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**DEVELOPMENT OF IMPROVED GASKETS, SEALANTS
AND CABLES FOR USE IN GEOTHERMAL WELL
LOGGING EQUIPMENT.**

Interim Summary Report, January 1—December 31, 1977

**By
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January 1978

Work Performed Under Contract No. EG-77-C-03-1325

**Hughes Aircraft Company
Culver City, California**

MASTER

**U. S. DEPARTMENT OF ENERGY
Geothermal Energy**

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INTERIM SUMMARY REPORT

Contract EG-17-C-03-1325

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AND CABLES FOR USE IN GEOTHERMAL
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I. ABSTRACT

This report presents the work conducted for the Department of Energy to investigate materials which could be used for fabricating elastomeric seals for geothermal well logging equipment.

A literature search was made to obtain data on carborane-siloxane polymers, synthesis routes for fluorinated elastomers, and high temperature hydrolytic stability tests of elastomers. Information was obtained on the first two topics, but very little was available on hydrolysis testing.

A number of compounds, based on carborane-siloxane, were formulated and cured. Compression set, hardness and shrinkage tests with post-cure variations were made on the most promising formulations. Hydrolytic stability tests at 275°C (525°F) and 830 psi and thermodynamic calculations indicated that the carborane and the siloxane bonds were easily broken after short exposure periods. Work on this polymer was therefore discontinued.

Synthetic efforts to produce a perfluorinated elastomer are still continuing. The first such compound, an acetylene terminated amide showed poor hydrolytic stability. The acetylene terminated ketone version of the basic perfluoroelastomer gum in preliminary tests showed promising results in the hydrolytic stability tests. A large amount of gum stock is being prepared so reinforced compounds can be made for test.

A second elastomer "Fasil," not in the original proposal, based on a fluorinated siloxane, was also synthesized. A gum stock was prepared and subjected to the hydrolytic stability test. Extensive deterioration was observed after a short period of time. Since this compound also had a siloxane backbone, which was found previously to be unstable, work was discontinued on this polymer.

Additional hydrolysis tests were run on other promising polymers. These included polyphenylene oxide, polyphenylene sulfide and pentaphenyl oxide. Good resistance was shown by the phenylene oxides and the polyphenylene sulfide.

Recommendations were made to continue work on the perfluoroalkylene elastomer and initiate work on the polyphenylene oxide and/or the polyphenylene sulfide.

II. INTRODUCTION

This report summarizes the work done by Hughes Aircraft on DOE contract EG-⁷47-C-03-1325 during the period of 1 Jan. 1977 to 31 Dec. 1977. The objective of the project during this time was to investigate materials and techniques which would be the basis for elastomeric seals for use in geothermal well logging equipment. Specifically the elastomers would have to withstand, without significant deterioration, temperatures up to at least 257°C (525°F), in a high pressure humidity environment. The major emphasis of the project was to be directed towards the development of elastomeric compounds formulated from two base polymers: (a) methylphenyl carborane-siloxane, obtained from the Union Carbide Co., and (b) a perfluoro elastomer to be synthesized at Hughes Aircraft.

With the successful development of either of the compounds, O-ring type seals, cable terminations and small lengths of insulated cable were to be fabricated.

III. WORK PERFORMED

A. LITERATURE SEARCH

During the period in which materials were ordered, but not yet received, a literature search was made to uncover information which might aid the synthesis approach and produce any data relating to compounding of either of these materials. The search was made using the computer facilities of the Defense Documentation Center and covered the period from 1952 to 1977. NASA documentation from 1962 to 1977 was also searched. Both of these searches were specifically on fluoroelastomers. A third literature search was made somewhat later in the program using the computer facilities of Wesrac (NASA Industrial Application Center) at the University of So. Calif. This search was specifically directed at information on high temperature hydrolysis tests of elastomers. This search covered NASA Publications, Chemical Abstracts, NTIS, and Engineering Index. In addition manual searches were made in "Rubber Chemistry and Rubber Chemistry and" Technology at UCLA and USC libraries. The net result of the searches, which included hundreds of references, were several good references on synthesis techniques, descriptions of new rubber compounds (fluoroelastomers and silicones) and on conventional tests of fluoroelastomers. Very little information was obtained on hydrolysis tests, except in several Dupont papers. Only the most pertinent of these references are included in this report, under References.

B. CARBORANE-SILOXANE POLYMERS

Because of the very high cost of the carborane-siloxane polymer ($\approx \$4000.00$ per lb) only a very small amount (100 gm) initially was ordered.

It was procured as a millable gum stock. In order to do standard rubber formulating, in which the gum was mixed with the catalyst, the filler, the stabilizer, etc., an extremely small mill was procured. With this equipment, known as a Micromill, it was possible to prepare well milled 3-4 gm compounds using as little as 2 gm of the base polymer. This mill is shown in Figure 1. A small mold was also made so that test "buttons" $1/4$ in. diameter x $1/8$ high could be molded. Each button took approximately 0.3 gm of compound. A small formulation of 3-4 gm therefore, could be used to mold 10 to 12 "buttons." While it was not possible to run conventional tensile and elongation tests on the "buttons," it was possible to determine hardness changes as a result of thermal aging. Compression set tests could be run, using miniature compression set fixtures, and standard thermo-mechanical analysis tests (TMA), thermo-gravimetric tests (TGA), and differential scanning tests (DSC) could also be run. Thus a considerable amount of information could be obtained from the small buttons.

Later in the program, when promising formulations were developed, another small mold was prepared so that $1-1/2 \times 3/8 \times 1/8$ in. "slabs" could be prepared. A miniature tensile specimen die was also built so that tensile-elongation samples could be stamped out.

Figure 1. Rubber Laboratory Micromill.

A number of formulations were made based mainly on the use of magnesium oxide and an activated silica, Tullanox 500, as the filler. The catalysts used were Vulcup 40KE, bis(t-butylperoxy)diisopropylbenzene, and Varox, 2,5-bis(t-butylperoxy)hexane, with iron oxide as the stabilizer. Variations were made in both the cure cycle and the post-cure heat treatment. Table I shows the formulations, and the cure and post-cure cycles.

In order to determine the completeness of cure a DSC (differential scanning calorimeter) test was made on one of the first formulations. It showed no evidence of either an exothermic or endothermic reaction. Since all the compounds were made with substantially the same proportion of curing agent to polymer, it was decided not to run any more DSC tests, until the optimum formulation was developed, or near development. Figure 2 shows the DCS curve for formula #2. Figure 3 shows a DCS for a material with a pronounced exotherm.

Thermogravimetric analyses, TGA, were run on one sample of compounded material to determine the effect of high temperature on the carborane-siloxane polymer. The TGA test showed a very slight loss of weight, starting at approximately 300°C (600°F). The tests were continued to 800°C (1450°F), over an 80 minute time span. The final weight was 3-1/2 percent. No other tests were made since the formulation, #2, was considered representative of all the formulations, i. e., each compound contains approximately the same amount of carborane-siloxane, and all the fillers are high temperature resistant inorganic materials. The TGA curve is shown in Figure 4. Figure 5 shows a typical decomposition curve of a 40 percent glass filled, high temperature resistant plastic, polyphenylene sulfide.

Four thermomechanical tests were conducted on postcured samples using a DuPont #900 Thermomechanical Analyzer. The results on the first four compounds were inconclusive. Three compounds, initially penetrated 10 percent, showed expansion while incrementally heated, then increased penetration during 2 hours of isothermal heating at 300°C (600°F). Sample #4, which was much less rubbery than the other samples, showed very little change during the tests. This indicated the value of high filler loading.

TABLE I. CARBORANE-SILOXANE FORMULATION DATA

Compound No.	Date	Polymer		Reinforcement		Stabilizer		Cure Agent		Cure Schedule				Post Cure		Hardness Shore A	Thickness in.	Remarks
		Type	gm	Type	gm	Type	gm	Type	gm	Min	°F	Min	°F	Hr.	°F			
1	3-17-77	CBS	100	Tullanox	45	Fe ₂ O ₃	3.9	Vulcup R	2.5	20	250	20	350	24	450-600	55		
2	3-17-77	CBS	100	MgO	31.6	Fe ₂ O ₃	2.5	Vulcup R	1.66	20	250	20	350	24	450-600	30-35		Sticky
3	3-23-77	CBS	100	MgO	84.8	Fe ₂ O ₃	2.5	Vulcup 40KE	2.5	20	250	20	350	24	450-600	60-62		
4	3-23-77	CBS	100	Asbestos	101.2	Fe ₂ O ₃	2.5	Vulcup 40KE	2.5	20	250	20	350	24	450-600			Crumbly
5	3-23-77	CBS	100	Tullanox Asbestos	49.7 9.9	Fe ₂ O ₃	2.5	Vulcup 40KE	2.25	20	250	20	350	24	450-600	--		Crumbly
6	3-31-77	CBS	100	Asbestos	70	Fe ₂ O ₃	2.5	Vulcup 40KE	2.5	20	250	20	350	24	450-600	60-65		Crumbly
7	4-5-77	CBS	100	Tullanox MgO	15.0 15.9	Fe ₂ O ₃	2.5	Vulcup 40KE	3.1	20	250	20	350	24	450-600	45-50		Soft and sticky
8	4-5-77	CBS	100	Tullanox MgO	10 29.2	Fe ₂ O ₃	2.5	Vulcup 40KE	2.6	20	250	20	350	24	450-600	50		
9	4-5-77	CBS	100	Tullanox Mica	10 25.4	Fe ₂ O ₃	2.65	Vulcup 40KE		20	250	20	350	24	450-600	50		
10	4-15-77	CBS	100	MgO	59.8	Fe ₂ O ₃	2.67	Vulcup 40KE	2.57	20	250	20	350	24	450-600	--		
11	4-15-77	CBS	100	MgO	20.4	Fe ₂ O ₃	2.6	Vulcup 40KE	2.5	20	250	20	350	24	450-600	--		
12	4-15-77	CBS	100	MgO Tullanox	60 20.3	Fe ₂ O ₃	2.62	Vulcup	2.5	20	250	20	350	24	450-600	--		
13A-1	5-9-77	CBS	100	Tullanox MgO	12.3 30.0	Fe ₂ O ₃	2.3	Vulcup 40KE	2.3	20	250	20	350	8 8	450 525	64		
13A-2	5-9-77	CBS	100	Tullanox MgO	12.3 30.3	Fe ₂ O ₃	3.3	Vulcup 40KE	2.3	120	300			8 8	450 525	64		
13A-3	5-31-77	CBS	100	Tullanox MgO	12.3 30.0	Fe ₂ O ₃	3.3	Vulcup 40KE	3.3	120	300			8 8	450 525	54-55		
13B-1	5-9-77	CBS	100	Tullanox MgO	12.3 30.0	Fe ₂ O ₃	3.6	Vulcup 40KE	1.2	20	250	20	350	8 8	450 525	40		
13B-2	5-9-77	CBS	100	Tullanox MgO	12.3 30.0	Fe ₂ O ₃	3.6	Vulcup 40KE	1.2	120	300			8 8	450 525	38		
13B-3	5-31-77	CBS	100	Tullanox MgO	12.3 30.1	Fe ₂ O ₃	6.6	Vulcup 40KE	4.2	120	300			8 8	450 525	56		
14A-1	5-9-77	CBS	100	Tullanox MgO	12.5 30	Fe ₂ O ₃	5.0	Vulcup 40KE	5.0	20	250	20	350	8 8	450 525	61		
14A-2	5-9-77	CBS	100	Tullanox MgO	12.5 30	Fe ₂ O ₃	5.0	Vulcup 40KE	5.0	120	300			8 8	450 525	60		
14A-3	5-31-77	CBS	100	Tullanox MgO	12.5 30	Fe ₂ O ₃	8.9	Vulcup 40KE	8.9	120	300			8 8	450 525	65		

(Table I, continued)

Compound No.	Date	Polymer		Reinforcement		Stabilizer		Cure Agent		Cure Schedule				Post Cure		Hardness Shore A	Thickness in.	Remarks
		Type	gm	Type	gm	Type	gm	Type	gm	Min	°F	Min	°F	Hr.	°F			
15	6-6-77	CBS	100	Tullanox MgO	12.5 30	Fe ₂ O ₃	5.5	A29 bis-propionitrile	5.5	120	250			8 8	450 525	No cure		
16A	6-7-77	CBS	100	Tullanox MgO	15 35	Fe ₂ O ₃	3.75	Vulcup 40KE	3.75	30	340			8 8	450 525	50		
16B	6-7-77	CBS	100	Tullanox MgO	26.7 62.3	Fe ₂ O ₃	3.75	Vulcup 40KE	3.75	30	340			8 8	450 525	59		
17A	6-9-77	CBS	100	Tullanox MgO	15 35	Fe ₂ O ₃	3.75	Varox	3.75	30	340			8 8	450 525	45		
17B	6-9-77	CBS	100	Tullanox MgO	26.7 62.3	Fe ₂ O ₃	3.75	Varox	3.75	30	340			8 8	450 525	69		
18	6-14-77	CBS	100	Tullanox MgO	15 35	Fe ₂ O ₃	5	Varox	5	30	340			16 48	450 525	43	0.125	
19	6-14-77	CBS	100	Tullanox MgO	15 35	Fe ₂ O ₃	10	Varox	10	30	340			16 48	450 525	45	0.126	
20	6-14-77	CBS	100	Tullanox MgO	20 45	Fe ₂ O ₃	12.5	Varox	12.5	30	340					53	0.131	
21	6-16-77	CBS LVS-76 ^o	150 50	Tullanox MgO	30 70	Fe ₂ O ₃ CaO	5 3	Varox	5	30	340							No cure
22	6-16-77	CBS LVS-76	100 100	Tullanox MgO	30 70	Fe ₂ O ₃ CaO	3.5 6.0	Varox	3.5	30	340							No cure
23	6-16-77	CBS LVS-76	50 150	Tullanox MgO	30 70	Fe ₂ O ₃ CaO	2.5 9.0	Varox	2.5	30	34							No cure
24	6-16-77	LVS-76	200	Tullanox MgO	30 60	CaO	10	None								84	0.129	Cured
25	6-17-77	CBS LVS-76	150 50	Tullanox MgO	30 70	Fe ₂ O ₃	1.5	Varox	1.5									No cure
26	6-17-77	CBS LV-76	50 150	Tullanox MgO	6? 25?	Fe ₂ O ₃ CaO	10 5		30	340						45	0.1258	
27	6-20-77	CBS	100	Tullanox MgO	10 30	Fe ₂ O ₃	5	Varox	5							42	0.1225	
28	6-20-77	CBS	100	Tullanox MgO	12.5	Fe ₂ O ₃	3	A20 bis-propionitrile	30	320	350							No cure
29	6-27-77	CBS Fluorel LVS-76	50 50	Tullanox MgO	15 35	Fe ₂ O ₃ CaO	6.5	None	None	30 90	60 120	340°						Did not cure
30	6-28-77	CBS Fluorel LVS-76	75 25	Tullanox MgO	15 35	Fe ₂ O ₃ CaO	6	None	None	30	60	340°						Did not cure
31	7-7-77	CBS	100	Tullanox MgO	15 20	Fe ₂ O ₃	5.0	Varox	2.0	30	340					45		Soft and sticky

(Table I, concluded)

Compound No.	Date	Polymer		Reinforcement		Stabilizer		Cure Agent		Cure Schedule				Post Cure		Hardness Shore A	Thickness in.	Remarks
		Type	gm	Type	gm	Type	gm	Type	gm	Min	°F	Min	°F	Hr.	°F			
32	7-7-77	CBS	100	Tullanox MgO	15	Fe ₂ O ₃	2, 5	Varox	2, 5	30	340						40-50	Sticky
33	8-1-77	CBS	100	Tullanox MgO	13, 3 31, 9	Fe ₂ O ₃	8, 3	Valcup	3, 75	30	340			48	450 ⁰		53, 3	70 79
34	8-1-77	CBS	100	Tullanox MgO	5, 87 14, 3	Fe ₂ O ₃	12, 5	Varox	12, 5	30	340			48 48	450 525		52, 6	61 72
35	8-9-77	CBS	100	Tullanox MgO	5, 87 14, 3	Fe ₂ O ₃	12, 5	Vulcup	3, 75	30	340			48 48	450 ⁰ 525		42, 5	45 49
36	8-9-77	CBS	100	Tullanox MgO	20	Fe ₂ O ₃	12, 5	Vulcup	3, 75	30	340			48 48	450 525		48, 2	60 63
37	8-9-77	CBS	100	Tullanox MgO	20 50	Fe ₂ O ₃	12, 5	Varox	12, 5	30	340			48 48	450 525		56	67 70
* LVS-76 - 3M Fluoroelastomer with an internal catalyst.																		

PART NO. 900326

INSTRUMENTS

Figure 2. DSC on formulation number 2 (MgO filler).

PART NO. 900325

DUPONT INSTRUMENTS

SAMPLE: <u>5T</u>	SIZE <u>DSC 23.95mg</u>	ATM. <u>Pressure 0.21/mm</u>	RUN NO. _____
	REF. <u>DSC Propyl p. sec</u>	T _____ ΔT _____	DATE <u>3-29-77</u>
ORIGIN: <u>Perkins</u>	PROGRAM MODE <u>Cycle</u>	SCALE SETTING <u>20</u> $^{\circ}\text{C}$ <u>0.1</u> $^{\circ}\text{C}$	OPERATOR <u>BK</u>
	RATE <u>5</u> $^{\circ}\text{C}/\text{min}$ START <u>27</u> $^{\circ}\text{C}$		

Figure 3. DSC on plastic material.

PART NO. 950252

CUPERT INSTRUMENTS

Figure 4. TGA on formulation number 2 (expanded scale).

PART NO. 950252

DUPORE INSTRUMENTS

Figure 5. TGA on Ryton (polyphenylene sulfide) plastic.

The most significant mechanical property tests run on the compounded materials were the compression set tests. For these tests a miniature compression set fixture (Ref. ASTM D395) was constructed which would compress the 1/4 diameter "buttons" 20 percent, and hold them in the compressed state during the high temperature exposure.

Compression set tests were made on the first series of compounds which appeared promising. The compounds tested were 7, 8 and 10 which had been kept for 25 days at 275°C (525°F), in a circulating oven. At the same time, and in the same fixture, buttons of compounds 14B, 16B and 17B, with short [18 hours at 230°C (450°F) and 8 hours at 257°C (525°F)] post-cures were also tested. The results are shown in Table II.

TABLE II. INITIAL COMPRESSION SET TESTS

Compound	Original Thickness, in.	Shore A Hardness	Final Thickness, in.	Shore A Hardness	Set,* %
7	0.116	71-74	0.099	76	81
8	0.119	67	0.100	70	73
10	0.119	82	0.0976	85	82
14B	0.1155	70	0.088	80	108**
16B	0.114	68	0.088	80	108
17B	0.114	69	0.091	76	96

*Samples were inadvertently kept for 136 hours in the compression set fixture.

**Evidently shrinkage occurred in addition to set accounting for "set" over 100%.

Compression set tests were run on the later formulations, however, only on the samples post cured at 300°C (575°F). The results of these tests are shown in Table III, along with the curing agent types and amounts, and the filler types and amounts. No appreciable improvement was noted, except that the higher percent of filler was effective in reducing the set in the Vulcup cured material.

An effort was made to optimize the later formulations with regard to hardness and shrinkage changes after prolonged, cumulative, oven aging. The results of these tests are shown in Figures 6 and 7. Figure 6 shows the changes in Shore hardness of various buttons, made from some of the formulations shown in Table I. Figure 7 shows the average decremental changes in thickness (due to shrinkage), of each formulation. It should be noted that on each plot two sets of data are shown for each formulation. The solid line in each case represents the average changes in the button samples after 48 hours at 230°C (450°F), followed by up to 215 hours at 275°C (525°F). The dotted lines, starting after 48 hours at 275°C (525°F), shows the changes in other buttons after 48 hours at 300°C (575°F) for two buttons of each group.

TABLE III. FINAL COMPRESSION SET TESTS

Formulation	Curing Agent		Filler		Final Hardness		Comp. Set. %
	Type	%*	Type	%	Cure	Cure	
33	Vulcup	3.75	Tullanox MgO	13 32	70	79	93-100
34	Varox	12.5	Tullanox MgO	13 12	61	82	98
35	Vulcup	3.75	Tullanox MgO	5.87 14.3	45	49	122
36	Vulcup	3.75	Tullanox MgO	20 50	60	63	81
37	Varox	12.5	Tullanox	20 50	67	70	100
*By weight of polymer							

Figure 6. Hardness changes in carborane-siloxane "buttons" during post-cure.

Figure 7. Decremental thickness changes in carborane-siloxane "buttons" during post-cure.

Since the buttons were quite small, and somewhat soft, measurements, of thickness and hardness were required which were not dependent on operator "feel." To this end thickness determinations were made using a Randal and Stickney stand mounted dial gage equipped with a 85 gm load. Hardness measurements were made using a Shore A-2 Durometer mounted on a stand, with a total load of 1258 gm. Measurements were taken approximately 1 second after load application.

It should be noted that the final hardness and shrinkage of the samples post cured 215 hours at 275°C (525°F) are not markedly different from those cured 48 hours at 300°C (575°F). It should also be noted that there appears to be a fair correlation between the amount of shrinkage and the hardness change; i. e., the greater hardness changes also show the higher shrinkages. This would be expected if the changes were due to cross-linking.

After development of what appeared to be promising formulations, a simple hydrolysis apparatus was assembled. This consisted of placing samples in small nickel wire cages and then placing the assembly in an iron pressure bottle, along with ≈100 ml. of water. The end of the bottle was immersed in a 275°C (525°F) Wood's metal bath. Figure 8 shows the equipment. Figure 9 shows a larger, somewhat improved version of the same apparatus, except equipped with a pressure gage. By use of standard steam tables the internal temperature could be more easily checked than was the case with the original set-up. The results of several tests with the carborane-siloxane formulations showed the material to be completely disintegrated in 24 hours. Analysis of the deionized water, when the button was contained in a sealed glass ampoule, as shown in Figure 10, showed 40 ppm of boron. (Normal tap water in Culver City, has approximately 5 ppm). It was thus concluded that the boron cage was being broken. Further tests, using commercially available 50 Shore silicone rubber showed the same type of deterioration. It was thus concluded that both the carborane moiety and the siloxane were extremely vulnerable to hydrolytic deterioration at the temperature and pressures used. The disintegration of the carborane was confirmed by a thermodynamic calculation of the reaction:

Figure 8. Initial hydrolysis equipment.

4R-50459

Figure 9. Improved hydrolysis equipment.

Figure 10. Hydrolysis test sample ampoule.

The total ΔH of the reaction was found to be -348 K Cal/mole, which indicated that the reaction once started was strongly endothermic. The calculations, of course, did not indicate the rate at which the reaction would take place. However, the hydrolysis test showed that the rate was appreciable at the temperatures used. The decomposition was also accelerated by the relatively high pressures involved. Based on these findings, work was discontinued on the carborane-siloxane polymers.

C. PERFLUORO ELASTOMER

The synthesis of the perfluoroelastomer was initiated using an acyl terminated perfluoroalkylene ether procured from the PCR Co. of Florida. Using this starting material, the polymer was to be terminated with acetylene groups so long chain polymerization could be accomplished. The specific steps in accomplishing these tasks are contained in the proprietary supplements to the bi-monthly reports. (These supplements are available to the Department of Energy.)

It was found that inducing the perfluoro compound to react to form the acetylene termination was quite difficult. It was, however, possible to form an acetylene terminated perfluoroalkylene oxide amide, which was polymerized to a thermosetting oligomer at temperatures from 175°C to 250°C. This material, which was a hard, thermosetting resin, was found to be resistant to dry heat temperatures up to 350°C. The amide formation reaction, which was a relatively simple, one step reaction, showed the basic soundness of the acetylene termination scheme in producing a polymerizable material. The incorporation of a small amount of non-cross-linkable moieties in the prepolymer was the approach taken to provide an elastomer. Such a compound was prepared in which a non-acetylenic end group was used on one end of the amide prepolymer. A mixture of the acetylene terminated prepolymer and the non-acetylene terminated prepolymer was thermally cured at 210°C to result in a rubbery end product. The material, however did not withstand the hydrolysis tests. This was due, no doubt, to the vulnerability of the amide functional group to attack during hydrolysis.

A more promising approach, then, was initiated to form an acetylene terminated perfluorinated alkylene ether ketone. In such a structure the

ketone functional group should be less vulnerable to hydrolysis attack. The same basic combination of an acetylene-terminated prepolymer reacted with a partially acetylene-terminated ketone prepolymer was used.

A thermodynamics calculation for the reaction $R_3CF + H_2O \rightarrow R_3COH + HF$ indicates that the reaction could be either a -9 K Cal or +13 K Cal; i. e., either slightly endothermic or exothermic, depending on the R group. Thus, the HAC-synthesized fluoroelastomer might, depending on the backbone, be resistant to hydrolysis at 275°C, or if vulnerable, might disintegrate at a very slow rate. The first hydrolysis tests on an impure gum ketone sample, and a purified sample, indicated that this premise was correct. (See Table IV for hydrolysis test results). Currently additional precursor acyl terminated fluoroalkyl ether is being procured from PCR, and other intermediates are being prepared, so optimum gum stocks can be prepared for compounding.

When the new reactants are synthesized, a small amount will be used first to determine if a rubbery polymer can be made. The polymer will then be immediately tested for high temperature hydrolysis resistance. If good hydrolysis resistance is found then varying proportions of the reactants will be combined to produce an optimum polymer which can be formulated with fillers, catalyst, stabilizers, etc. to form a sealant elastomer.

D. "FASIL" ELASTOMER

A new fluoroalkylene siloxane polymer, "Fasil," was also synthesized for test. This material, although not in the original proposal, was considered theoretically promising and work was initiated. The specific steps to form the intermediates are as shown below:

TABLE IV. HYDROLYTIC STABILITY TESTS

Test No.	Material	Visual Results	Chemical Analysis				Remarks
			Gas Evol.	pH	F ⁻ Ion	CCl ₄ Ext. of H ₂ O	
1	Carborane-siloxane rubber	Complete deterioration	Yes	--	--		
2	HAC amide fluoroelastomer (solid)	Bad disintegration	Yes	--	--		
3	Krytox 143-AC perfluoroalkyl polyether lubricating oil mol wt = 5000	Very little or no effect seen	No	6	Neg	Neg	Oil on bottom matches IR lines non-volatile residue-negative
4	OS-124 (pentaphenyl oxide)	Appeared significantly affected, water very cloudy	No	6.8	--	Neg	Phenol spot test negative no phenol odor
5	Braycote 816Z perfluoroalkyl polyether copolymer lubricating oil mol wt = 13000	Slight cloudiness in solution breakdown?	No	6	Positive	Neg	Oil characteristic non-volatile residue negative
6	Teflon TFE	No discernible effect	No	6	--	--	Clear colorless
7	Diphenyl ether	Large amount of cloudiness emulsification?	--	--	--	--	--
8	Polyphenylene oxide pellets	Pellets melted together, but showed no evidence of depolymerization. Slight odor of phenol	--	--	--	--	--
9	HAC ketone fluoroelastomer unpurified, Ag containing powder	Significant deterioration*	Yes	10	Positive	Neg	Ag found nonvolatile residue-degradation products
10	HAC ketone fluoroelastomer** (purified)	Material appeared substantially unchanged, slight odor in water, some deterioration	No	4.5	Positive	Siloxane CH ₃	Look intact
11	Silicone rubber - 50 Shore	Complete depolymerization*	--	--	--	--	
12	Polyphenylene sulfide***	No apparent effect except lighter color	Yes	6.8	--	Neg	Slight swelling =16% no IR change - sulfur order
13	Kalrez***	No apparent effect	Yes (High)	<1	Strong Positive	Neg	No IR effect - SiO ₂ residue =5% swell
*These tests run at 235°C (450°F) and 400 psi **Run for 45 hours at 235°C ***These tests were run at 275°C for 72 hours							

I

The Grignard reagent formed from m-dibromobenzene is added to dichlorodimethylsilane to give 1,3-bis(chlorodimethylsilyl)benzene, (Ref. 1, 2, 3, 4) which is subsequently hydrolyzed to the dio(I) (Ref. 5.)

The co-reactants were prepared by reacting diethylamine with dichloromethyl(3,3,3-trifluoropropyl)silane and dichloromethylvinylsilane to give the substituted diamino derivatives II and III (Ref. 6 and 7).

II

III

The vinyl siloxane was used to provide sites for cross-linking the polymer.

Compounds I and II were reacted in tetrahydrofuran, Ref. 8, to give a viscous liquid material of the structure

The infrared spectrum showed the presence of absorptions consistent with the presence of Si-CH₃, Si-C₂H₅, Si-O-Si, and CF₃ groups.

The NMR spectrum indicated the presence of four different types of protons with the following ratios:

Proton type	Aromatic	-Si-CH ₃	-Si CH ₂	-CH ₂ CF ₃
Theoretical Ratio:	4	15	2	2
Experimental Ratio	4	~13	2	~3
Chemical Shift (CC/4):	7.5 ppm	0.2 ppm	~0.65 ppm	~1.8 ppm

Polymer molecular weight as determined by vapor pressure osmometry was 10,200 g/mole.

The subsequent polymerization reaction (Ref. 8) using all three compounds I, II, and III in the ratio 50:48:2 was carried out in tetrahydrofuran. The polymer (V) was synthesized from 8.91 g. of bis(hydroxydimethylsilyl)-benzene (I) and 0.51 g. of bis(diethylamino)methylvinylsilane (III) and 10.76 g. bis(diethylamino)methyl(3,3,3-trifluoropropyl)silane with evolution of diethylamine. The reaction was continued for a week with increased heating by oil bath and application of vacuum to remove the gaseous amine. The polymer formed was viscous, brown and weighed 11.54 g. Further work on this polymer was stopped when it was discovered that siloxane type polymers did not withstand high temperature hydrolysis tests. (See Hydrolytic Stability Tests).

$$a = 48; b = 2$$

E. HYDROLYTIC STABILITY TESTS

Because of the results secured in the hydrolysis tests of the carborane-siloxane and the "Fasil" materials a series of additional hydrolytic stability tests was initiated on a number of selected polymers. The purpose of these tests was to:

- (1) Determine if the relatively simple apparatus was truly effective in causing deterioration of a number of different polymers and/or if resistant polymers could be found.
- (2) Establish a convenient hydrolysis test, e. g. , 24 hours at 275°C in saturated steam.
- (3) Most important, establish the resistance of some selected, supposedly resistant, polymers to the hydrolysis test, so they can be used as standards against which the new synthesized materials can be compared.

The first tests made, after the carborane-siloxane tests, were of small pieces of commercially available 50 Shore A silicone rubber. This material depolymerized in 16 to 24 hours in a manner similar to the carborane-siloxane. These tests were also made with the samples in small wire cages, as shown in Figure 8. Later tests were made with the samples in deionized water filled glass ampoules. With this technique, deterioration products in the water can be collected for analysis, without contamination from rust, etc. from the pressure bottle. See Figure 10.

The materials so far tested for 16 to 72 hours of approximately 234°C (≈450 psi) and 275°C (approximately 850 psi from steam tables) include the following, shown in Table IV.

IV. CONCLUSIONS

1. The carborane-siloxane and siloxane bonds are apparently not resistant to the deteriorating effects of hydrolysis at 275°C (525°F). Since in service an unlimited supply of water will be available the usual concept of using an additive or a buffer material is not considered practical. Polyphenyl oxide or sulfides appear resistant. Either of these, modified to be elastomeric, should be satisfactory in hydrolysis resistance.
2. Based on the preliminary results of the hydrolysis tests on the purified HAC compound, and the tests on similar fluorinated products, the possibility of obtaining a highly resistant polymer appears very promising.
3. The simple hydrolysis apparatus appears satisfactory for running hydrolytic screening tests. After the initial tests, if a compound appears satisfactory, then a solution containing NaCl , CO_2 and/or H_2S would probably be used.

V. RECOMMENDATIONS

1. Work should be continued on synthesis at fluorinated alkylene ether ketones with an altered structure to incorporate elastomeric properties into the polymer. Enough material should be produced for extensive testing and manufacturing of seals.
2. Hydrolysis tests should be continued on the synthesized gumstock polymers and compounds, and on any new materials believed promising.
3. In particular, an investigation should be made into the possibility of creating elastomeric polyphenylene oxide or sulfide compounds. A proposed mechanism for such an elastomer block copolymer is shown in Figure 11.

Figure 11. Proposed block copolymer synthesis.

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