A REVIEW OF SELECTED U.S. GOVERNMENT RESEARCH AND DEVELOPMENT REPORTS OTR-138

Synthesis of Thermally Stable Elastomers

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This study is one of a series of reviews of selected Government research and development reports. It highlights significant technical information for the attention of the industrial community. These reports may offer ideas for materials and product development and/or means of reducing production costs.

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SYNTHESIS OF THERMALLY STABLE ELASTOMERS

ABSTRACT

Significant reports covering the period since 1960 were selected for this study with reference to relevant earlier works. Recent Government-sponsored research and development (R&D) in high temperature elastomers has been directed along two lines: (1) new polymer synthesis and (2) evaluation of compounds to improve the thermal stability of current elastomers. Progress has been made in each of these areas. Large groups of inorganic and semi-inorganic polymer systems were evaluated. Systems included silazanes, siloxanes, and fluorocarbons.

KEY WORDS

Elastomers, Polyester, Polymer, Polymer Synthesis, Thermally Stable Elastomers, Polyester Elastomers, Elastomer Synthesis, Heat-Resistant Inhibitors, Vulcanization, Elastomeric Gums, Copolymers.

REVIEW OF RESEARCH REPORTS

Introduction

The increasingly stringent environmental requirements of space age design has resulted in a rising need for elastomeric materials that are resistant to the effects of high temperatures. In the recent past, the upper temperature limit at which elastomers maintained their properties was about 600° F. Beyond that point, their tensile strength, modulus of elasticity, or hardness degraded appreciably. Concurrent requirements are that these elastomers possess reasonable properties at low temperatures, resist ozone and weathering, and be impervious to solvents and oils.

The development of suitable materials has been an area of exceptional difficulty, and the Government has sponsored a number of programs over the past decade in an attempt to obtain significant breakthroughs. The goal has been to extend the useful upper temperature limit to at least 800° F with an ultimate objective of 1000 - 1200° F.

Programs have generally had two goals: (1) new polymer synthesis, and (2) improved compounding to increase the thermal stability of available elastomers. A lesser objective has been to achieve improved radiation stability either separately or in conjunction with improved heat stability.

Two factors are required for a polymer to exist at elevated temperatures: (1) no significant portion of its chemical bonds should degrade at elevated temperatures, and it should retain its elasticity, (2) the intermolecular forces and molecular entanglement responsible for elasticity must remain effective. The main cause of strength loss is a reduced filler reinforcement at elevated temperatures and an increased molecular motion of the chains because of thermal excitation.

Large groups of inorganic and semi-inorganic polymer systems have been investigated in the past few years in an attempt to develop new elastomers and to improve the properties of those currently known. The principal areas investigated included silazanes and fluorocarbons. Polyesters have been studied intensively in an effort to meet the need for polymers with better heat and radiation resistance. Present polyesters, in general, exhibit high tensile strengths, good tear resistance, high abrasion resistance, fair elasticity, good solvent resistance, and excellent ozone and oxidation stability. Although significant improvements in materials have been obtained, total success has been elusive and much remains to be done to find materials that are altogether satisfactory. Research has been so intense and the need is so great that the field of thermally stable and high temperature elastomers is tending to become a distinct area of chemistry. Reports from many of these Government-sponsored research programs are available from the Clearinghouse for Federal Scientific and Technical Information (CFSTI), Department of Commerce.

Those interested in the subject matter of this report may also be interested in additional information in related fields such as high temperature adhesives, finishes, coatings, elastomeric insulating materials, and sealants. Titles of Government reports related to these areas may be obtained by contacting CFSTI or by checking the indexes of *U.S. Government Research and Development Reports (USGRDR)* which can be obtained from the GPO. Other related reference sources are the following Selected Bibliographies (SB's) which contain bibliographies of reports listed in the CFSTI semimonthly announcement journals, *USGRDR* and *Technical Translations.*

SB–400	Polymer Research (Plastics), 1959.
SB–493	Fluorocarbons, 1962.
SB–507	Polymers, Organic (Organic Catalysts, Part III), 1962.

Synthesis of Polyester Elastomers

A program for the synthesis of polyester elastomers was conducted by the Rock Island Arsenal (AD–275 520) to obtain polymers of increased heat and radiation stability. Polyester-based polymers having functional groups to serve as cross-linking sites were investigated. This work was directed to the improvement of heat stability of the polyesters by incorporating thermally stable organic substituents.

The effect of combining the carbon-fluorine bond and the benzene ring in a polyester repeating unit was studied. Carbon-black filled compounds exhibited poor mold flow and cure characteristics. Vulcanizates based on aromatic fluorinated polyester elastomers did not have improved heat resistance when compared with saturated aliphatic polyester-based vulcanizates. All of the experimental polyesters had poor compression set, poor properties at low temperature, and good resistance to hydrocarbon oils. The best balance of physical properties was exhibited by the polyester based on 1,10-decanediol and isophthalic acid. The general conclusion to be drawn from this study is that the presence of benzene and carbon-fluorine groups in the molecule does not overcome the weak link (the ester group) of polyesters, especially when aged at high temperature.

Synthesis of Polyesters From Diepoxides and Anhydrides

Since aromatic systems are resistant to degradation by heat, they were incorporated into a polyester type polymer and studied as a means of enhancing the thermal stability of such material.

Rock Island Arsenal Laboratory sponsored a program (AD–259 551) to synthesize polyester based elastomers which would retain their elastomeric properties over the temperature range of −70° F to 500° F and be resistant to various lubricants, fluids and fuels. Low molecular weight, rubber polymers were prepared from 1,3-bis [3 (2,3-epoxypropoxy) propyl] tetramethyldisiloxane and phthalic anhydride using tertiary amines as catalysts. Attempts to obtain rubbery polymers of high molecular weight proved unsuccessful. The vulcanizates based on these polymers had excellent hydrocarbon oil resistance; their properties were poor at low temperature. The heat resistance was much lower than expected and the stress-strain properties were poor compared to those of the control vulcanizates. The control vulcanizates were based on butadiene/acrylonitrile and polyethylene/propylene succinate.

Synthesis of Polymers Containing Silicon-Nitrogen Bonds

The U.S. Army sponsored a program (AD–289 547) to study polymers containing silicon-nitrogen bonds as part of a broad program of the search for materials useful as elastomers, lubricants, sealants, adhesives, and structural materials. Polymers such as silazanes have wide variety of physical states including liquids, oils, greases, elastomers, and vitreous solids. They have a higher degree of thermal and chemical stability than siloxanes and fluorocarbons and thus greater potential stability toward the diverse effects of heat, water, air, or liquid oxygen.

Polymers were obtained through two different reactions: (1) silicon tetrachloride and ammonia and (2) methyl or phenyl dichlorosilanes with ammonia and amines. The dichlorosilane polymers exhibited exceptional stabilities to heat, reagents, and solvents, although they proved to be somewhat sensitive to moisture and acids. Possible uses include coatings to protect metals from attack by air and chemicals, coatings for electrical insulation and flexible impregnating agents for gaskets.

Silicon tetrachloride reactions were not productive because extreme care was required to protect the products from moisture, and the products did not consistently react with polymer-forming reagents. Silazanes prepared from difunctional derivatives of silicon yielded a wide range of physical states of relatively low molecular weights from mobile liquids to heavy greases. Diamines offered intriguing possibilities for making silazane polymers. In spite of complications such as hydrochloric acid precipitating salts of the desired reaction product, silazane was obtained. Heavy greases were obtained through catalytic polymerizations. However, much additional work is required to gain an understanding of the structure so that high polymers can be produced by simplified methods. Hexamethylcyclotrisilazane was converted to a compound of higher molecular weight by heating it with potassium hydroxide. The product obtained was a grease; however, only a three-fold increase in molecular weight was obtained and it could not be considered high polymer.

Resilient and rigid solids have been obtained by condensation polymerization of some silazanes at temperatures in the range of 750 - 940° F. These products have good chemical and thermal stability. Rigid polymers are brittle but have exceptional thermal stability. Polymers that are both flexible and reasonably tough have been obtained by choosing the proper silazanes as raw materials.

Hexaphenylcyclotrisilazane, when polymerization was stopped before completion, resulted in a benzene-soluble material with a lower melting point and lower volatility than the original compound. This partially polymerized compound was suitable for application to metal panels for subsequent complete polymerization to coatings. When a thick film was applied, the resulting polymer was a foam because solidification occurred while volatile products were escaping. Films of less than 1 mil thickness cured at 840 - 940° F resulted in a hard, transparent, brittle coating. Condensation polymers have exceptional thermal and chemical stability with no known solvent except boiling sulfuric acid.

Attempts to make salts with acids under anhydrous conditions, employing the amine group of silazanes, yielded no satisfactorily pure products. The end product was a brittle, vitreous, colorless solid which decomposed at temperatures above 400° F.

An elastomer made from ethylenediamine silazane adhered well to metals and was not attacked by moisture, acids, or alkali. It remained resilient longer at 840° F than either a silicone rubber (Silastic 80) or a fluorocarbon rubber (Viton A) and also maintained its resiliency at −110° F. However, its tensile strength was low.

It was found to be possible to make sheets of cured silazane condensation polymers. A limited investigation disclosed that they are relatively impervious to gases and liquids and will remain flexible for many hours at 750° F.

In another U.S. Army-sponsored program to develop methods for synthesis of thermally stable elastomers based on polymer chains containing silicon atoms bonded directly to nitrogen (AD–614 473), linear silicon-nitrogen polymers with molecular weights of 7500 to 15,000 were obtained from diazasilacyclopentane derivatives. Polymers obtained by splitting out ammonia ranged from viscous oils to rubbery solids. Polymers obtained by splitting out methylamine ranged from viscous liquids to brittle solids.

Numerous cyclotrisilazane compounds were prepared and evaluated. Ethyl-substituted derivatives proved to be more stable than methyl-substituted cyclotrisilazane. Polymers were also obtained from silazanes and organic diols. Their character ranged from elastic gums to solids at room temperature and their thermal stability was relatively poor.

Silcarbane Siloxane Elastomers Synthesis

At Rock Island Arsenal, the U.S. Army supported an experimental program (AD–296 822) to synthesize silcarbane elastomers having potential use in the temperature range of 500 - 810° F. Silcarbane polymers were prepared from silicon dihydrides and 1,6-heptadiene, usually yielding rubbery products curable by conventional techniques. A silcarbane type elastomer was prepared having a molecular weight of 100,360 which was the highest molecular weight known at that time for this polymer type.

Silicate Polymers Synthesis

Rock Island Arsenal sponsored an extended program to prepare thermally stable, flexible, and elastic silicates (AD–286 464). Two areas of investigation were pursued: (1) the modification and reaction of the natural silicates, asbestos and mica, and (2) the investigation of polymers derived from a reaction of a silicate with an organohalosilane.

The preparation of elastic silicates from naturally occurring silicates depends on the ability to modify the existing crosslinking of the silicate chains without materially or totally destroying the chain structure itself. Several methods of extracting metallic ions from the matrix of asbestos and mica to modify the crosslinking were investigated. These methods consisted of treatment with chelating agents, leaching with acid and alkali, and sublimation with sodium. Some success was achieved with the leaching and sublimation process.

One approach to the improvement of the physical and mechanical properties of a polymer is to increase the molecular weight of the material. Investigations were made on the effects of increasing the temperature and reaction times and to variations of solvents to improve miscibility and solubility of the materials. This was based on the premise that if the solubility of the polymer in the reaction medium could be increased, the molecular weight could be increased. Results showed that raising the temperature and increasing the time of reaction had little or no effect on the molecular weight, thus it can be concluded that such simple methods have little effect on the solubility of the polymers in the medium. However, increases in the molecular weight of the polymer can be achieved by the use of a crosslinking agent such as methyltrichlorosilane. Polymers were also prepared which contain a substantial percentage of phenyl groups.

Silicone, Fluorocarbon, and Diene Elastomers Synthesis

Rock Island Arsenal of the U.S. Army sponsored a program to synthesize chemicals not commercially available which would function to increase the heat stability of various types of elastomers (AD–290 757). The classes of compounds selected for synthesis were: (1) derivatives of dithio-oxamide, and (2) organometallic chelates. Silicone, fluorocarbon, and diene elastomers were evaluated. This program was devised in order to broaden research on the heat stabilization of elastomeric vulcanizates. The degradation mechanism under temperature was determined to be derived from free radical formation; also traces of soluble heavy metal salts which are introduced during the processing may be contributory.

Dithio-oxamide derivatives were investigated since they were theoretically good stabilizers for elastomers; however, in actual tests of the 37 derivatives of dithio-oxamide prepared, only two—N,N′-bis (hydroxyethyl) dithio-oxamide cobalt (II) and N,N′-dibenzyl-dithio-oxamide cobalt (II)—showed promise. Their utility was limited to the case of the fluoroelastomers.

Sixteen organometallic derivatives were also evaluated, but only nickel chelates of benzoin oxime and ethylene-diamine-o-cresol, in admixture with pentaerythritol and a proprietary amine, exhibited better resistance to degradation at 300° F than did the control. They did not, however, provide protection equal to that offered by the best inhibitor system found to date, which is cadmium-barium fatty acid soaps-chelator mixture and a proprietary amine.

Also, protection for fluoroelastomers was provided by cobalt and nickel chelates of 8-hydroxy-quinoline during a 24-hour exposure at 600° F; but, these stabilizers lose their effectiveness when the exposure is extended to 48 hours.

Polyphenylether-Siloxane Compound Synthesis

Siloxane compounds have been developed to the point where they are now comparable to natural and synthetic organic rubbers. Related to these materials are the cometalloxanes which contain silicon, oxygen, and a metal in the polymer chain.

The U.S. Army sponsoced a program (AD–600 121) to prepare high temperature, thermally stable elastomers from polyphenylether-siloxane compounds. Research was separated into three following problem areas (AD–268 261):

a. Synthesis of the desired monomer blocks (p,p′-dihydroxypolyphenylether)

b. Condensation of these blocks with silane groups to yield high molecular weight block copolymers.

c. Development of vulcanizing systems appropriate for these high temperature block copolymers.

Polymerization with diethoxysilanes yielded low melting, low molecular weight, soluble thermoplastics. Polymerization with dichlorosilanes resulted in polymers of low molecular weight which were converted into insoluble, infusible products during storage at 285° F in vacuo. One fairly successful copolymer was prepared in xylene solution from very pure monomers and the extent of reaction was indicated by an increase of relative viscosity to 190 in 193 hours. Shortly thereafter the polymer precipitated from solution as an insoluble, infusible material. The thermal stability of this copolymer is excellent; it is a brittle glass at room temperature and exhibits rubbery characteristics at about 122° F.

Polymerization with dianilinosilanes resulted in a product whose characteristics were outstanding. It exhibits rubbery characteristics only at temperatures above 400° F and retains its rubbery characteristics to temperatures of approximately 1850° F when heated rapidly. At room temperature it is a hard solid and is tough rather than brittle.

This work demonstrated that condensation of dihydroxy monomers with dichlorosilanes or dianilinosilanes can result in block copolymers of the desired structure with sufficient structural regularity and of sufficiently high molecular weight to possess rubbery characteristics at elevated temperatures. The difficulty with these polymers is that while high molecular weight is necessary if the copolymer is to have good physical properties, the glass transition temperatures of these copolymers increases with molecular weight and is as high as 400° F before they begin exhibiting rubberlike elasticity.

Bulk polymerization was found to be preferable over solution polymerization, with higher temperatures and higher concentrations resulting in faster polymerizations.

The major reason for high glass-transition temperatures is crystallization brought about probably by the regularity of the polymer molecules. This temperature can be lowered without destroying thermal and radiation stability of the polymers by a number of methods. These include introducing irregularity into the polymer molecules to achieve random orientation of the phenylether blocks, and the use of bulky, pendant groups to prevent the microcrystallization of the neighboring polymer molecules.

Fluorine-Containing Polymers Synthesis

The Quartermaster Corps sponsored a program (AD–613 945) to investigate fluorine-containing polymer systems for the development of high strength chemical resistant rubbers for use at temperatures down to −65° F, and chemical resistant rubbers that have high strength and rubberlike properties at temperatures at 600° F and above. The program investigated (a) block copolymers consisting of fluorocarbon units alternating with fluoroalkyl siloxane units and (b) polyethers derived by the condensation of diols with diolefins or from oxetanes.

As a result of this investigation, a new elastomer was discovered which was obtained from the condensation of a fluorine-containing diol with a fluorocarbon diene; it has a glass transition temperature of −70° F. In addition, hydrogen-containing oxetanes were prepared by the photolysis of hexafluoroacetone with ethylene and vinylidene fluoride. These products were all of low molecular weight.

Attempts to use the thermal cycloaddition of fluorocarbons as a polymer forming reaction proved unsuccessful.

Synthesis of Elastomers Containing Boron

A program by the Rock Island Arsenal Laboratory to prepare boron containing elastomers that have high temperature resistance, low-temperature flexibility, and inertness toward solvents is described in AD–432 014. The development of elastomers having extended resistance to temperatures at the 670° F level and upwards, high oxidative stability, and resistance toward solvolysis by water and organic solvents, yet retaining their usefulness at subzero temperatures, is a growing requirement in view of the advances in equipment technology.

None of the materials studied yielded satisfactory properties, although individual properties such as increased temperature tolerance were obtained.

Monomers were prepared from substituted acetylenes and dicarboran. A tough elastomer was produced by the emulsion copolymerization of butadiene and isoprophenylcarborane.

Polyesters were prepared from bis (hydroxymethyl) carborane and succinic, perfluoroglutaric, adipic, and terphthalic diacid chlorides. The polycarbonate adipate was a soft, tough, partially elastomeric material of low melting point. No press cure of this material was obtained, but with diisocyanate the material set up into a tough leathery product. Weight losses after air oven aging of the raw polyesters were evaluated and found to be lower than a typical commercial polyester.

High crosslinking was obtained in a polymer prepared from bis (acryloxymethyl) carborane and methylphenylsilane.

Metallosiloxane Elastomers Synthesis

The Department of the Army sponsored the development of a new class of semiorganic elastomers that would provide the proper tensile strength, adhesion, and strain tolerance as well as thermal insulation capability for rocket liner applications (AD–293 422). A number of random cometalloxanes, including various arsenosiloxanes, aluminosiloxanes, stannosiloxanes, and titanosiloxanes were synthesized. Copolymers of these types were compounded with fillers, cured in panel form, and evaluated as thermal insulation materials.

In torch test evaluations, the ablative insulation capability of stannosiloxane-based compositions derived from chain-extended copolymers was found to be superior to silicone-based compositions both in insulation index and erosion rate. These elastomers had stress-strain properties comparable to commercial silicone rubbers.

Similar torch test evaluations of metallosiloxane polymer-based insulation compounds showed that none of the latter compositions compared favorably with commercial nitrile rubber-phenolic resin compositions.

An ancillary result of this work was the development of technology for preparing copolymers by an interfacial cohydrolysis technique for the processing of these polymers into high molecular weight elastomeric gums by means of chemical grafting or chain-extending reaction. Also developed were methods for compounding and curing of these gums into stannosiloxane rubbers.

Synthesis of Inhibitors

Rock Island Arsenal pursued a program (AD–268 271) to synthesize chemicals which would serve as heat-resistant inhibitors for diene vulcanizates as typified by SBR rubber. These vulcanizates are adversely affected by heat above 212° F. Classes of materials synthesized included substituted ferrocene derivatives, substituted resorcinol-formaldehyde derivatives, and polymeric secondary aryl amines.

Nine ferrocene derivatives proved to be inactive as heat-resistant inhibitors in both sulfur and nonfree sulfur-cured formulations. This lack of utility was attributed to nonresonance stabilization of the free radicals formed on initial thermal breakdown.

An investigation of resorcinal-formaldehyde derivatives also showed no significant stabilization of these vulcanizates. Some of the compounds inhibited curing of the vulcanizate at low concentration and accelerated aging of the cured vulcanizate when used at high concentrations. Most of the resoles, where the resorcinol substituent was greater than ethyl, adversely affected the sulfur and nonfree sulfur curing systems of the SBR compositions except for a 4-(Panarez-Resin) resorcinol which yielded a fair state of cure when used with a sulfur system. Some resoles were used as mixtures with powdered molecular sieves in an attempt to stabilize the resole against premature crosslinking during the vulcanization reaction; however, the sieve degraded the properties of the cured aged vulcanizate.

The failure of the resoles to inhibit heat degradation of SBR vulcanizates indicates that free radicals formed on degradation are not stabilized by the resorcinol derivatives and thus they are not satisfactory for such applications.

Polymeric secondary aryl amines had little affect in inhibiting the degradation of aged SBR vulcanizates. Several derivatives yielded noncurable vulcanizates in a nonfree sulfur system.

Polymeric secondary amine derivatives mixed with the proprietary fatty acids soaps-chelator mixture yielded an improvement which was marginal compared to the use of the soap-chelator mixture by itself.

One polymeric amine significantly inhibited degradation of both the sulfur and nonfree sulfur vulcanizates during short term heat aging; however, when the aging period was extended to 48 hours it was not as effective as the best inhibitor previously tested. Vulcanizates containing this material also exhibited lower tensile strength, which indicates some interference with nonfree sulfur-cured systems.

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(1961-1965)

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AD–259 551 Rock Island Arsenal Labs., Rock Island, Ill. SYNTHESIS OF ELASTOMERIC POLYESTERS BASED ON DIEPOXIDES, R. R. Freeman, Apr. 61, 20p., CFSTI 50 cents.

This report describes work to synthesize polyester-based elastomers which will exhibit elastomeric properties over a wide temperature range while maintaining resistance to various oils and solvents. Polymerization was conducted by bulk, emulsion, and solution techniques. The procedures are described and the results tabulated. Several literature references are included.

AD–268 271 Resin Research Labs., Inc., Newark, N. J. HEAT STABLE INHIBITORS FOR DIENE VULCANIZATES, G. A. Baum and A. Goldberg, Nov. 61, 55p., CFSTI $5.60.

Describes work to synthesize special chemicals to serve as heat-resistant inhibitors in diene rubber vulcanizates. Details of the program include procedures for synthesizing the compounds, experimental details, and test results. Tabular data of properties for various formulations of each of the compounds and many literature references are included.

AD–275 520 Rock Island Arsenal Lab., Rock Island, Ill. SYNTHESIS OF POLYESTER ELASTOMERS FOR POTENTIAL HIGH TEMPERATURE USE, R. R. Freeman, Feb. 62, 17p., CFSTI $1.10.

Work was directed toward the synthesis of polyester-based polymers with functional groups that may serve as crosslinking sites for the formation of elastomers. The experimental procedures are described in detail and the test results of the preliminary evaluation of the experimental polyesters are tabulated. Literature references are included.

AD–286 464 Aerojet-General Corp., Azusa, Calif. RESEARCH AND DEVELOPMENT OF HIGH-TEMPERATURE-STABLE INORGANIC RESINS AND ELASTOMERS, J. Feltzin, Aug. 62, 45p., CFSTI $4.60.

Treats the preparation and evaluation of thermally stable, flexible, and elastic silicates including the modification of natural silicates, asbestos and mica, and the silicate-silane reaction. The work was divided into two phases: (1) a treatment phase and (2) a reaction phase. Treatment involved chelation, leaching with acid or alkali, and sublimation. Reaction was concerned with partially degrading and reacting treated materials with salts and other chemicals. Details of experimental procedures are given and the results are tabulated. Areas covered include reactions of asbestos and mica to various conditions, molecular weight studies, crosslinking agents, vinyl-containing polymers, phenyl polymers, and various polymer structures. References are included.

The following progress reports prepared for this program are available:

AD–262 167 Annual Summary, June 61, 26p., CFSTI $2.60.
AD–267 203 Quart. Rept. No. 1, Sept. 61, 16p., CFSTI $1.60.
AD–271 979 Quart. Rept. No. 2, Dec. 61, 15p., CFSTI $1.60.

AD–289 547 Southern Research Inst., Birmingham, Ala. A STUDY OF POLYMERS CONTAINING SILICON-NITROGEN BONDS, R. E. Burks, Jr., and T. W. Ray, Feb. 61, 48p., CFSTI $5.60.

The synthesis and preliminary evaluation of polymers containing silicon-nitrogen bonds is discussed. Experimental details are described regarding difunctional derivatives of silicon. Thermal and chemical stability tests are detailed. Practical applications of ethylenediamine silazane, hexaphenylcyclotrisilazane, and other compounds are included.

AD–290 757 Resin Research Labs., Inc., Newark, N. J. SYNTHESES OF ADDITIVES FOR IMPROVING HEAT STABILITY OF ELASTOMERIC VULCANIZATES, A. E. Weinberg and R. H. Cook, Nov. 62, 79p., CFSTI $7.60.

Described are the synthesis of chemical additives for use as heat stabilizers in elastomeric vulcanizates. Procedures and test results are given. Data tabulated include recipes for each of the formulations and properties measured for various conditions.

AD–293 422 Hughes Aircraft Co., Culver City, Calif. ROCKET LINER PROGRAM, S. B. Eglin and A. L. Landis, Oct. 62, 114p., CFSTI $9.60.

Describes the preparation of metallosiloxane elastomers for use as insulators in rocket motor cases. A number of random cometalloxanes were synthesized and representative copolymers were compounded with fillers, molded into test panels, and evaluated. Investigations were made of silicon polymers containing titanium, arsenic, aluminum, lead, or nitrogen. The report describes procedures for preparation of the polymers and intermediates and includes recipes for the various mixtures. Tables of density, insulation index and erosion rate are given. References are included.

The following progress reports prepared on this program are available:

AD–274 393 Quart. Rept. No. 6, Jan. 62, 27p., CFSTI $3.60.
AD–275 140 Quart. Rept. No. 7, Apr. 62, 29p., CFSTI $3.60.
AD–284 194 Quart. Rept. No. 8, July 62, 20p., CFSTI $2.60.

AD–296 822 Rock Island Arsenal Lab., Rock Island, Ill. SYNTHESIS OF SILCARBANE POLYMERS USING CONVENTIONAL AND RADIATION INITIATION, R. R. Freeman, Dec. 62, 20p., CFSTI $1.60.

This is a detailed record of the synthesis of silcarbane elastomers with potential use in the temperature range of 500 - 810° F. Five silane monomers were synthesized and compared with various commercial monomers. The procedure followed and the results of the synthesis of silcarbane and silcarbane-siloxane polymers from silicon dihydrides and diolefin silanes are described in detail. Literature references are included.

AD–432 014 Rock Island Arsenal Labs., Rock Island, Ill. SYNTHESIS OF ELASTOMERS CONTAINING BORON, L. G. Wiedenmann, Jan. 64, 19p., CFSTI 75 cents.

Research into boron-containing elastomers that have high temperature resistance, low temperature flexibility, and inertness toward solvents is described. Polymers studied included structures with carbon chain backbones with the carborane groups pendant, structures with the carborane group in the main chain, and structures with the various groups separated by very short carbon chains. Data given include recipes, physical properties, and weight loss after aging. Several references are included.

AD–600 121 United States Rubber Co., Naugatuck, Conn. SYNTHESIS OF REGULATED STRUCTURE POLYPHENYLETHER-SILOXANE BLOCK COPOLYMERS, R. MacFarlane, Jr., and E. S. Yankura, Jan. 64, 34p., CFSTI $1.00.

This report covers the processing of block copolymers which are thermally stable and maintain their properties at elevated temperatures. Polyphenylethers and mono- and disiloxanes were selected because their thermal and radiation resistance is well known. The preparation of suitable polymers from dichlorosilanes and dianilinosilanes are described.

The following progress reports prepared on this program are available:

AD–268 261 Quart. Rept. 1, Sept. 61, 12p., CFSTI $1.60.
AD–272 671 Quart. Rept. 2, Dec. 61, 13p., CFSTI $1.60.
AD–276 089 Quart. Rept. 3, Mar. 62, 31p., CFSTI $3.60.
AD–282 458 Quart. Rept. 4, June 62, 10p., CFSTI $1.60.
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AD–418 105 Quart. Rept. 8, July 63, 15p., CFSTI $1.60.
AD–424 642 Quart. Rept. 9, Oct. 63, 20p., CFSTI 60 cents.

AD–613 945 Food Machinery and Chemical Corp., Princeton, N. J. QM ELASTOMER CONTRACT, J. A. Gannon, et al, Progress Report No. 4, June 64, 36p., CFSTI $2.00, MF 50 cents.

Previous and present experiments, along with supporting results, are detailed in this report. Although much of the experimental work is incomplete and is being carried on, favorable results are indicated by condensing a fluorine-containing diol with a fluorocarbon diene along with a new method to produce linear polyethers.

The following reports prepared on this program are available:

AD–428 799 Rept. No. 1, Sept. 63, 12p., CFSTI $1.60.
AD–602 530 Rept. No. 2, Dec. 63, 11p., CFSTI $1.00, MF 50 cents.
AD–606 286 Rept. No. 3, Apr. 64, 38p., CFSTI $2.00, MF 50 cents.

AD-614 473 Midwest Research Inst., Kansas City, Mo. SYNTHESIS OF ELASTOMERS CONTAINING Si-N BONDS IN THE MAIN CHAIN, L. W. Breed and R. L. Elliott, Feb. 65, 47p., CFSTI $3.00, MF 75 cents.

Methods are detailed for synthesizing thermally and hydrolytically stable elastomers based on polymer chains containing silicon atoms bonded directly to nitrogen. The report describes the preparation of monomers and intermediates as well as the polymerization of (a) the diazasilacyclopentane group, (b) diaminodiorganosilanes and N-substituted cyclotrisilazanes, (c) silazanes and organic diols, (d) siloxanes, (e) phenylene-linked silazane, (f) silicon-nitrogen polymers containing piperazine, (g) N-silylated derivatives of silazanes. Discussed are the reaction of organic isocyanates for crosslinking silazane polymers of peroxide-catalyzed polymerization of model compounds, and the reactions of cyclic silazanes under the influence of acids and bases. Many tables are included containing experimental data related to this program. References are included.

The following progress reports prepared on this program are available:

AD-282 206 Summary Rept. No. 1, 23p., CFSTI $2.60.
AD-409 894 Summary Rept. No. 2, 27p., CFSTI $3.60.
AD-432 392 Summary Rept. No. 3, 22p., CFSTI $2.60.
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AD-299 294 Rept. No. 2, Nov. 62, 56p., CFSTI $6.60.

AD-406 932 Rept. No. 3, Mar. 63, 54p., CFSTI $5.60.

Rock Island Arsenal Lab., Ill.

AD-275 520 SYNTHESIS OF POLYESTER ELASTOMERS FOR POTENTIAL HIGH TEMPERATURE USE, Rept. No. 62-650, Feb. 62, 17p., CFSTI $1.10.

AD-407 780 SYNTHESIS AND EVALUATION OF POLYURETHANE ELASTOMERS, Rept. No. 63-1242, Apr. 63, 14p., CFSTI 50 cents.

AD-423 192 HEAT RESISTANT ELASTOMER PROGRAM, Nov. 63, 14p., CFSTI $1.60.

AD-434 350 IMPROVEMENT OF HIGH TEMPERATURE PROPERTIES OF A FLUOROELASTOMER, Oct. 63, 18p., CFSTI 75 cents.

The Northern Polytechnic., Great Britain. HIGH-TEMPERATURE OR LOW-TEMPERATURE RESISTING ELASTOMERS CONTAINING BORON.

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AD–434 905 Tech. Status Rept. No. 2, Feb. 64, 38p., CFSTI $3.60.

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PB–130 097 Rock Island Arsenal Lab., Ill. EVALUATION OF HEAT AND OIL RESISTANT SPECIALTY POLYMERS FOR ORDNANCE APPLICATION. R. R. Freedman, Dec. 56, 17p., CFSTI $3.30.

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PB–161 813 Trionics Corp., Madison, Wis. HEAT RESISTANT ELASTOMERIC MATERIAL COMBINATIONS AND FORMS. R. E. Stapleton and J. Pappis, Jan. 59, 44p., CFSTI $1.25.

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