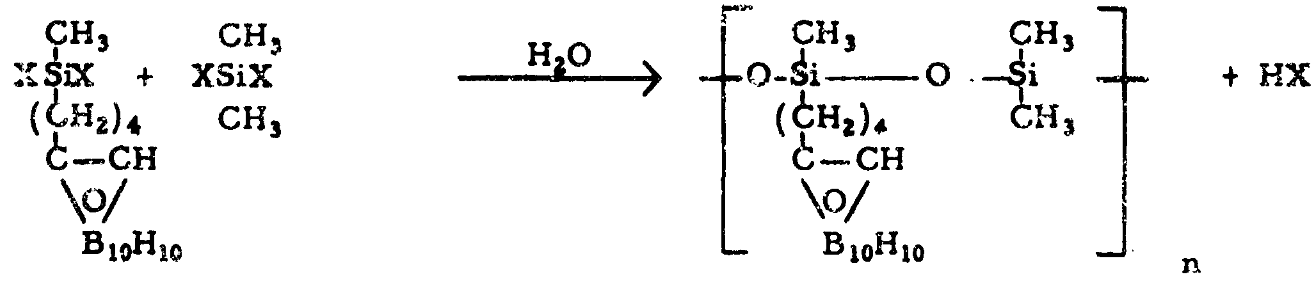
where R = $-CH_3$ and R' = $-(CH_2)_4\underset{B_{10}H_{10}}{\underset{\backslash O /}{C-CH}}$

or



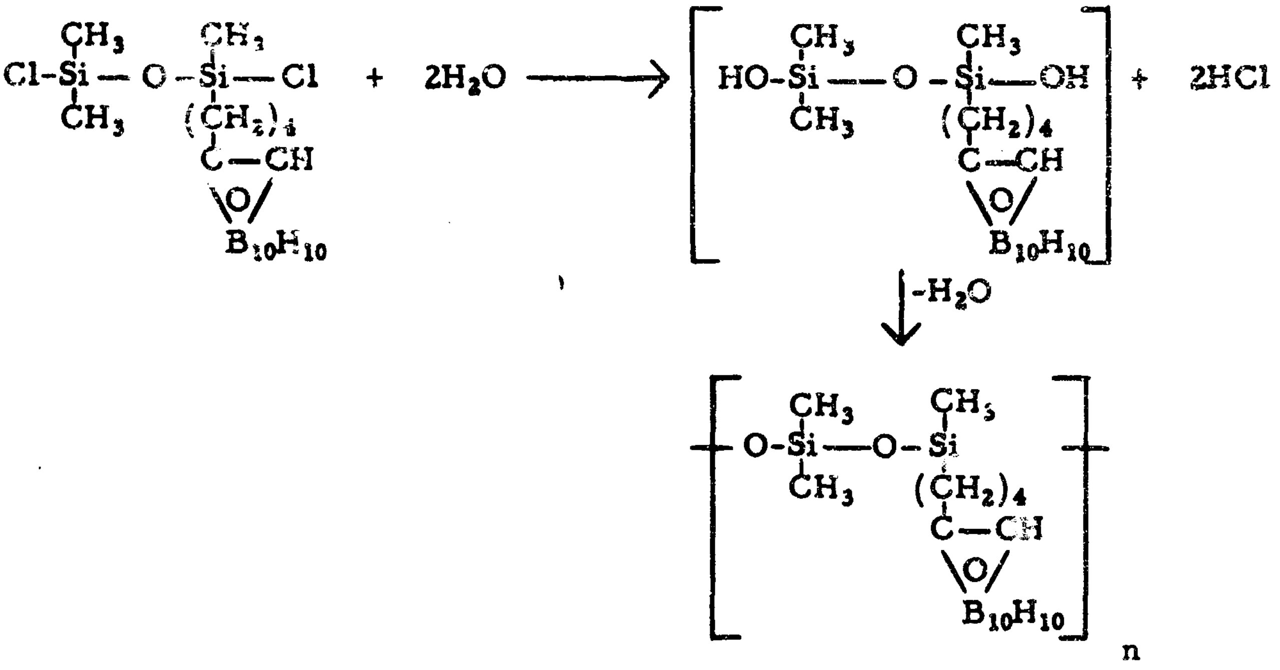
R = $-(CH_2)_4\underset{B_{10}H_{10}}{\underset{\backslash O /}{C-CH}}$ and R' = $-CH_3$

This slow polymerization yielded a mixture of cyclic compounds and linear copolymer of random orientation. Subsequently cohydrolysis of the appropriate dichloro or diethoxy silanes was found to be a must faster method of polymerization and yielded essentially the same products.

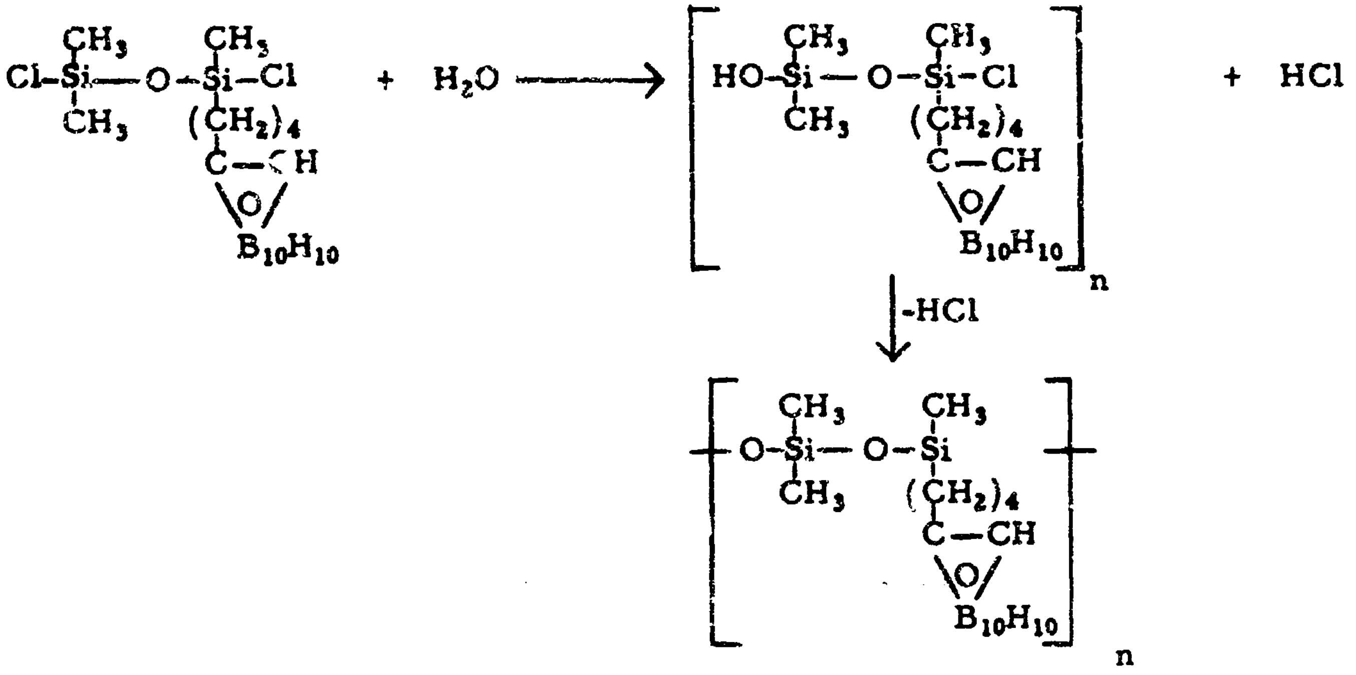


where X = -Cl or $-OC_2H_5$

It was found that the manner of hydrolysis could greatly affect the molecular weight of the resultant polymer; i.e., complete hydrolysis of the dichlorosilane followed by condensation of silyl hydroxy groups led to low polymers, but partial hydrolysis followed by condensation of silyl hydroxy groups with silyl chloride groups led to higher polymers. This was demonstrated in the polymerization of 1, 1, 3-trimethyl-3-(4-carboranylbutyl)-1, 3-dichlorodisiloxane

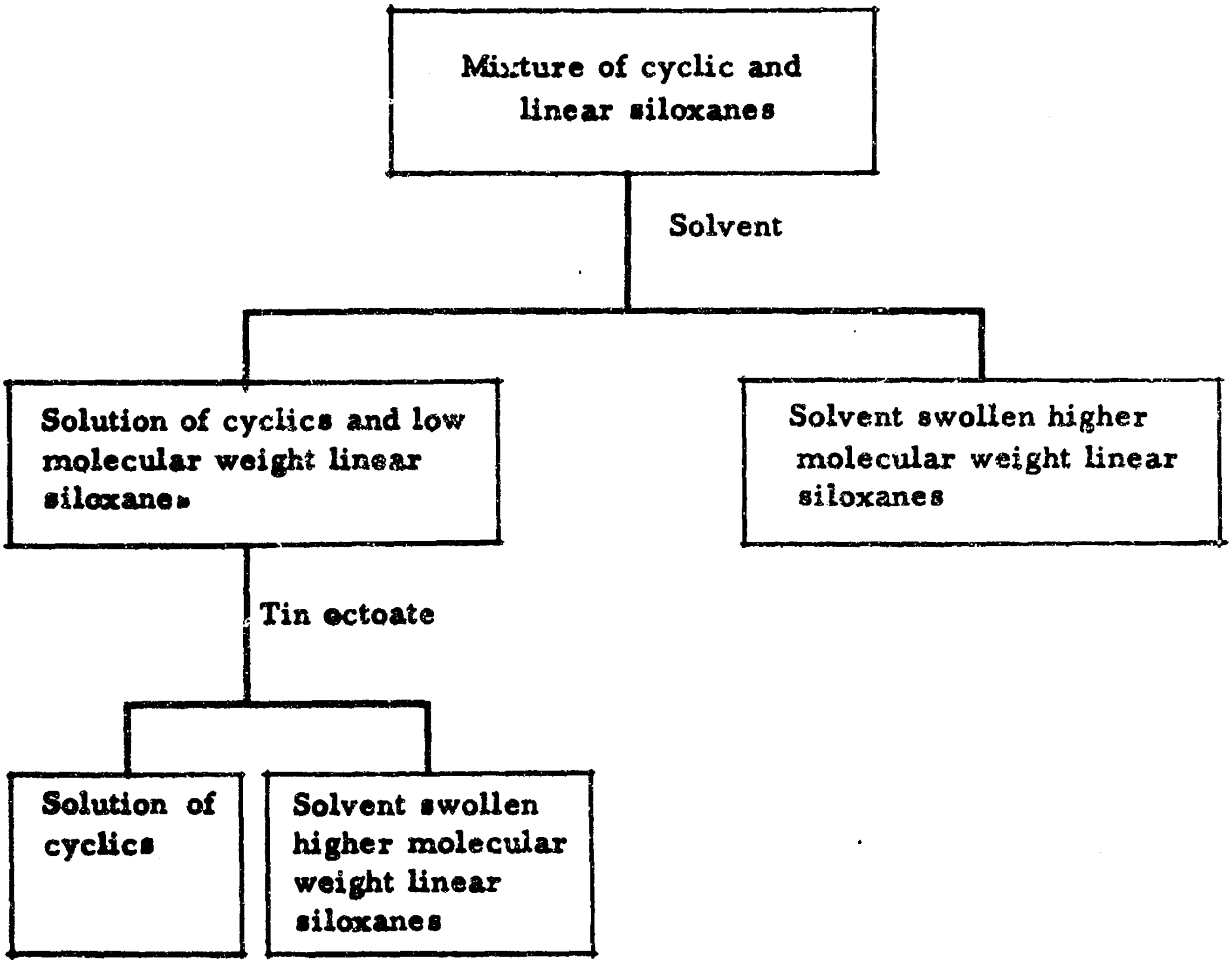


mixture of cyclics and low
molecular weight copolymer



mixture of cyclics and higher
molecular weight copolymer

The partial hydrolysis technique has now been applied to the cohydrolysis of dimethyldichlorosilane with (4-carboranylbutyl)methyldichlorosilane. The procedure is to slowly add half the equivalent quantity of water to a mixture of the dichlorosilane (one mole of water per mole of dichlorosilane) and then stir at 90-100° for at least 24 hours. The addition of excess water after this period insures the hydrolysis of any remaining silyl chloride groups. The product is a mixture of low and higher molecular weight siloxanes which may be solvent fractionated. The solvent used for fractionation has been benzene although other solvents such as toluene, ether, dimethyl formamide or acetonitrile may be used. Siloxanes of molecular weight lower than about 4000 are soluble; higher polymer is swollen by the solvent and forms a separate dense liquid phase. The soluble portion which contains linear and cyclic siloxanes may be treated with a catalyst such as tin octoate to increase the molecular weight of the linear portion. This makes possible the complete separation of linear and cyclic siloxanes by a second solvent fractionation.



The linear polymers obtained this way have molecular weights in the range of 7000-14,000. The cyclic siloxanes are about 900 average molecular weight. Both materials are essentially 1:1 dimethylsiloxane:(4-carboranylbutyl)methylsiloxane copolymers as shown by analysis for boron.

Calculated for $C_9H_{28}B_{10}O_2Si_2$: B, 32.53
Found for cyclic component: B, 32.24
Found for linear component: B, 33.62

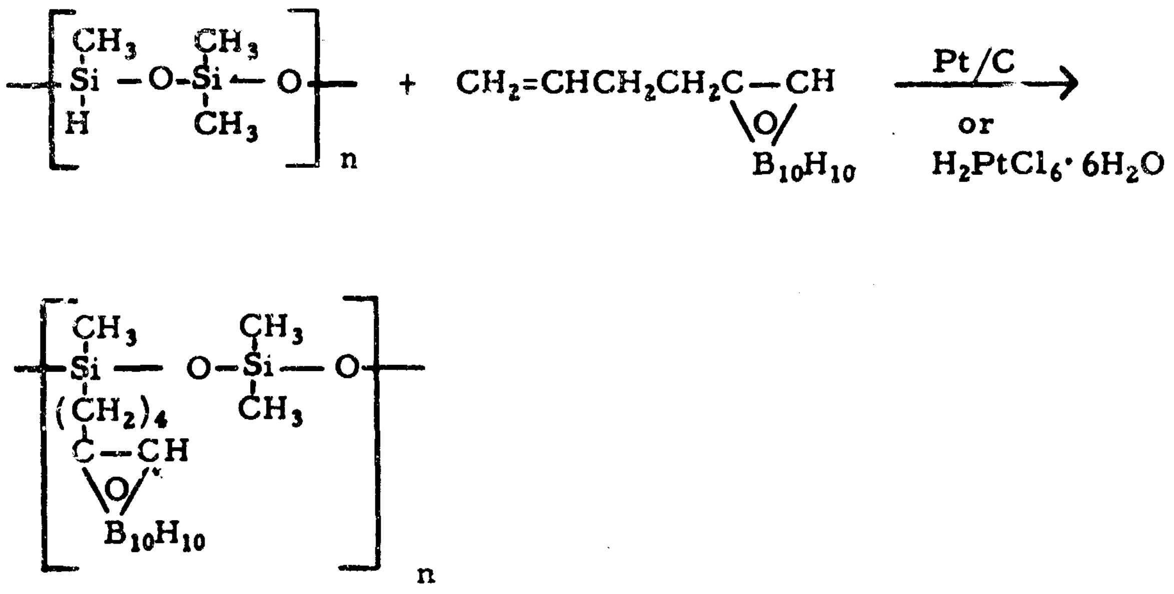
The proportion of linear to cyclic obtained from the cohydrolysis is approximately 1:1 although in some instances about 60 percent linear polymer has been obtained.

2. Polymerization of Cyclosiloxanes

Previous efforts to polymerize mixtures of cyclic carborane siloxanes through ring opening have not been successful. The only successful polymerization of this type was that of relatively pure (4-carboranylbutyl)heptamethylcyclotetrasiloxane. However, since the solvent fractionation of cohydrolysis product yields a large portion of cyclic carborane siloxanes it was important to study these materials and attempt to convert them to the more useful linear polymer. Consequently, the soluble low molecular weight fraction of cohydrolysis product was treated with acidic and basic catalysts and molecular weights determined before and after treatment. Neither sulfuric acid, potassium hydroxide, nor tetramethylammonium hydroxide produced a significant change in molecular weight. An attempt was made to purify the mixture and then treat with catalyst. It was distilled at 3×10^{-4}mm Hg to yield fractions at 130°, 260-270°, and 350°C. None of these were pure fractions as indicated by Schlieren lines; however, they were each treated with sulfuric acid and potassium hydroxide catalysts. No apparent polymerization was obtained although definite evaluation of these reactions is not possible at this time since the molecular weight determinations have not been completed.

3. Post-Carboranylation of Polysiloxane

A relatively simple method of preparing high molecular weight carborane siloxane polymer may be to allow high molecular weight polysiloxane containing silyl hydrogens to react with butenylcarborane.



$$\left[-\underset{H}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-\right]_n + CH_2{=}CHCH_2CH_2\underset{\underset{B_{10}H_{10}}{\backslash O/}}{C-CH} \xrightarrow[\text{or } H_2PtCl_6\cdot 6H_2O]{Pt/C}$$

$$\left[-\underset{\underset{\underset{\underset{B_{10}H_{10}}{\backslash O/}}{C-CH}}{(CH_2)_4}}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-\right]_n$$

This approach was tried using a polymer prepared by hydrolysis of equimolar quantities of dimethyldichlorosilane and methyldichlorosilane. The nonvolatile portion of the hydrolyzate, hydroxy terminated polymer of 7000 molecular weight, was used for further reaction. An attempt to add butenylcarborane in refluxing benzene in the presence of Pt/C catalyst led to about 30 percent reaction after 24 hours. The product, a rubbery gum, was partially crosslinked.

The reaction was further investigated using chloroplatinic acid catalyst with benzene solvent in one case and chloroform as solvent in another. The benzene reaction yielded a crosslinked product and the chloroform reaction resulted in almost complete reaction of butenylcarborane with no crosslinking. This product, a very rubbery gum, was completely soluble in chloroform and in acetone; however, on being exposed to the atmosphere it crosslinked and became brittle. Other reactions were attempted with siloxane polymers terminated with chlorine. The purpose was to carboranylate low molecular weight silyl chloride terminated polymer and subsequently hydrolyze to higher molecular weight. In every case in which siloxane polymers containing random silyl hydrogens were used incomplete reaction with butenylcarborane occurred. One reaction was allowed to continue two weeks without complete reaction of silyl hydrogens as determined by infrared spectroscopy.

A high molecular weight copolymer of 25 mole percent methylhydrogen siloxane and 75 mole percent dimethylsiloxane (Union Carbide Silicone Y-3510) was allowed to react with butenylcarborane in chloroform with chloroplatinic acid catalyst. Reaction occurred readily and was apparently complete within 24 hours as indicated by the absence of absorptions for silyl hydrogens in the infrared spectrum. The elastomeric product did not crosslink on exposure to the atmosphere and was still rubbery and soluble after several weeks.

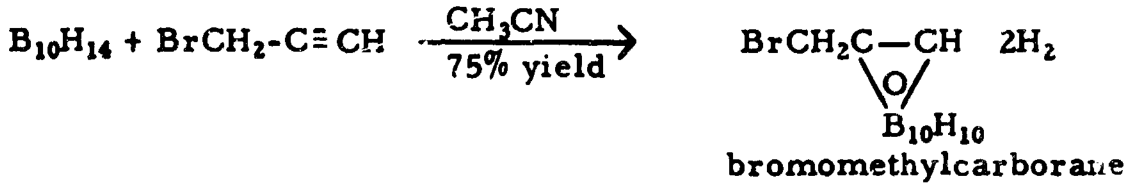
Calculated for $C_{13}H_{40}O_4B_{10}Si_4$: B, 22.49
Found: B, 20.02

The comparatively easy reaction of butenylcarborane with the Union Carbide siloxane polymer is probably due to the regular spacing of reaction sites. This polymer has a hydrogen on every fourth silicon atom and would present no problem of steric hindrance. The random copolymers undoubtedly have hydrogens on successive silicons and could be sterically hindered after partial reaction with butenylcarborane.

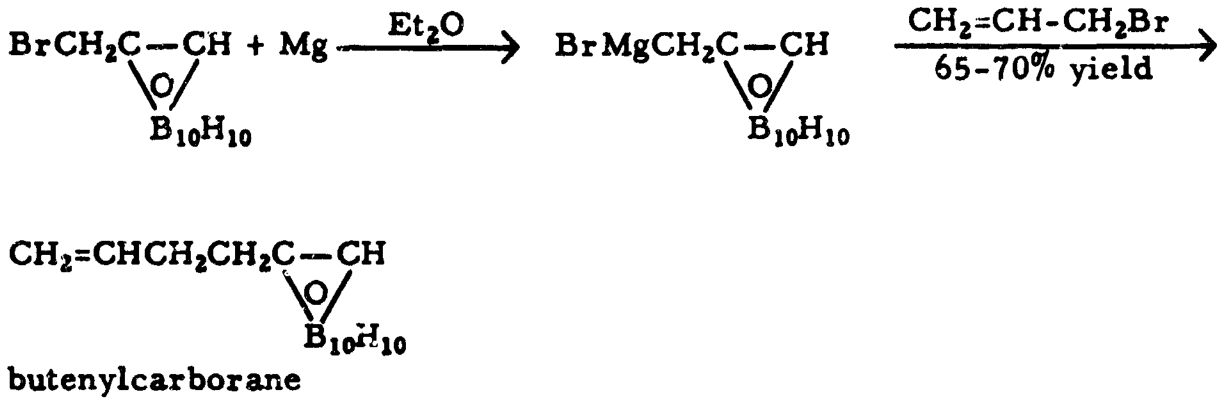
B. Scaleup

The bench-scale preparation of the carborane siloxane polymer and its precursors was completed during this report period. The polymer was prepared by the following series of reactions starting with decarborane:

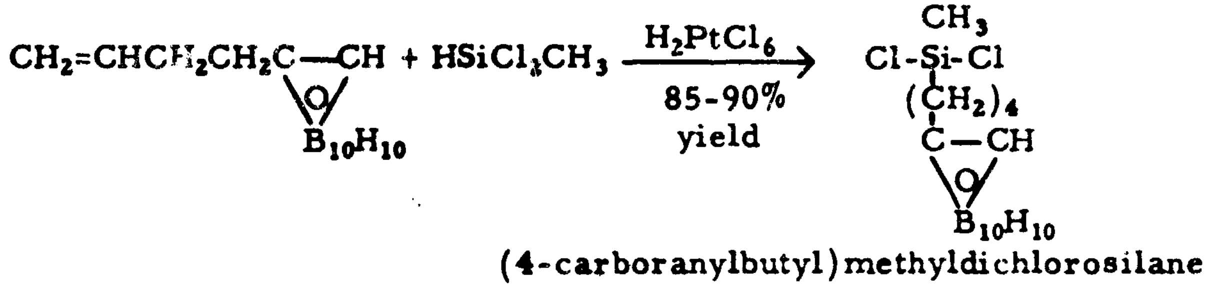
1.



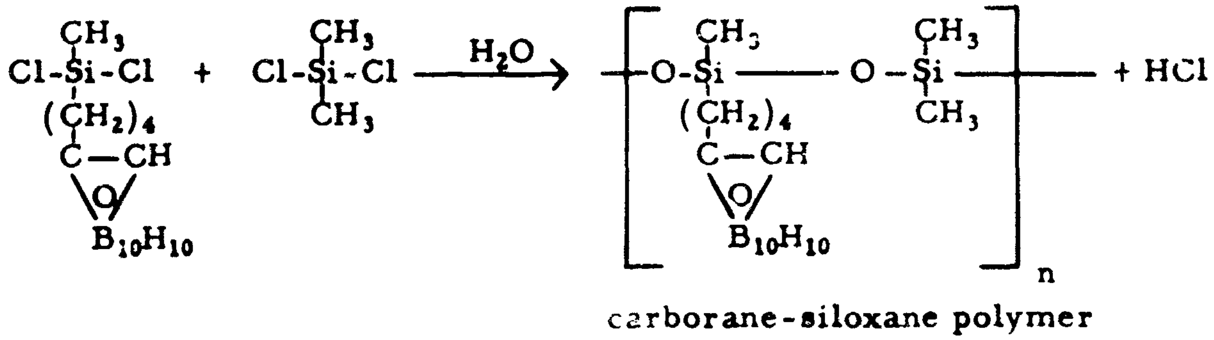
2.



3.



4.



The preparation of 38.5 lb of crude bromomethylcarborane was described in the previous report (Ref 4) with a description of the developmental reactions completed prior to this preparation. Previously bromomethylcarborane has been purified by distillation in vacuo (<0.5 mm); however, since pure bromomethylcarborane is a solid at room temperature, distillation of quantities of this size would be difficult and tedious. Therefore other methods of purification were investigated.

The impurities considered to be most harmful to subsequent processing are unreacted decaborane and/or decaborane derivatives. It was found that these materials could be eliminated by refluxing the crude product in methanol, dissolving in hexane, and filtering off insolubles (e.g., boric acid). The bromomethylcarborane treated in this manner (90 percent recovery) was pure enough for conversion to butenylcarborane.

An additional six bromomethylcarborane preparations were completed during this report period with a combined yield of 25 lb (after purification).

Bromomethylcarborane was converted to butenylcarborane according to reaction 2, above, using the process as described in the previous report. The product was purified by distillation even though the same problems associated with the distillation of bromomethylcarborane were again encountered. Distillation was necessary because no other method to remove the by-product, methylcarborane, has been found.

A total of seven butenylcarborane preparations were completed in this quarter with a combined yield of of 19 lb of distilled product. The combined distillation forecuts weighed 4.8 lb and probably contain additional butenylcarborane as well as methylcarborane.

The butenylcarborane was converted to 21 lb of distilled (4-carboranylbutyl)-methyldichlorosilane according to reaction 3, above. The butenylcarborane was charged to a kettle containing the silane and the catalyst at a rate such that the reaction was controllable. The reaction was exothermic and too rapid addition could have caused a sudden exotherm and loss of part of the more volatile silane. After allowing the mixture to stand overnight for maximum reaction, the product was distilled at 0.1mm/Hg, 153-156°C. A total of four reactions were completed.

Cohydrolysis of the (4-carboranylbutyl)methyldichlorosilane to carborane siloxane polymer was also done. This reaction occurred on the controlled addition of water to an equimolar mixture of the two intermediates (reaction 4, above).

Water addition was done with care to avoid silane loss by entrainment in the HCl stream. One mole of water was added per mole of dichlorosilane and the mixture was allowed to stir for 24 hours to insure complete reaction. After this period, excess water was added and the mixture was stirred and heated for an additional 4 hours.

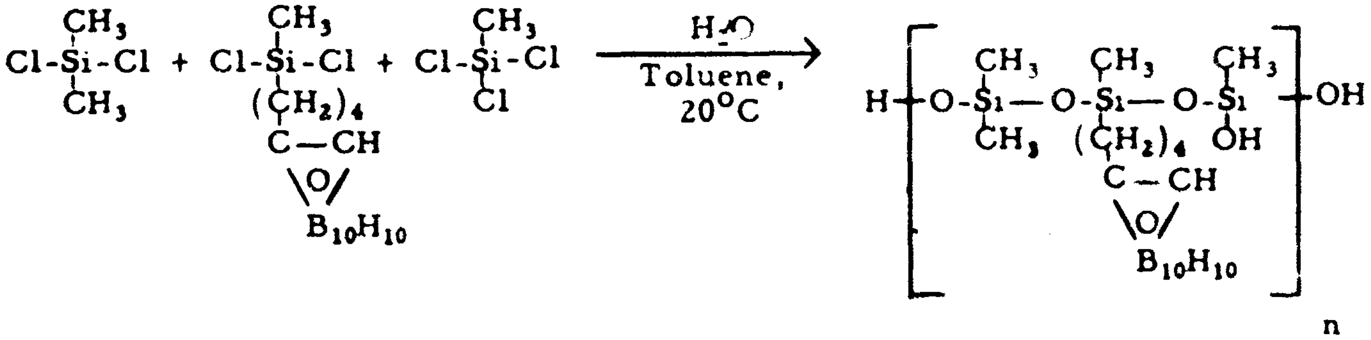
Two cohydrolysis reactions were completed. The products were dissolved in benzene and washed with distilled water to neutrality. At this point a large excess of benzene was added to precipitate the high molecular weight fraction. A total of 10.5 lb of the high molecular weight polymer was obtained from a 21 lb charge of (4-carboranylbutyl)methyldichlorosilane. Recovery of the low molecular weight fraction from the benzene is in progress

C. Curing Studies

1. Resins for Varnishes and Laminates

One potential use of the carborane siloxane polymer is as a varnish, whereby it would be placed in a suitable solvent, applied as a coating and then cured while removing the solvent. Another use that involves a similar procedure is the preparation of resin bonded fiber glass laminates. Here the polymer, in solution is applied to the fiber glass cloth and the solvent is removed to yield dry pre-preg sheets. This is followed by stacking and curing under pressure to yield the laminates. To investigate these applications carborane siloxane polymers containing multiple sites for curing were prepared in solvent and their curing behavior was investigated.

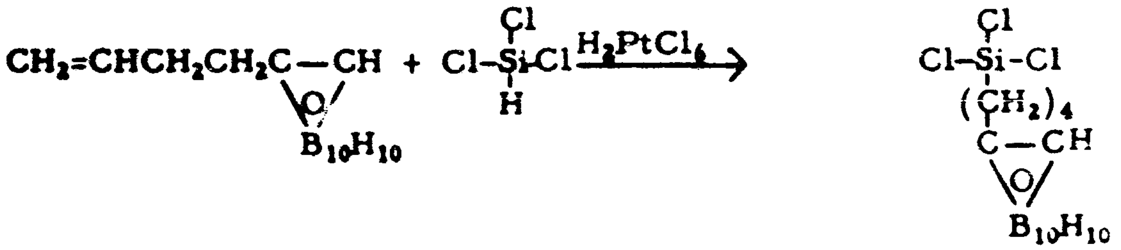
Polymers were prepared by cohydrolysis of dimethyldichlorosilane, (4-carboranylbutyl)methyldichlorosilane, and methyltrichlorosilane in toluene at 20°C. The ratios of silanes were varied so that polymers with 10, 20 and 30 mole percent of functional hydroxy units were obtained.



The polymers did not crosslink during preparation because of the mild conditions used. At higher temperatures gelation would be expected. The polymers were cured using (4-carboranylbutyl)methyldiethoxysilane or tetraethoxysilane as a curative and tin or lead octoate as a catalyst. Tetraethoxysilane was generally unsatisfactory as a curative because it migrated to the surface and evaporated during removal of solvent and degassing. The result was no cure or only surface curing. Tin octoate catalyst gave very fast cures at the temperatures necessary for degassing and solvent removal (80-100°C) and curing started before these operations were completed. Good cured products were obtained using (4-carboranylbutyl)methyldiethoxysilane and lead octoate. Curing for 24 hours at 100°C produced glassy brittle products for the 30 and 20 mole percent functional siloxanes and flexible products for the 10 percent material.

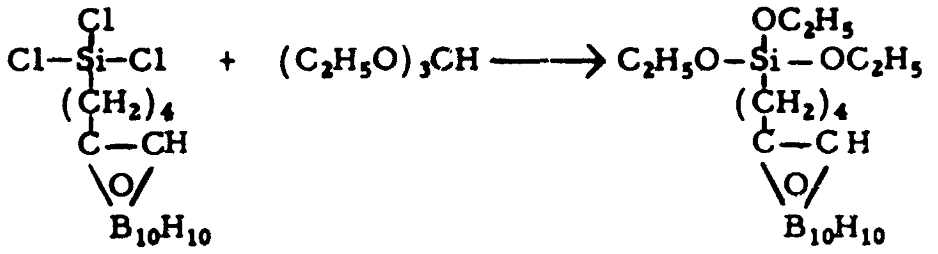
2. Elastomers and Plastics

The polymers of 7000-14,000 molecular weight obtained by solvent fractionation (cf. Phase I, A1) have silyl hydroxy terminals as curing sites. The cured products have potential application as elastomers and resins. Curing of the linear difunctional polymers was studied using tetraethoxysilane and tin or lead octoate. Benzoyl peroxide was also investigated as a curative. Tetraethoxysilane and tin octoate were unsatisfactory for the reasons already given (cf. Phase I, C1) and benzoyl peroxide did not cure the polymer. An ethoxy silane of low volatility was necessary; however, the carboranyl diethoxysilane used for the multi-functional polymers could not be used to cure difunctional polymers. A tri or higher ethoxysilane was necessary and accordingly (4-carboranylbutyl)triethoxysilane was prepared by reaction of butenylcarborane with trichlorosilane followed by reaction with ethylorthoformate.



bp 140-142°/0.04 mm Hg
mp 59-62°

Analysis calculated for $C_6H_{19}B_{10}Cl_3Si$: C, 21.72; H, 5.78; B, 32.60
Found: C, 21.86; H, 5.97; B, 33.65



bp 146-147°/0.02 mm Hg
n_D^{25} 1.4912

Analysis calculated for $C_{12}H_{34}O_3B_{10}Si$: C, 39.85; H, 9.48; B, 29.90
Found: C, 39.79; H, 9.36; B, 29.41

The carborane triethoxysilane was used in conjunction with lead octoate to cure the difunctional linear polymer and good cures were obtained. The products were flexible resins rather than elastomers. Higher molecular weights are probably necessary to obtain elastomers.

The polymer before curing was a highly viscous liquid or sticky gum and it was difficult to mix with curative and degas. Mixing on a roll mill without the addition of filler was unsuccessful due to sticking to the rolls. It was finally necessary to mix while hot (80-100°C) in vacuum to prevent air entrapment and cure in a mold. Some reasonably good cured samples were obtained but air entrapment remains a problem. At this writing injection molding techniques are being tried to obtain cured samples free of voids or air pockets.

PHASE II. THERMAL EVALUATION OF CARBORANE SILOXANE POLYMERS

A. Application Study in Sealed DC Electric Motor Tests

A potential application of carborane siloxane polymers is as insulation in sealed DC electric motors. Conventional silicones are presently used for this purpose; however, they are unsatisfactory because they degrade at the operating temperature of the motor (185°C) to yield products which promote corrosion of the carbon brushes.

Samples of carborane siloxane polymer, both uncured and cured, were tested at USNASL to determine their effect upon carbon brush corrosion in a simulated sealed DC electric motor operating at 185°C. The results shown below indicate that both uncured and cured carborane siloxane polymer produce no corrosive action on the brushes during a 72 hour test period. Brush corrosion was apparently limited to that caused by normal friction, the difference being within experimental error. Conventional silicones, under the same conditions, caused corrosion up to 850 percent greater than normal friction, a value which is sufficiently high to prohibit their use as insulation in sealed DC electric motors.

Material	Brush wear, inches
Control (no siloxane present)	0.006
Perphenylated polysiloxane (USNASL product)	0.007
Carborane siloxane, uncured	0.010
Carborane siloxane, cured	0.010
Silicone rubber, conventional type	0.084

III. CONCLUSIONS

A method was developed to prepare carborane siloxane polymer in large quantity by the cohydrolysis of dimethyldichlorosilane and (4-carboranylbutyl)methyldichlorosilane. A total quantity of 21 pounds of polymer was prepared during the scaleup procedure. The yield of linear polymer was about 50 percent of the total product. The crude cyclics could not be polymerized.

Hydrogenmethylsiloxane/dimethylsiloxane copolymer may be post-carboranylated with butenylcarborane to near completion if the silyl hydrogens are adequately separated in the polymer.

Proximity of silyl hydrogens results in steric hindrance to reaction after an initial partial reaction. The product obtained from the post-carboranylation of a high molecular weight silicone is a rubber which may be cured with benzoyl peroxide.

Carborane siloxane polymers may be cured through silyl hydroxy groups using ethoxy silane derivatives and tin or lead octoate catalysts. Lead octoate is preferable to tin octoate because the lead compound gives a longer pot life. A new compound (4-carboranylbutyl)triethoxysilane was prepared and shown to be useful as a high temperature curative.

Cured products that vary from brittle to flexible may be obtained by regulating the number of crosslinks in the polymer. Products cured this way are suitable for varnish or glass-resin laminate applications.

Evaluation of these polymers in simulated sealed DC electric motors operating at 185°C shows that they do not contribute to brush wear as do conventional silicones.

IV. REFERENCES

1. Report RMD 1147-E1, Development of Solid Propellants for Application in Extended Temperatures or Space Environment Conditions, Thiokol Chemical Corporation, Reaction Motors Division, Contract AF33(616)-6424.

2. Contract NObs-78416, Index No. SR-007.

3. Report RMD 2034-F, Ultra High Temperature Dielectric Materials, Thiokol Chemical Corporation, Reaction Motors Division, Contract NObs-78416.

4. Report RMD 5038-Q1, Dielectric Materials for High Temperature Application, Thiokol Chemical Corporation, Reaction Motors Division, Contratc NObs-90065.

APPENDIX

INVESTIGATION OF THERMAL STABILITY OF BORON-SILICONE COPOLYMER

(Technical Memorandum)

U.S. Naval Applied Science Laboratory
Naval Base
Brooklyn, New York

Lab Project 9400-31
SR-007-03-03, Task 1000

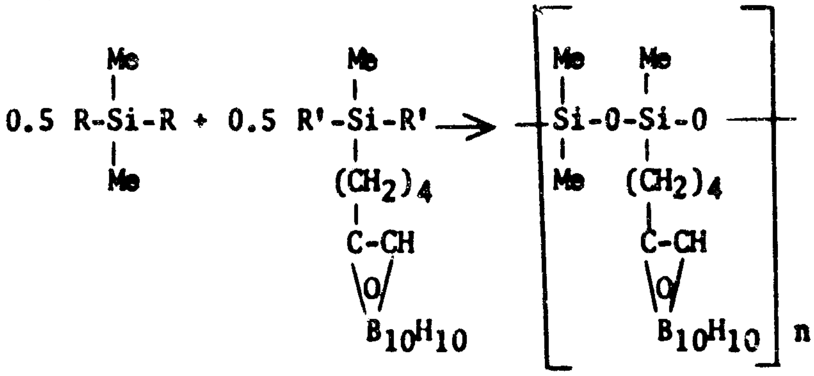
Lab. Project 9400-31
Technical Memorandum 2

Ref: (a) BUSHIPS ltr R007 03 03 Ser 634C4-457 of 11 May 1962
(b) Visit of J. Green (Thiokol Chemical Corp.) to NAVAPLSCIENLAB (Code 9420) of 11 Dec 1963
(c) Green, J., Fein, M.M., Loprest, F.J., Lum, A., and Mayes, N. "Thermally Stable Boron-Containing Polymers", presented at the Symposium on Thermal Stability of Polymers, Battelle Memorial Institute, Columbus, Ohio, 5-6 Dec 1963
(d) Visit of J. Green and R. Crooker (Thiokol Chemical Corp.) to MATLAB NAVSHIPYDNYK of 2 Apr 1963
(e) BUSHIPS ltr SF 013-12-09 Ser 660E-2939 of 28 Jun 1963

Encl: (1) Thermogram of Reference (b) Polymer - Heated in Nitrogen Atmosphere
(2) Thermogram of Reference (b) Polymer - Heated in Air
(3) Thermogram of Polymer 171431 - Heated in Nitrogen Atmosphere
(4) Thermogram of Polymer 171431 ($FeCl_3$ Catalyst) - Heated in Nitrogen Atmosphere
(5) Thermogram of Polymer 171436-1 - Heated in Nitrogen Atmosphere
(6) Thermogram of Polymer 171441 - Heated in Nitrogen Atmosphere

1. As authorized under reference (a), the U. S. Naval Applied Science Laboratory is conducting a program to develop new, thermally stable polymers for naval use. In addition to in-house efforts to synthesize novel heat resistant inorganic polymers, study is being undertaken of similar research work conducted by other laboratories under government sponsorship. This memorandum covers investigation of an experimental polymer developed by the Reaction Motors Division of Thiokol Chemical Corp. under sponsorship of the Bureau of Ships, Department of the Navy, under Contracts NObs 84774 and 88318.

2. An experimental quantity of a tough, flexible solid polymer was submitted to this Laboratory during the reference (b) visit for investigation of its pyrolytic stability when heated in air and in nitrogen atmospheres. As indicated in references (b) and (c), this material was obtained by condensation reactions such as



$$0.5\ \mathrm{R{-}\overset{Me}{\underset{Me}{Si}}{-}R} + 0.5\ \mathrm{R'{-}\overset{Me}{\underset{\substack{(CH_2)_4\\ C-CH\\ \backslash O/\\ B_{10}H_{10}}}{Si}}{-}R'} \longrightarrow \left[\mathrm{\overset{Me}{\underset{Me}{Si}}{-}O{-}\overset{Me}{\underset{\substack{(CH_2)_4\\ C-CH\\ \backslash O/\\ B_{10}H_{10}}}{Si}}{-}O}\right]_n \qquad (1)$$

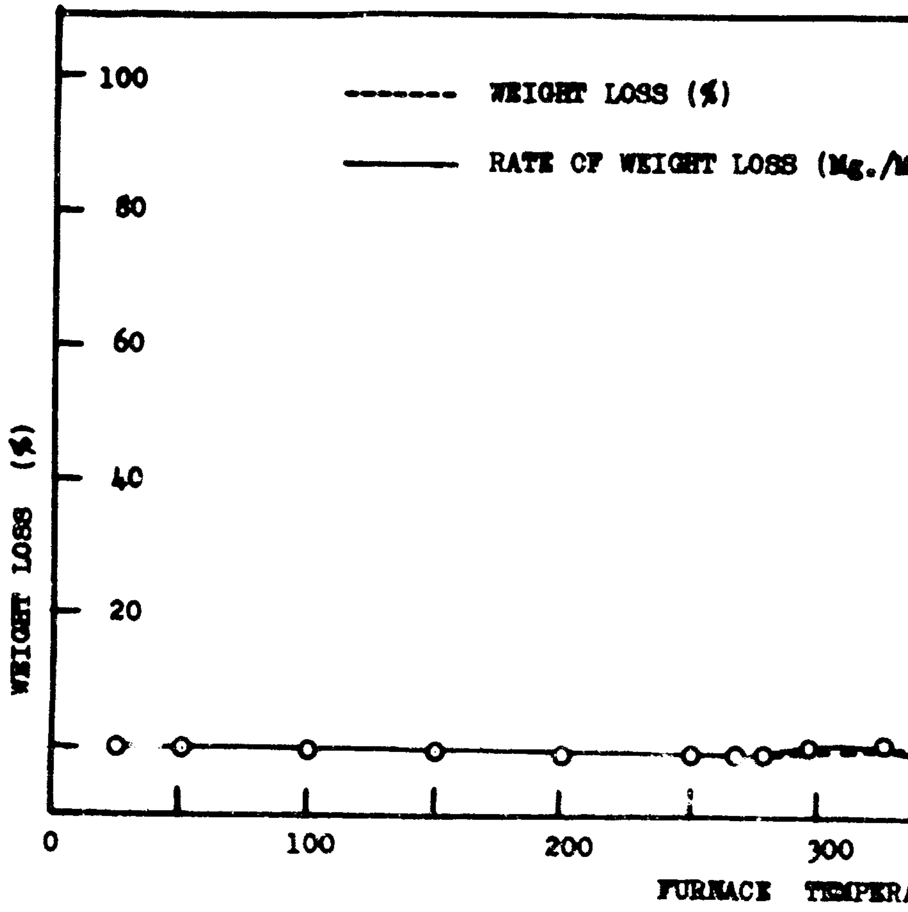
where R, R', and Me represent halogen atoms, alkoxy groups, and methyl radicals, respectively.

3. Samples of the polymer, 200 mg. each, were subjected to thermogravimetric analysis (TGA). The results of TGA analysis of a specimen heated at 180°C/hr. in the presence of nitrogen flowing at 10cc/min. is presented in enclosure (1). These data indicate that, under these conditions, the polymer shows a weight loss of only 6% when heated to about 450°C. Above this temperature the material volatilizes rapidly, attaining a maximum rate of weight loss of approximately 6 mg./min. at 495°C. The small losses in weight occurring at 250-280, 280-370, and 370-425°C are probably due to the volatilization of impurities in the polymer. An amber colored, hard, brittle residue was recovered after the sample was heated to 600°C.

4. The results of TGA analysis of the polymer, heated in air in similar manner, are shown in enclosure (2). While a comparison of the data in enclosures (1) and (2) shows a very close similarity, the nature of the residues differed. The white powder residue, obtained from the heating in air, probably consists of silicon and boron oxides. The brownish polymer obtained from heating in nitrogen-air mixture suggests that under these conditions only partial oxidation takes place. Subsequent heating in air of the brown residue resulted in complete charring of the specimen, indicating the presence of some organic matter.

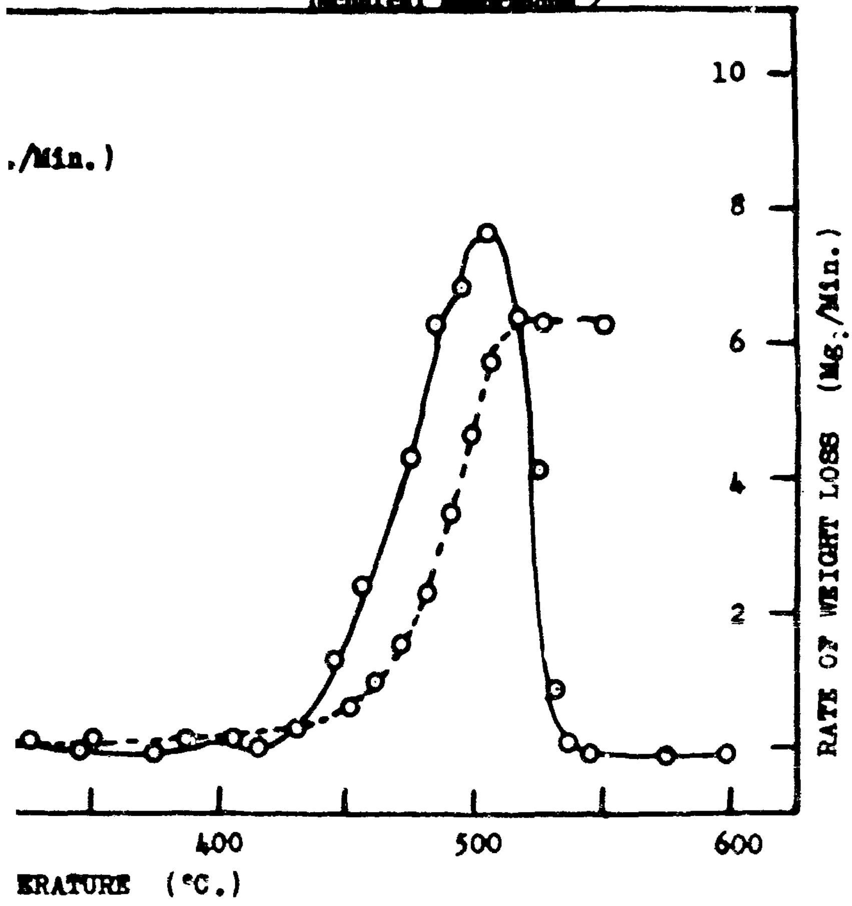
5. For comparison purposes, TGA data of specimens provided this Laboratory during the reference (d) visit are given in enclosures (3) through (6). It is evident from these results that the thermal stability of the polymer supplied during the reference (b) visit closely parallels that of the material designated by the Thiokol Chemical Corp. as 171431, obtained under reference (d). The ferric chloride catalyst treated 171431 material shows appreciable weight losses at temperatures below 450°. This might be attributed to large amounts of impurities in the specimen or to differences in molecular bonding. The thermal resistance of the substances designated as 171436-1 and 171441 are similar to each other, to specimen 171431, and to the material provided under reference (b). It is suggested that the resistance of these carboranesilane-methylsilane copolymers to heat degradation is not appreciably influenced by minor variations of molecular structure or by differences in molecular weight.

6. Additional application studies of the reference (b) polymer are now underway. These investigations are being made in conjunction with studies of excessive brush wear in totally enclosed electric D.C. motors containing silicone type insulating materials, authorized under reference (e), Bureau of Ships Subproject SF 013-12-09, Task 4643. This phase of the work will be reported under Lab. Project 9400-7.

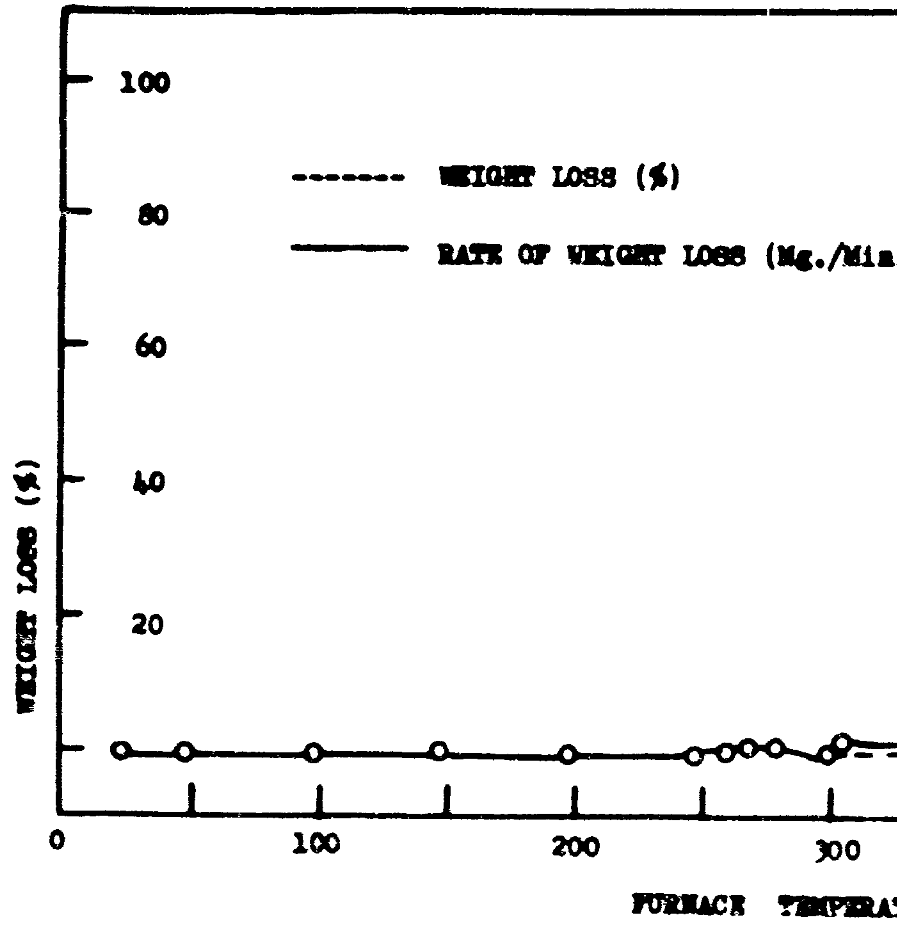


THERMOGRAM OF REFERENCE (b) POLYMER –

Enclosure (1)

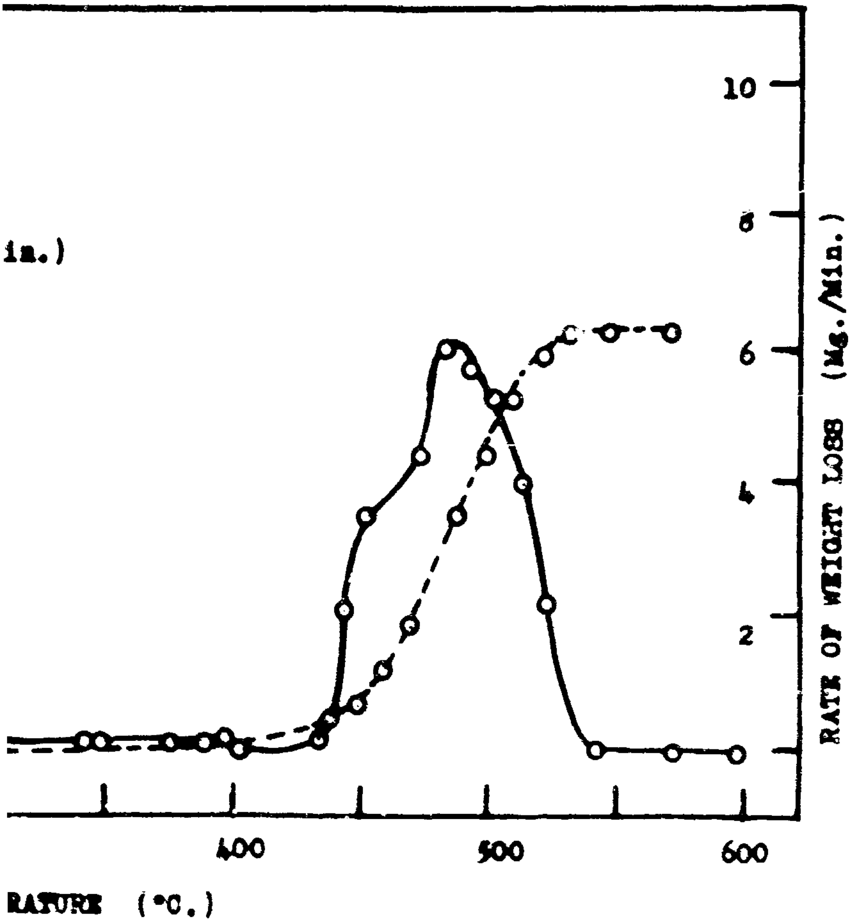


-- HEATED IN NITROGEN ATMOSPHERE

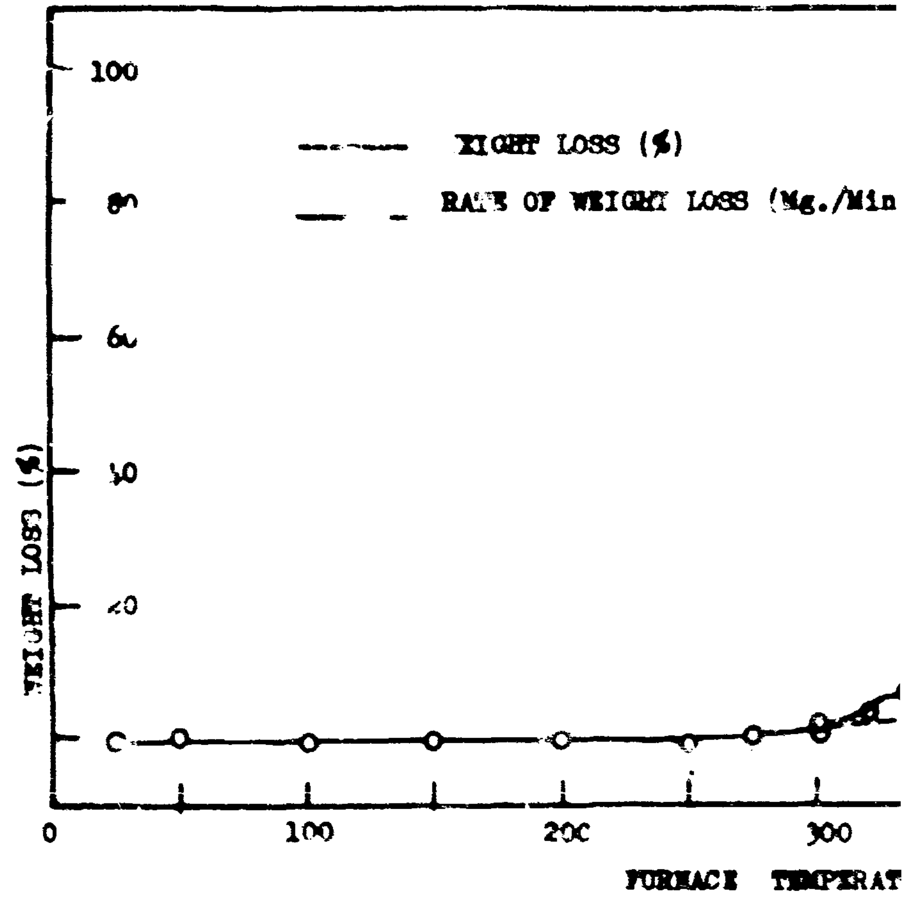


THERMOGRAM OF REFERENCE (b) PO

Enclosure (2)

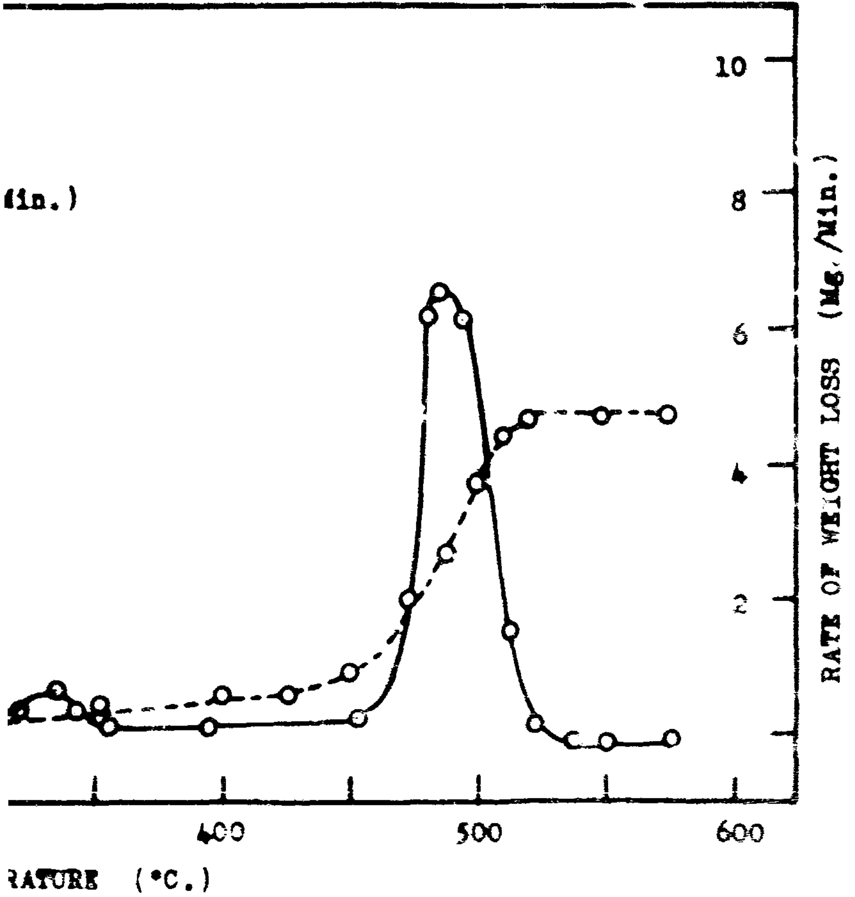


POLYMER - HEATED IN AIR



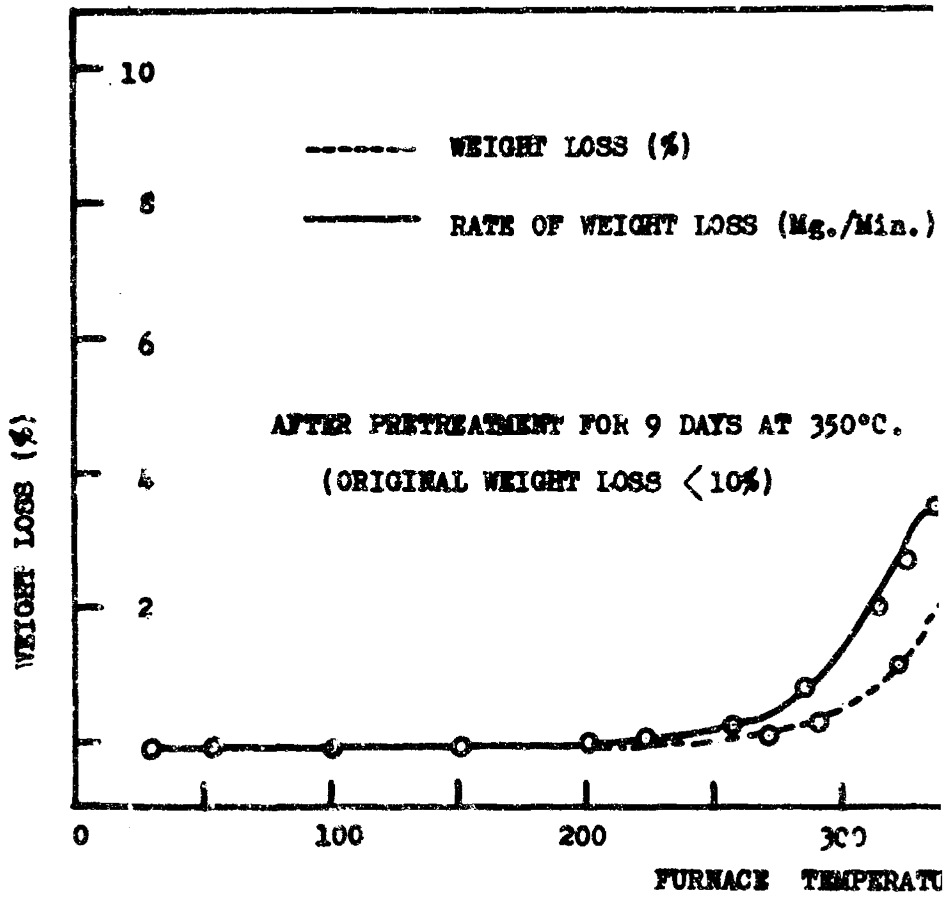
THERMOGRAM OF POLYMER 171431 - HEA

Enclosure (3)



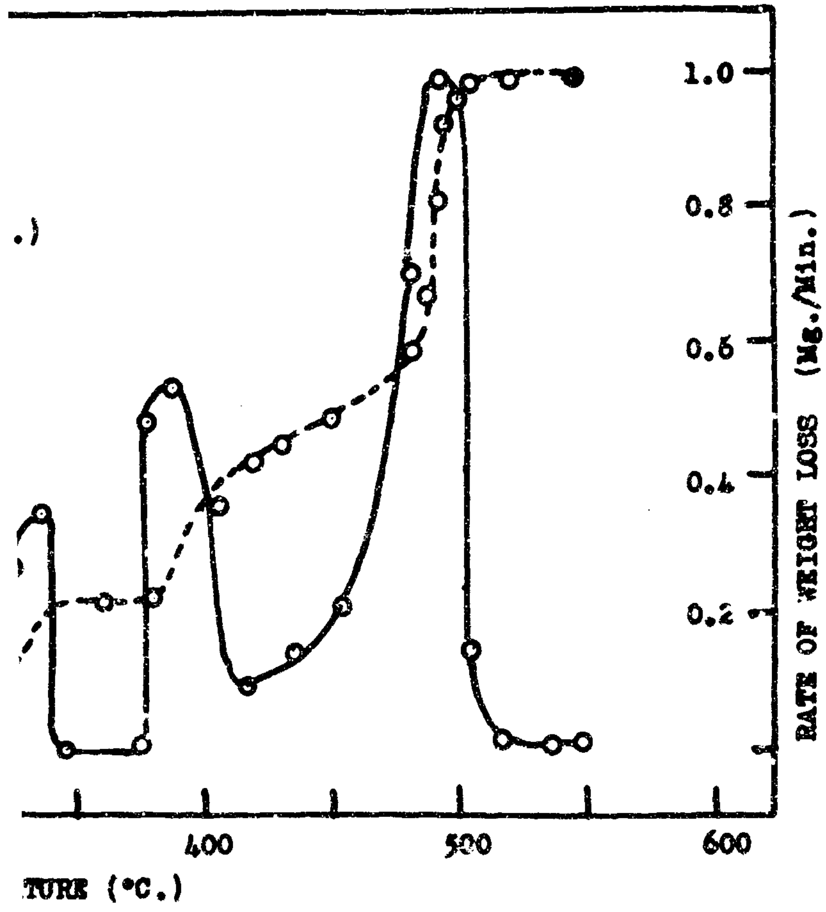
HEATED IN NITROGEN ATMOSPHERE

Thiokol
REACTION MOTORS DIVISION



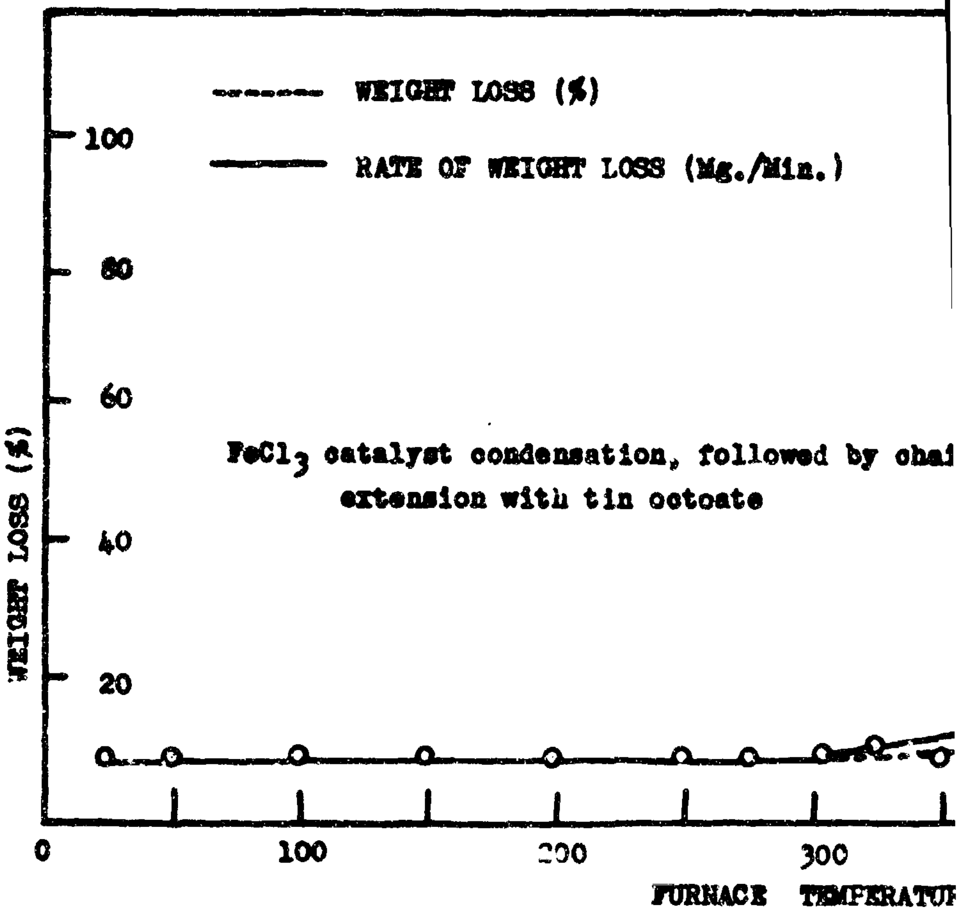
THERMOGRAM OF POLYMER 171431 ($FeCl_3$ CATALYST)

Enclosure (4)



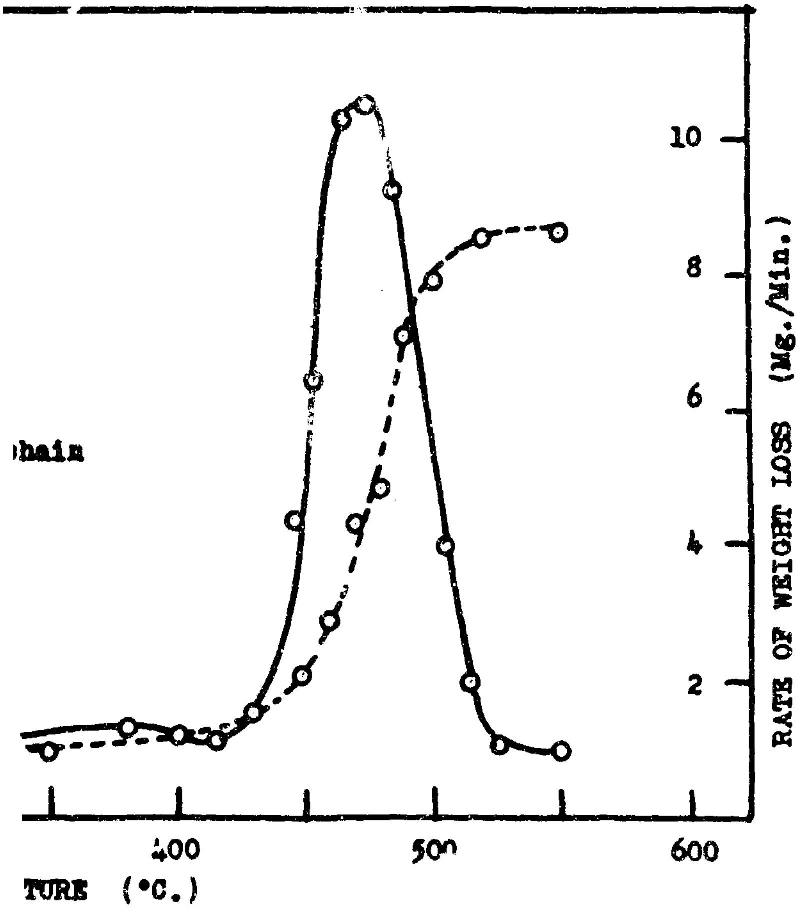
T) - HEATED IN NITROGEN ATMOSPHERE

Naval Applied Science Laboratory



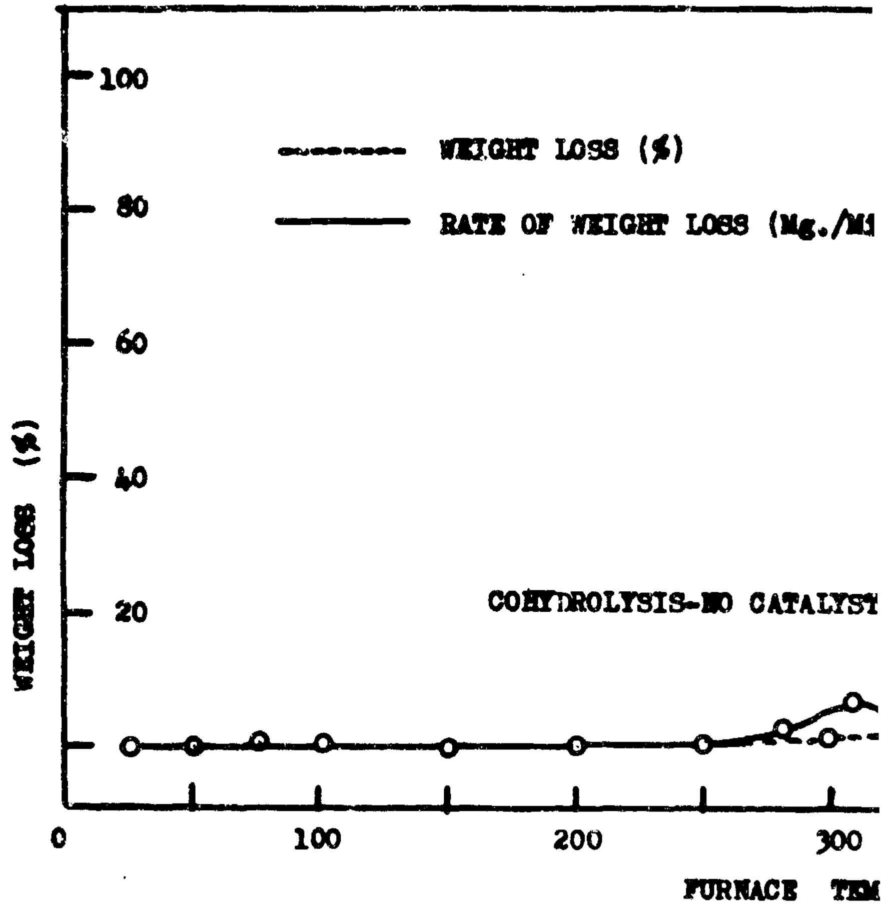
THERMOGRAM OF POLYMER 171436-1 - HEATED

Enclosure (5)



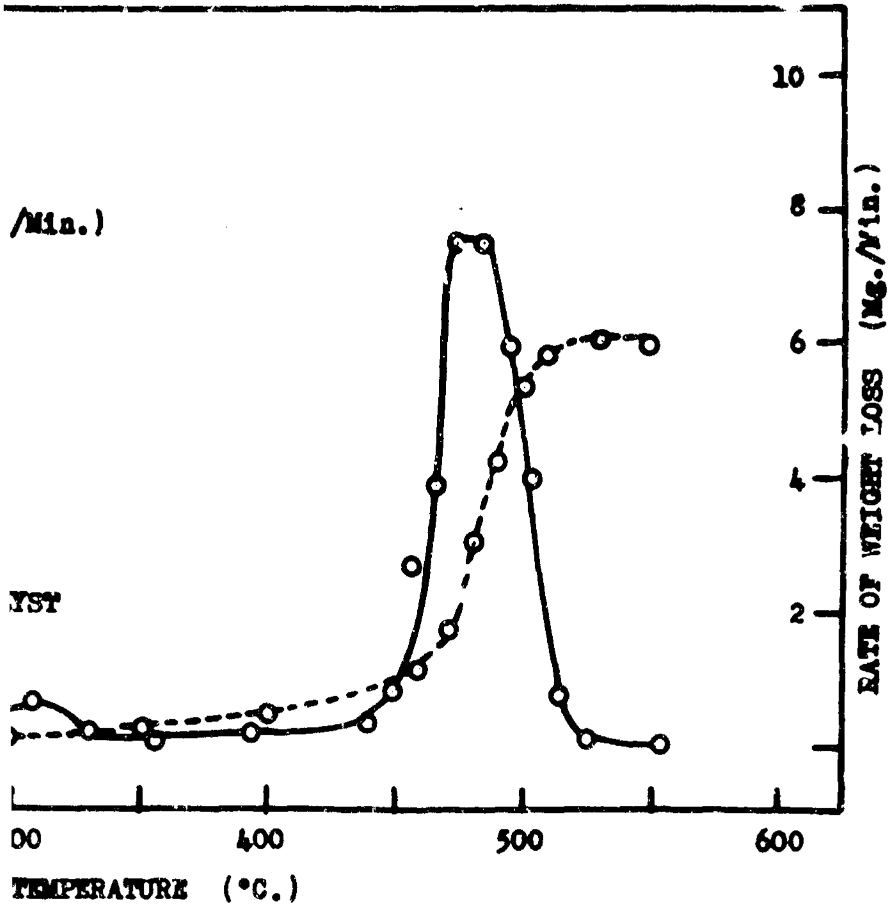
ED IN NITROGEN ATMOSPHERE

Naval Applied Science Laboratory



THERMOGRAM OF POLYMER 171441 - HE

Enclosure (6)



HEATED IN NITROGEN ATMOSPHERE