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Development and Evaluation of Elastomeric Materials for Geothermal Applications

Annual Report, October 1976 – October 1977

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W. W. Reilly
J. D. Ingham

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Prepared for

Department of Energy
Division of Geothermal Energy

by

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California

DEVELOPMENT AND EVALUATION OF ELASTOMERIC MATERIALS FOR GEOTHERMAL APPLICATIONS

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(JPL PUBLICATION 78-69)

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NOTICE

NOTICE

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ABSTRACT

The goal of this work is the development and evaluation of elastomeric materials for geothermal applications. A survey of organizations with experience in petroleum and geothermal drilling and logging operations was performed to obtain detailed information on service requirements for geothermal elastomers. On the basis of results of this survey, it was decided to attempt to develop a material for a casing packer for service at 260°C (~500°F) and 10.3 MPa (1500 psia) for 24 hours in a geothermal environment.

Work was divided into synthesis of new elastomers (block copolymers) and formulation of available materials. Formulation includes use of commercial elastomer gumstocks and also crosslinking of plastic (high T_g) materials and examination of their properties at high temperatures.

The synthetic part of the program has progressed to where constituent hard and soft blocks of candidate block copolymer compositions have been synthesized. The hard blocks are poly (phenyl quinoxalines) and the soft blocks are ethers or hydrocarbons. Present work is focused on placing suitable reactive end groups such as halides and phenolic hydroxyls on the polymer blocks, and coupling them together to form the elastomer.

Fibrous reinforcement of fluorocarbon rubbers has been emphasized in the formulation of available elastomer gumstocks. Organic fiber reinforcement (Kevlar*) did not increase hot properties significantly. Glass fiber reinforcement gives significant increases in tensile properties at low levels of fiber addition. Elongation is reduced, and the glass-reinforced compositions examined so far do not hold up well in the geothermal environment. Colloidal asbestos fibers, treated with a coupling agent, are also being investigated.

All compositions have been cured in nitrogen at or above the target operating temperature of 260°C, which is significantly higher than the usual processing temperatures. Substantial additional curing has been found to occur with the fibrous fillers under these conditions, and modified compositions are being evaluated to improve elongation and mitigate the effects of over curing.

A sample of new hydrofluorocarbon rubber from Japan (AFLAS 150H) has been tested with encouraging results, and additional formulation studies with this material are planned.

Crosslinking of plastics has not given very good results so far. A few experiments with polyphenyl ether (NORYL) gave material with low tensile strength and high compression set. The polyphenyl ether itself has good hydrolytic stability under geothermal conditions. Similar

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*Manufacturers of the trade-named products mentioned in this report are identified in Appendix A.

experiments are being done with polystyrene; however, so far, no crosslinked, molded sheets have been produced.

As a result of the work to date and discussions with other investigators in this field, the performance goals have been revised, and are now a tensile strength of 400 psi and 50% elongation at 260°C, with service life as before. Work carried out to date suggests that new synthetic polymers, such as those being investigated, will be required for service in geothermal environments at high temperatures. A possible alternative may be chemical modification of known polymer systems with second order transition temperatures, Tg, of about 100°C.

SECTION I

INTRODUCTION

A total of five types of geothermal energy resources have been defined (Ref. 1) and environmental resistance of elastomers for geothermal applications will depend on resource characteristics. The types of resources are as follows:

(1) Hydrothermal convective resources can be either vapor-dominated or liquid-dominated and are characterized by relatively high temperatures at shallow depths.

(2) Geopressured resources consist of pressurized water reservoirs in sedimentary basins. They often contain dissolved methane, and are capable of supplying both heat and mechanical energy.

(3) Hot, dry rock resources are nonmolten but very hot rock structures with insufficient water to be considered as type 1 (hydrothermal convective resources).

(4) Normal or near-normal gradient resources are conduction-dominated areas and are the result of radiogenic heat production, heat flows and the thermal conductivity of rocks. They exhibit temperatures from 15°C (60°F) to about 300°C (570°F).

(5) Magma resources consist of molten rock at temperatures exceeding 650°C (1200°F).

Resources (4) and (5) can be neglected at the present because their successful utilization is considered to be far in the future.

For materials applications involving resources of types (1), (2), and (3), the high temperature environment is from about 150 to 390°C (302 to 734°F) or higher. In addition, salinity can be low (<1000 ppm) to high (~250,000 ppm), H_2S and CO_2 may be present, and pressures vary from about 3.45 MPa (500 psia) to over 82.7 MPa (12,000 psia). The highest pressures have been found in geopressured resources. Elastomeric materials exposed to these environments may thermally, hydrolytically or chemically degrade, may absorb water or gases and later rupture at lower pressures (i.e., experience the "bends"), or they may undergo viscous flow to result in failure.

A very important additional consideration in the application of elastomers at high temperatures is the essentially reversible loss in tensile properties at the higher temperatures. For example, Viton* may have a tensile strength of about 10.3 MPA (1500 psi) at room temperatures,

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*Manufacturers of the trade-named products mentioned in this report are identified in Appendix A.

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but, even in the absence of degradation, the tensile strengths at 149°C (300°F) and 260°C (500°F) are only of the order of 4.14 MPa (600 psi) and 1.72 MPa (250 psi), respectively. Since this type of behavior is typical of all elastomers, there appear to be only two ways to obtain better high temperature performance. One is to formulate or modify the base elastomer in some way that increases the high temperature tensile properties, and the other is to prepare new elastomers that are designed to have better high temperature properties. It has been reported* that, at present, the maximum use temperature for elastomers in petroleum applications has been found to be about 205°C (400°F). If Viton was used, this condition corresponds to a tensile strength of 2.76 MPa (400 psi) to 3.10 MPa (450 psi); therefore, for applications at 260°C, it appears that the tensile strengh should be above 2.76 MPa (400 psi) at that temperature, or at least 80% higher than currently available compositions. Since this is an estimate based on several assumptions, there are some uncertainties, but it can be taken as a tentative criterion for a selection of materials for downhole testing.

As a result of some of the above considerations, the specific objective of this work for the first year was development of one material for at least one specific application for service at 260^0F ($\sim500^0$F) and 10.34 MPa (1500 psia) for 24 hours in a geothermal environment. The specific application proposed is a casing packer.

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Private communication from personnel at Dresser Industries.

SECTION II

MATERIALS SURVEY

A. INTRODUCTION

A survey was conducted to determine the geothermal environmental capabilities of existing commercial polymeric materials in order to tentatively evaluate them for specific applications, and to determine which applications are considered to be the most critical with respect to materials requirements.

As a part of this survey, several companies and laboratories were visited, including Baker Oil Tools, City of Commerce, CA; Smith Tool Company, Irvine, CA; Los Alamos Scientific Laboratories, Los Alamos, NM; Sandia Laboratories, Albuquerque, NM; Dresser Industries, Dallas TX; Dresser Environmental Technical Division, Santa Ana, CA; and Dyna Drill (Division of Smith International, Inc.), Long Beach, CA.

B. RESULTS

1. Baker Oil Tools

Baker obtains molded elastomers for packers from other companies. Packer failures were described as being caused by elastomer degradation, followed by extrusion. They use only conventional commercial elastomers, and for high temperature applications the packers are designed with backup rings; the packer cannot be reset and is not retrievable.

2. Smith Tool Company

Smith Tool is the bit manufacturing arm of Smith International, Inc. Mr. Allen Newcomb described their drilling experiences at the Geysers. Production sealed bearing bits failed because of elastomer degradation in face seals and O-rings. They now drill using air as the drilling fluid with air bearing bits. The air stream downhole reaches sonic velocity, and the combination of high air velocity and entrained rock chips is extremely abrasive and requires frequent replacement of bits and drill pipe. Therefore, they have been evaluating Vespel (polyimide) and Kalrez (perfluoromethyl vinyl ether-tetrafluoroethylene copolymer) as O-ring materials in sealed bearing bits to allow drilling with liquid drilling fluid. Vespel was found to be too hard and nonelastic to be assembled in current bit designs. Initial work indicated that Kalrez appears more promising. In their production bits they use nitrile rubber, which fails in a few hours at bearing temperatures of about 150°C. Their composition has a durometer (Shore A) hardness of 70 and, although a hardness of 90 might result in longer times to failure, assembly is again a problem. Their criteria for O-ring selection include resistance to tearing, high temperature and fluids. Tensile strength is a secondary consideration.

Mr. Newcomb expressed a willingness to test new O-ring compositions, if preliminary evaluation indicates that a particular composition has merit. Testing involves making separate drawings, having their supplier make O-rings, producing a special bit, testing, and interpretation of results. Total time required would be 9 to 12 months.

3.   Los Alamos Scientific Laboratories

The contact at Los Alamos Scientific Laboratories (LASL) was John Rowley, Associate Division Leader, Energy Division. The LASL project involves extraction of energy from hot, dry rock. Two holes are drilled into a suitable formation, the rock is fractured, cold water is pumped down one hole and hot water retrieved from the second hole. LASL normally drills using water and does not seem to have any particular problem with bits, drill pipe, etc. They do have a problem with directional drilling which they say they must be able to do in order to accurately drill into fracture zones. They have used the Dyna Drill, but its life is only a few hours under their conditions, and they are working with Maurer Co., Houston, to develop a turbodrill.

Their principal problems are logging and packing. They have not been able to pack off an uncased hole ($T \sim 200°C$), but have been successful in a cased hole using a packer from Lynes, Inc., Houston. Their need is for a 6 ft long, 12 in. diameter packer to pack off against a relatively large, possibly fractured granitic hole wall for a minimum of several hours, preferably 2-3 days. They report existing pressures across the packer of 6500 psi at 200°C. Logging under these conditions causes failure of electronic equipment. They have developed instruments in which the electronics are cooled in ice-filled Dewar flasks. These packages require good sealing, and they have found Kalrez O-rings to be satisfactory. They can also use Viton O-rings, but must change them every time the instrument comes out of the hole, since they harden and set.

Their main problem in logging is with the cable head and cable used to transmit signals to the surface. The cable insulation resistance drops from 10 MΩ to 200 KΩ at 200°C, and to 10 KΩ at 220°C. This is not a serious problem at 200°C, but certainly will be at 275°C, their target temperature. Present cable is insulated with "Tefzel", an ethylene-tetrafluoroethylene copolymer. They are getting a new cable insulated with PFA, a fluoropolymer with an upper service temperature of 550°F, compared with 400°F for Tefzel, but with inferior mechanical properties. Vector Cable is making a new cable configuration, a coaxial type with six twisted pairs instead of the usual 7 conductor type. More troublesome than the cable itself has been the cable head connector. Apparently the conventional ones are poor performers, and they have designed their own in which the entire head is potted with an RTV silicone. The main drawback with this design is the 24 hour cure requirement for the silicone; however, they say it is satisfactory in other respects. LASL has several contracts out for instrument development.

4.   Sandia Laboratories

        Max Newsom of the Drilling Research Division was the contact at
Sandia Laboratories. Sandia divides their drilling research into
fossil energy and geothermal energy programs. In the fossil energy area
they have projects to improve the performance of elastomers, steels,
drilling mud, and diamond bits. The elastomers improvement program
consists of applying thin coatings to Viton and Kalrez O-rings by glow
discharge polymerization, and incorporation of a hydrogen sulfide
"getter" in an O-ring formulation. The metals improvement is concerned
primarily with drill pipe. They have found that specifications for
pipe can be met with a wide variation in metallurgy and performance.
They are looking at the effects of heat treatment, brine composition,
and hydrogen sulfide on performance, with a view to obtaining an
improved performance specification.

        The drilling mud project is concerned with measuring true mud
viscosity under actual conditions and developing mud field test equipment.
They are attempting to provide a more detailed picture of mud performance
than is presently available, and in this respect the mud and steel
projects are similar. They also have a project to improve the bond
between diamonds and bit heat in a diamond bit.

        In the geothermal areas they are doing some work on logging equip-
ment in conjunction with LASL, mainly concerned with cable head develop-
ment. They are also developing a spark drill, a device similar to a
large spark plug with several electrodes. The spark energy causes
fracture of the rock ahead of the spark, and the chips are removed as
usual. No bit rotation is necessary. Firing small projectiles ahead
of the bit is another scheme under investigation, as is a chain bit, a
device that they regard as a downhole replaceable drill bit.

5.   Dyna Drill (Division of Smith International, Inc.)

        The contact was John E. Tschirky, V. P., Engineering. Dyna Drill's
main project is a downhole drilling motor that is basically a Moyno
pump in which the shaft is rotated by the drilling medium (gas or
fluid). The motor stator is a large (29.5 kg (65 lb)) elastomer molding
of 70 durometer (Shore A) nitrile rubber, probably a composition quite
similar to that used by Smith Tool for O-rings.

        The Dyna Drill has been tried at the Geysers, but was unsuccessful
because of elastomer failure. The tool lasted for only 10 hours when
exposed to steam at 283-288°C (450-550°F), at which time large chunks
of elastomer came out. Mr. Tschirky says they have tried EPDM,
polyurethane, and metal-filled materials, and test about 20 formulations
per year in a small test motor. He reports that rubber compounders
have been able to achieve only marginal improvements. Gas permeability
is sometimes a problem with the Dyna Drill in that, when the motor is
withdrawn from the hole, gas evolution has caused the stator to explode.
They initiated a quality control program with their supplier and
improved their product significantly within the last five years.

Tschirky summed up his views by saying that the problems in geo-thermal exploration are materials problems, that an order of magnitude improvement in elastomers is needed and that the most immediate drilling need is for steel for an abrasion-resistant drill string. The latter area is being investigated by Sandia.

6.   Dresser Industries

The two contacts with Dresser Industries personnel were extremely beneficial. The first was a meeting with a large number of representa-tives from various Dresser divisions and subsidiaries at the Dresser Environmental Technical Division in Santa Ana, CA. The main contact was J. D. Foster, Marke ing Manager, Gulberson Division. They indicated that they do all their own compounding and, for O-ring; at 260°C (500°F), no material is really acceptable. They log holes at 204°C (400°F) but the duration is only about 30 minutes. For most applications, it has been found that Viton is better than other materials, but Dresser had not been very interested in evaluations of Kalrez because of its cost and processing limitations. They indicated that they would like to have a material for use at 315°C (600°F) in steam at pressures of over 13.8 MPa (2000 psi). They offered to submit a letter indicating that they would provide a summary report on elastomers that have been evaluated for downhole petroleum applications (cf. appendix of the original proposal for this task). The report was received and is included in Appendix B of this report. The second meeting was at the Gulberson Elastomer Research and Development Laboratory in Dallas, TX. The main purpose was to examine their processing and test facilities. The summary report from the Gulberson Division was prepared by M. B. (Dub) Jett, who was the main representative at the second meeting.

Although tensile strength is not the only important parameter that determines materials capabilities for packer seal,, an approximate correlation of tensile strength vs. differential pressure capability of oil field packers was ived from Figures 1 and 2 of the report by Jett, and is shown in Figure 1. Since only data for 4 hours in a test well and 6 months in oil wells were available, the middle curve in Figure 1 for 24 hours was derived by interpolation using log time. It can be seen that, on the basis of this curve, for a differential pressure of 10.34 MPa (1500 psi), the minimum tensile strength can be estimated to be 2.34 MPa (340 psi). To prevent cracking, M. B. Jett has indicated that elongation should probably be no less than 50%. Therefore, for service at 260°C for 24 hours in a geothermal environment at differential pressure of 10.34 MPa (1500 psi), the estimated target properties are that the elastomer should be thermally stable for 24 hours in a geo-thermal environment and should have about 2.75 MPa (400 psi) tensile strength, and at least 50% elongation.
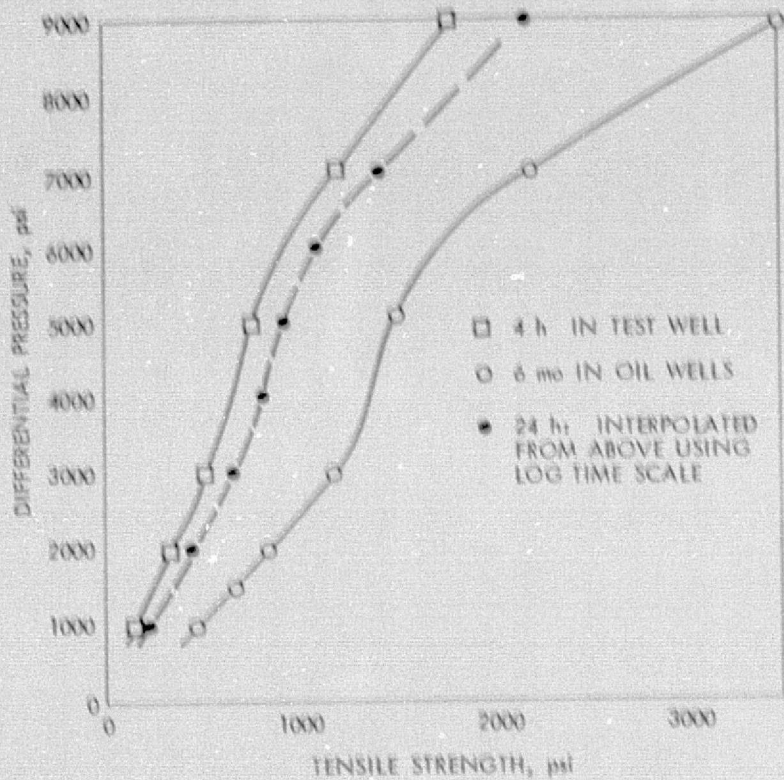
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Figure 1. Estimated Correlation of Differential Pressure
Capability of Packers With Elastomer Tensile Strength

EVALUATION OF COMMERCIAL ELASTOMERS

A.   INTRODUCTION

In most specific well applications, there are some fundamental differences between elastomer requirements for oil wells and geothermal resources. For example, oil resistance is not required for most operations in geothermal environments, and resistance to higher temperature brine may not be needed for some petroleum wells. Another difference is that, normally, for oil production, improved elastomers are required because of the need to develop deeper wells in which temperatures and pressures correspondingly increase. For deep wells, temperature may be about $260^{\circ}C$ ($500^{\circ}F$) with pressures of 4.14 MPa (600 psi) or higher. However, for most geothermal resources, temperatures range from about 150 to over $300^{\circ}C$ ($302-572^{\circ}F$), and, because of the lower depths, pressures of these wells are of the order of 3.4 to 20.7 MPa (500 to 3000 psi). (This is not true for geopressured resources (Refs. 2 and 3) in which reservoir pressure may be over 82.7 MPa (12,000 psi) and temperatures may be only as high as $149^{\circ}C$ ($300^{\circ}F$).)

As a consequence of these factors, properties and formulation variables are not necessarily the same for geothermal and petroleum applications; the objective in both cases, however, is to formulate materials that are stable and have maximum tensile strength and elongation at temperatures of 260°C (500°F) and above. For temperatures up to 149°C (300°F) the most commonly used elastomer for oil wells is acrylonitrile butadiene (NBR), particularly Hycar (cf. Appendix B). Comparable parts can also be formulated from epichlorohydrins (ECO), such as Hydrin and Herclor, but these cause some processing difficulties such as mill sticking and molding problems. Chlorinated polyethylene (CPE) elastomers do not appear to be useful because of poor mechanical properties and limited chemical resistance. Although silicones can be thermally stable at temperatures above 260°C (500°F), their mechanical properties are not very good even at room temperature and are very poor at high temperatures. Under geothermal conditions, it is doubtful that they would show adequate hydrolytic stability.   Fluorocarbons such as Viton and Fluorel are considered the best elastomers available at reasonable cost, but molding is difficult and they have limited steam resistance. Perfluoromethylvinyl ether-tetrafluoroethylene copolymer (Kalrez) is the most stable elastomer currently available, but it is extremely expensive ($4000/kg) and must be molded by DuPont. Furthermore, the maximum web thickness of molded parts is limited to about 0.635 cm (0.25 in.). Therefore, this elastomer cannot be used for packers, but can be useful for O-rings, backup rings or other small parts.

B. FORMULATION AND PROCESSING OF COMMERCIAL ELASTOMERS, PLASTICS, AND FIBERS

1. Viton

The basic Viton formulation is as follows:

Ingredient	Parts by Weight
Viton GH	100
MT Black (Thermax)	50
SRF Black (Pelletex NS)	10
Litharge [1]	3
Diak 7 [2]	2.5
Luperox 130-XL	2.5
VPA #2	2

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[1] Rubber grade.

[2] Triallylisocyanurate.

Enough material was used to make about 600 g of rubber. Viton was banded on the mill and the other ingredients added in the order listed in the formulation. The final milled sheet was about 0.32 cm (0.125 in.) thick. Sheets were then molded in a press at 177°C (350°F) for 10 minutes. Sheet thicknesses were 0.064 cm (0.025 in.) for stress relaxation measurements, and about 0.18 cm (0.07 in.) for tensile tests. The sheets were then postcured in a nitrogen atmosphere for 24 hours at 260°C (500°F). Test specimens were in the form of rings about an inch in diameter.

Vitron reinforced with Kevlar fiber was prepared by incorporating 7 phr of Kevlar fibers. These fibers were chopped to 0.64 cm (0.25 in.) in length, and coated with a resorcinol-formaldehyde tire cord adhesive. They were milled in directly on the mill after the black was added. Molding and cure cycles were as described above. Vitron was reinforced with glass fibers at the same level as Kevlar. The glass fibers (Johns-Manville 104/475 microfibers) were washed and treated twice with 1 wt % each time of UC A-172 silane coupling agent. They were dried 48 hours at 120°C (248°F).

Viton (300 g) was dissolved (some gel) in about 5 liters of acetone, and then treated fibers were dispersed in the solution by low shear mechanical mixing for 6 hours. The mixture was poured into drying trays, and the solvent allowed to evaporate. The residue was then dried in

vacuo at 90°C (194°F) for 20 hours. Some clumps of fibers were still evident. The resulting gum was milled with the other ingredients in the following recipe:

Viton GH	300	g
MT Black	150	g
Litharge	9	g
DIAK 7	7.5	g
Luperox 130-XL	7.5	g
VPA #2	6	g
Glass fibers	21	g

Milling, molding, and postcure were as before.

2.   Polyphenyl Ether (NORYL) - Crosslinking Experiments

NORYL SE-100 was molded at 190°C (374°F) into 0.0635 cm (0.025 in.) sheet from which tensile bars were cut. Also, NORYL was dissolved in chloroform, the solution was centrifuged to remove solids, and a clear film was cast from the supernatant liquid. The bars and film were irradiated in a cobalt-60 source to doses of 1, 12, and 107 megarads. The 1 and 12 megarad-dosed samples showed little change. The 107 samples were discolored, brittle, and had an oily appearance, but were soluble in chloroform. It was concluded that the main effect of radiation was chain scission, and no further work on radiation crosslinking was done.

Attempts were made to mold powdered mixtures of NORYL and Luperox 130-XL, a peroxide crosslinking agents on an inert carrier. Voids and visibly poor distribution of peroxide resulted. Luperox 130-XL dispersed in solutions of NORYL gave similar results. A procedure that worked involved dissolving the polymer in chloroform or methylene chloride (preferred), adding Luperox 130 (a soluble liquid peroxide), pouring the solution onto drying trays, and allowing the solvent to evaporate under ambient conditions. The use of chloroform required that the dried film be heated in vacuum to remove traces of solvent; methylene chloride would evaporate satisfactorily at room temperature and pressure.

To add carbon black, the first procedure tried was mixing in a Waring blender. This proved rather unsatisfactory in that molded sheets showed visible irregularities; dispersion appeared to be nonuniform due to material collecting on the walls of the blender.

A satisfactory procedure was to mill the polymer solution and black in a ball mill (steel balls), add curing agent with stirring, and evaporate the solvent as already described. A number of temperatures and times for molding were examined, and 160-165°C (320-329°F) for 4 hours at an initial molding pressure of about 60.34 MPa (7500 psi) was found satisfactory.

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3. Polystyrene

Initial experiments were done with Lustrex. This material was found difficult to mold in a heated press because of void formation. A polystyrene from Poly Sciences, Inc., molecular weight 100,000, was easily molded, and future experiments will be conducted using this material. Weight loss of polystyrene when exposed to geothermal brine at 260°C (500°F) for 24 hours was about 1% for uncrosslinked material.

4. Glass Fibers

This material was Johns-Manville microfibers, mentioned earlier. Exposure to geothermal conditions for 40 hours caused a weight loss of about 7%. Leaching with 6N hydrochloric acid for about 20 hours caused a weight loss of only 0.6%. No attempt was made to preleach or autoclave the fibers and then treat them with coupling agent. In view of the difficulty of dispersion and the susceptibility of these fibers to hydrolysis, no further experiments are planned.

5. Hydrolytic Treatment of Asbestos Fibers

It is necessary to remove a significant fraction of magnesium hydroxide from asbestos fibers while retaining the fibrous, open structure in order to ensure accessibility of silane coupling agents. Therefore, a series of hydrolysis experiments with asbestos fibers (Calidria HPO) was carried out (T ~ 25°C) as summarized below.

Reagent	Time, h	Yield
6N HCl	6	71%
6N HCl	16	48%
6N HCl	24	66%
50:50 HCl:Isopropanol	72	49%

*Not dispersed prior to hydrolysis.

The following procedure was adopted to prepare fibers: asbestos fibers (10 g) are placed in distilled water (500 ml) in a Waring blender and dispersed for 1-2 minutes. The pH of the solution is carefully adjusted with acetic acid while stirring until the onset of a marked change in viscosity accompanied by thixotropic behavior and a uniform, nonfibrous appearance. This mixture is then dispersed at a high shear condition for 5 minutes. The mixture is then removed from the blender and concentrated hydrochloric acid equal to the volume of water is added with stirring. The mixture is allowed to stand for a few hours and filtered. It is then washed thoroughly with distilled water to remove

acid and salts. It is important to keep the fibers wet at all times.
The material is then redispersed in distilled water in the blender until
the "colloidal" appearance and pronounced thixotropic behavior appears.
Some adjustment of pH may be necessary. The final pH should be about 4.
The suspension is then treated with the silane coupling agent in water,
filtered, and the cake dried at 120°C. The material is then ready for
use.

Although elastomers were not formulated and tested during the first
year's work, the above description is included for completeness. Results
on compositions containing asbestos will be discussed in subsequent
reports.

C. TESTING AND EVALUATION

A number of methods have been used to investigate modes of degrada-
tion of fluorinated elastomer formulations. The base elastomers included
Viton, Kalrez, and AFLAS 150H. Test methods included stress relaxation,
sol-gel determinations, swollen stress-strain measurements, weight loss,
and tensile tests after exposure to saline-carbon dioxide, saline-hydro-
gen sulfide solutions, and deionized water at elevated temperatures.

1. Stress-Relaxation (SR) Measurements

Chemical SR measurements can be used to determine degradation rates,
scission sites, crosslink densities, and the nature of the degradation,
i.e., whether chain scission and/or crosslinking take place (Refs. 4,5).
To make a measurement, the test specimen is strained a fixed distance
and the force at the % strain as a function of time is recorded. A
photograph of a stress relaxometer is shown in Figure 2. Figure 3 is
a schematic of a stress relaxometer. A diagram indicating the two types
of scissions, i.e., at the crosslinks, and in the main chains, is shown
in Figure 4. Two types of SR measurements are carried out: continuous
and intermittent. In continuous measurements, the sample is held at
constant extension (strain), and for intermittent experiments the sample
is strained only while the stress is being measured. It is assumed that
new bonds, such as crosslinks, formed during aging in a continuous
experiment will not contribute to the stress, but when new bonds are
formed in the unstretched condition (in intermittent SR) they will
contribute to the stress when the sample is strained. As a result, if
only scission occurs, the continuous SR curves will be essentially the
same as the intermittent, but if crosslinking takes place, the stress
observed is larger in an intermittent experiment than in a continuous
experiment at any given time. The stress may or may not increase above
the initial value depending on the rate of crosslinking versus scission.
Thus, from SR measurements, it can be determined whether only scission
or crosslinking, or both, are taking place. Also, the scission sites
can be established because in random chain scission the rate of stress
relaxation decreases when the initial crosslink density, v_e, is in-
creased. If scission occurs only at the crosslinks, the rate of stress
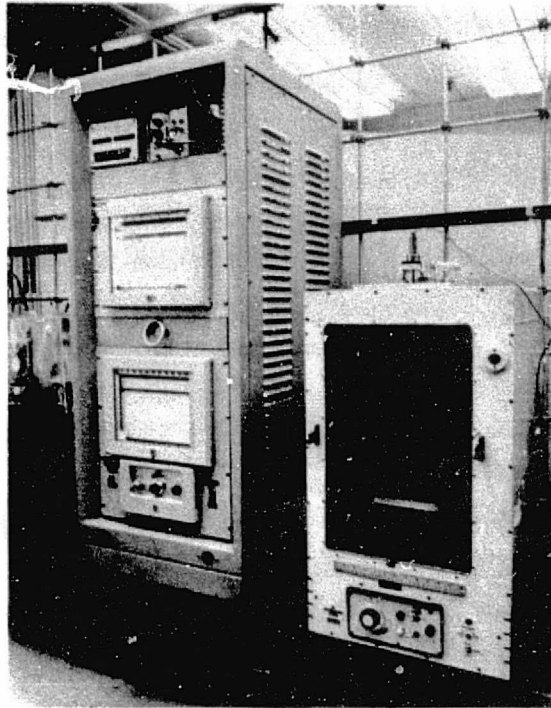relaxation is independent of the initial value of v_e.

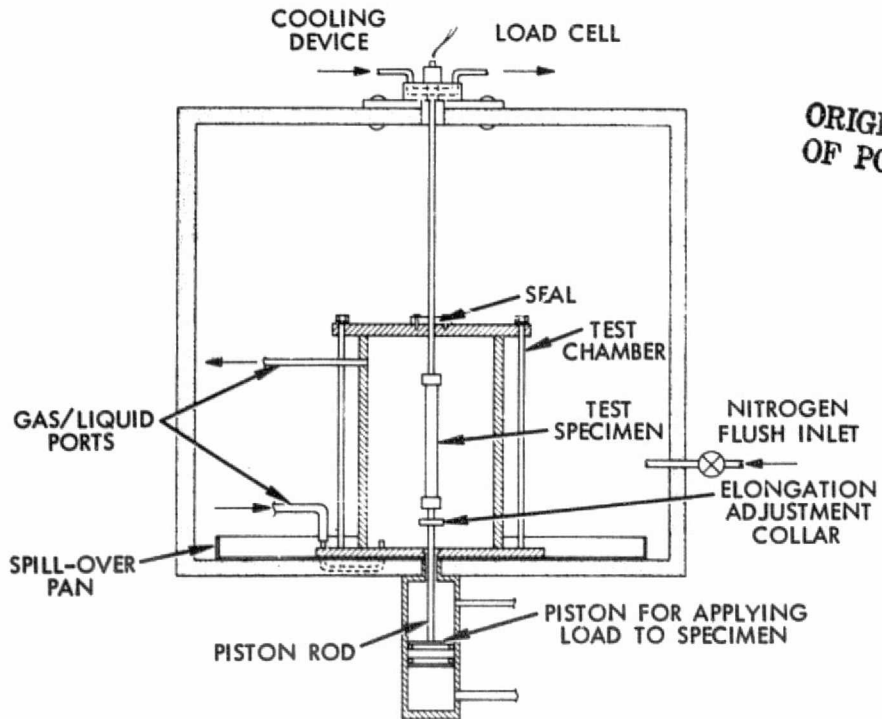Figure 2.   Stress Relaxometer for Stress Relaxation Measurements

Figure 3.   Schematic of High Temperature Gas and
Liquid Stress Relaxometer
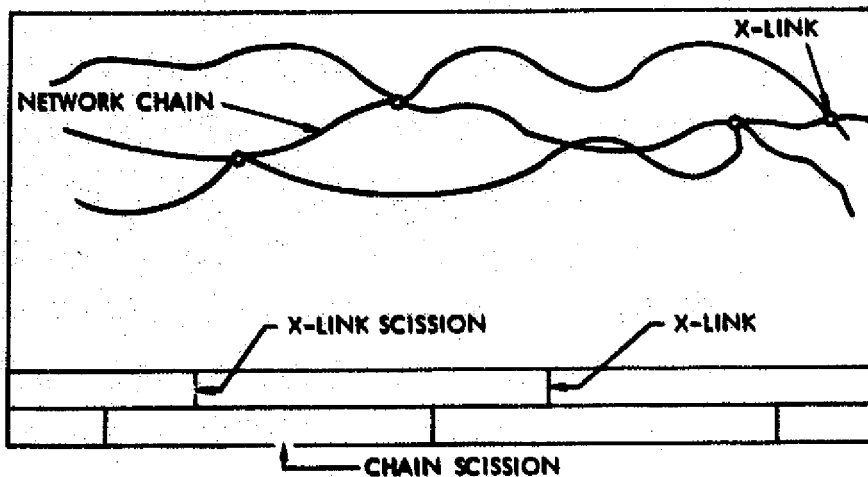
Figure 4. Scission in the Network

The equations used for calculation of the crosslink densities at time zero, $\nu_{e(0)}$, and at time t, $\nu_{e(t)}$, are

$$\nu_{e(0)} = \frac{f_o}{ART \left(\lambda - \frac{1}{\lambda^2}\right)} \tag{1}$$

$$\nu_{e(t)} = \frac{f_t^i - f_t^c}{f_o} \times \nu_e(0) \tag{2}$$

where i = intermittent, c = continuous, f_t = stress force at time t and t, A = the stressed area, λ is the extension ratio, and R and T are the gas constant and absolute temperature, respectively.

Figure 5 shows SR results for Viton. Viton 10K contains Kevlar fibers and 10G contains glass fibers. The data show that Viton 10 (without reinforcement) is superior to Viton 10K and that Viton 10G is the best formulation. Apparently, Kevlar affects curing and provides no improvement in aging behavior of Viton compositions.

Figure 5. Continuous Stress Relaxation of
Vitons at Various Temperatures
in Nitrogen Atmosphere

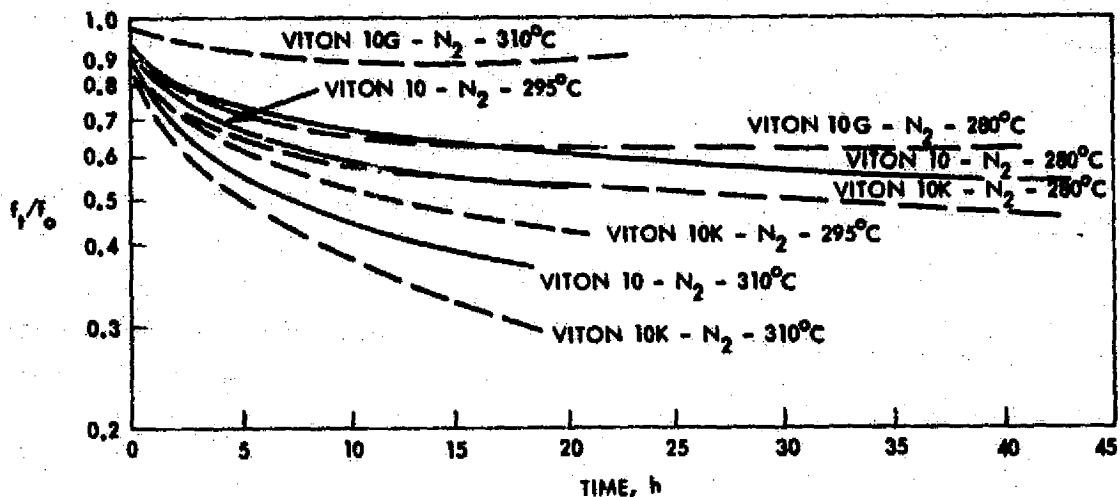Continuous and intermittent SR of Viton 10 and 10K in air and nitrogen are compared in Figure 6. It can be seen that these compositions undergo oxidative degradation and are significantly less stable in air than in nitrogen. It is also apparent from the wide separation of corresponding continuous and intermittent curves that, while bond scission is taking place, substantial increases in crosslinking are also observed.

Figure 7 shows some similar results for Viton 10G. From SR data, this elastomer composition appears to be very stable. However, it was postcured for 24 hours at 315°C, which might be a prohibitive processing condition for practical geothermal applications. Furthermore, although tensile data are not yet available, this composition is so highly crosslinked that it would not have sufficient elongation for normal packer operations.

Figure 8 shows the decrease in SR obtained by postcuring at 315°C for this composition. For the sample that was not postcured at 315°C, further curing occurred during the test, and it appears that substantially less than 24 hours is required to effect most of the postcuring at 310°C.

Results for Kalrez 3065 (which contains Kevlar fibers) and Kalrez 3050 (without Kevlar fibers) are shown in Figure 9. Kalrez behaves similarly to Viton, except that comparison of Figures 5 and 9 shows that Kalrez is significantly more thermally stable than Viton. In Figure 10, continuous and intermittent SR of Kalrez compositions are compared. Again, it is clear that both bond scission and crosslinking are taking place simultaneously.
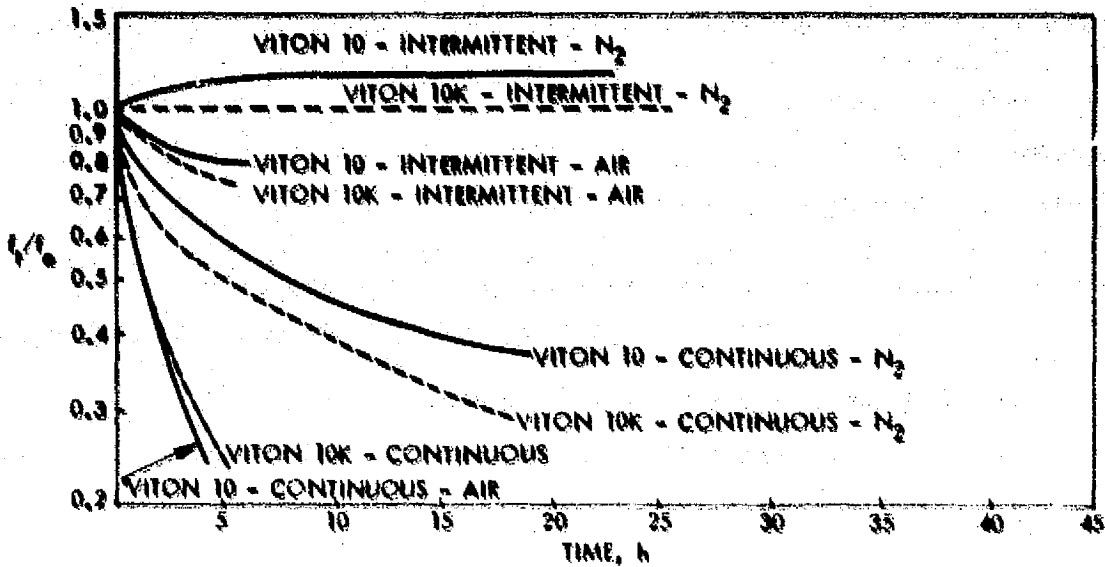
Figure 6. Comparison of Continuous and Intermittent
Stress Relaxation of Viton 10 and 10K in
Air and Nitrogen at 310°C
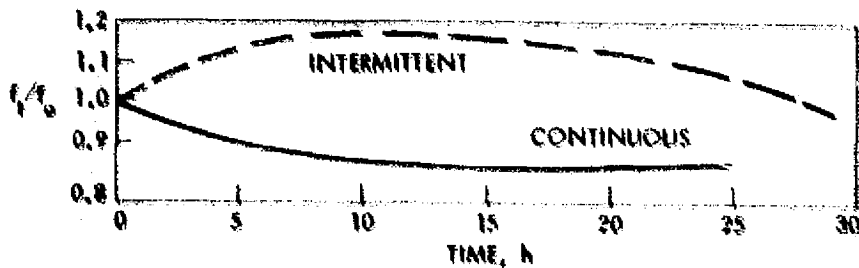
Figure 7. Intermittent and Continuous Stress
Relaxation of Viton 10G and 310°C -
Postcured 24 h at 260°C and 24 h
at 315°C

Figure 11 shows the concentration of new crosslinks (v_c, in moles/ m^3) formed at 315°C as a function of time for Viton 10 and 10K and for Kalrez 3050. It can be seen that crosslink density increases are greatest for Viton K and the least for Kalrez 3050. (Although not shown, crosslink density increases the most for Viton 10G). Larger increases in crosslink density result in less apparent stress relaxation; however, mechanical properties may still be affected adversely since insufficient elongation may remain after thermal aging. Also, although some formulations such as Viton 10G undergo little stress relaxation in nitrogen, the presence of water tends to reduce fiber-matrix bonding, leading to poor behavior in the geothermal environment.
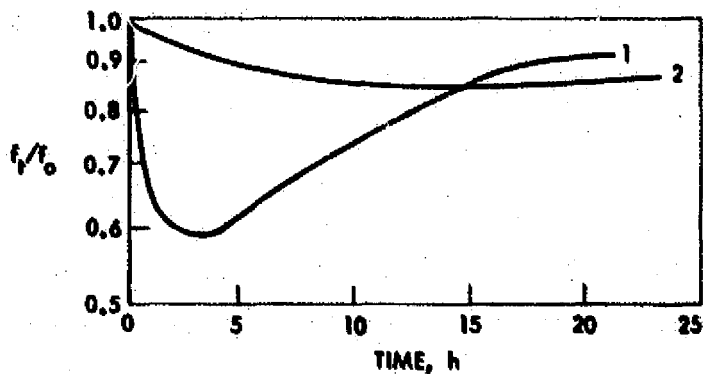
Figure 8. Stress Relaxation of Viton 10G in N_2 at 310°C:

    1. Postcured at 260°C in N_2 for 24 h

    2. Postcured at 260°C in N_2 for 24 h
       and at 315°C for 24 h
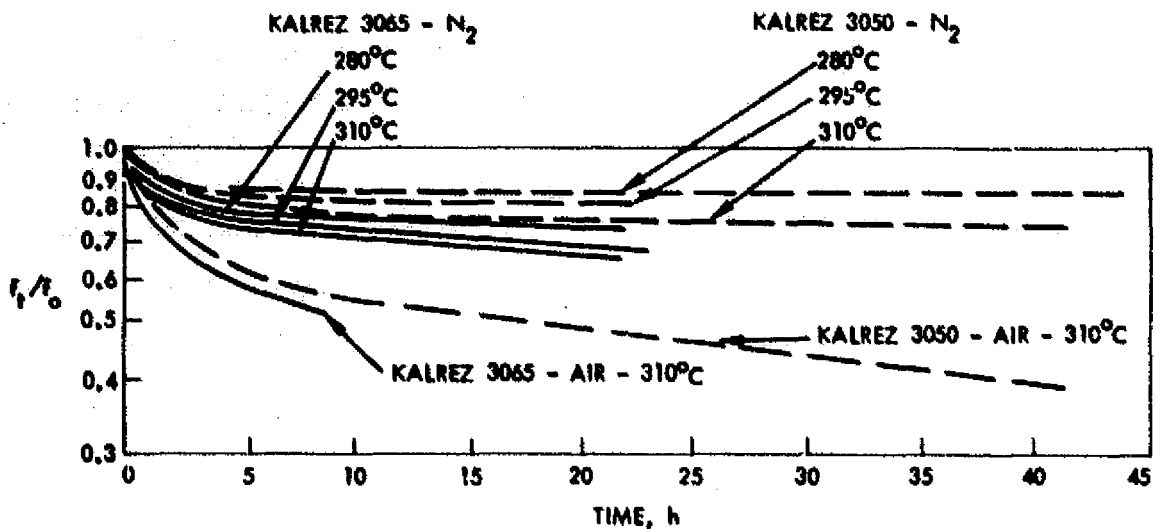
Figure 9. Continuous Stress Relaxation of Kalrez 3050 and
           3065 at Various Temperatures in Nitrogen and Air

The rates of stress relaxation of Vitons 10 and 10K and Kalrez
3050 and 3065 at 280, 295, and 310°C in nitrogen were used to calculate
their activation energies (cf. Figure 12). Activation energies are
high for Viton 10, Viton 10K and Kalrez 3050 (179, 168, 155 kJ,
respectively), and relatively low for Kalrez 3065 (87.7 kJ).
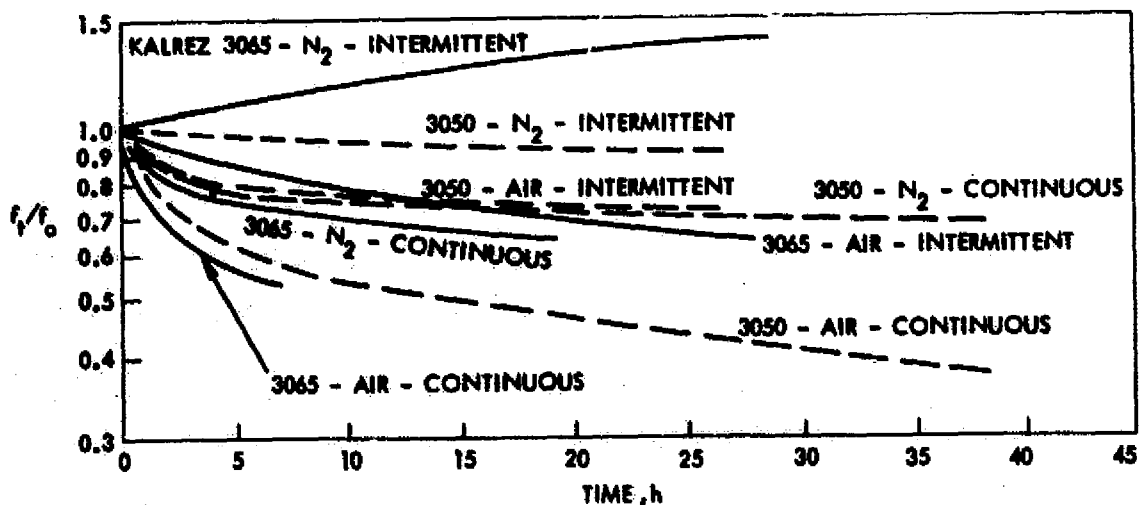
Figure 10. Comparison of Continuous and Intermittent
Stress Relaxation of Kalrez 3050 and 3065
in Air and Nitrogen at 310°C
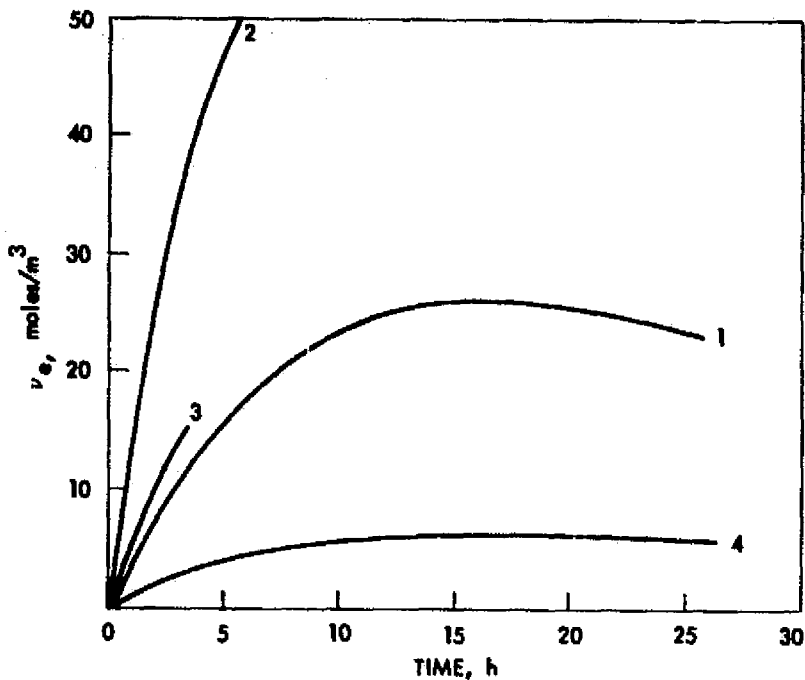
Figure 11. Additional Crosslinks Formed at 315°C

1. Viton 10 (N_2)

2. Viton 10K (N_2)

3. Viton 10 (Air)

4. Kalrez 3050 (N_2)
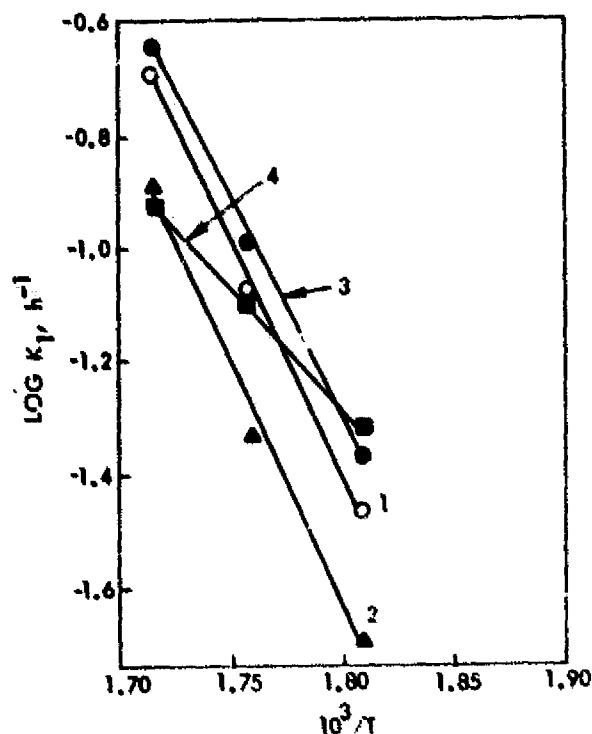
Figure 12.   Temperature Dependence of
K_1 ($K_1 = 1/t_{.30}$) for Stress
Relaxation of Fluorocarbon
Elastomers in Nitrogen
1.   Viton 10K (168.2 kJ)
2.   Viton 10 (179.0 kJ)
3.   Kalrez 3050 (154.6 kJ)
4.   Kalrez 3065 (87.7 kJ)

2.   Sol-Gel Determinations

Swelling measurements were carried out to determine crosslink
densities as a function of time of aging at 252°C in three different
aqueous systems: solution 1 contained 2.5% sodium chloride and 1000 ppm
carbon dioxide; solution 2 contained 2.5% sodium chloride and 300 ppm
hydrogen sulfide; and solution 3 was deionized water.   Swelling and
sol-gel measurements were made before and after heating for 20, 20,
and 60 hours in closed stainless steel tubes.   Swollen stress-strain
measurements were carried out using the apparatus shown in Figure 13.
The specimen was immersed in solvent and strain was measured with a
cathetometer.   The solvents were butyl acetate (Viton) and Freon TF (Kal-
rez).   Values for X_1, a solvent interaction parameter, were calculated
as described in Ref. 6.   The results were as follows: Kalrez 3065,
0.38; Kalrez 3050, 0.44; Viton 10, -0.92; and Viton 10K, -4.98.   The
values for the Vitons are outside the range expected for elastomers be-
cause interactions of the filler (~ 55 vol %) could not be taken into
account, and are larger than one would normally expect.   However, the
apparent v_e values (cf. Table 1) that are affected by filler inter-
actions are still valid for comparison of effects observed on aging
in water and brine.

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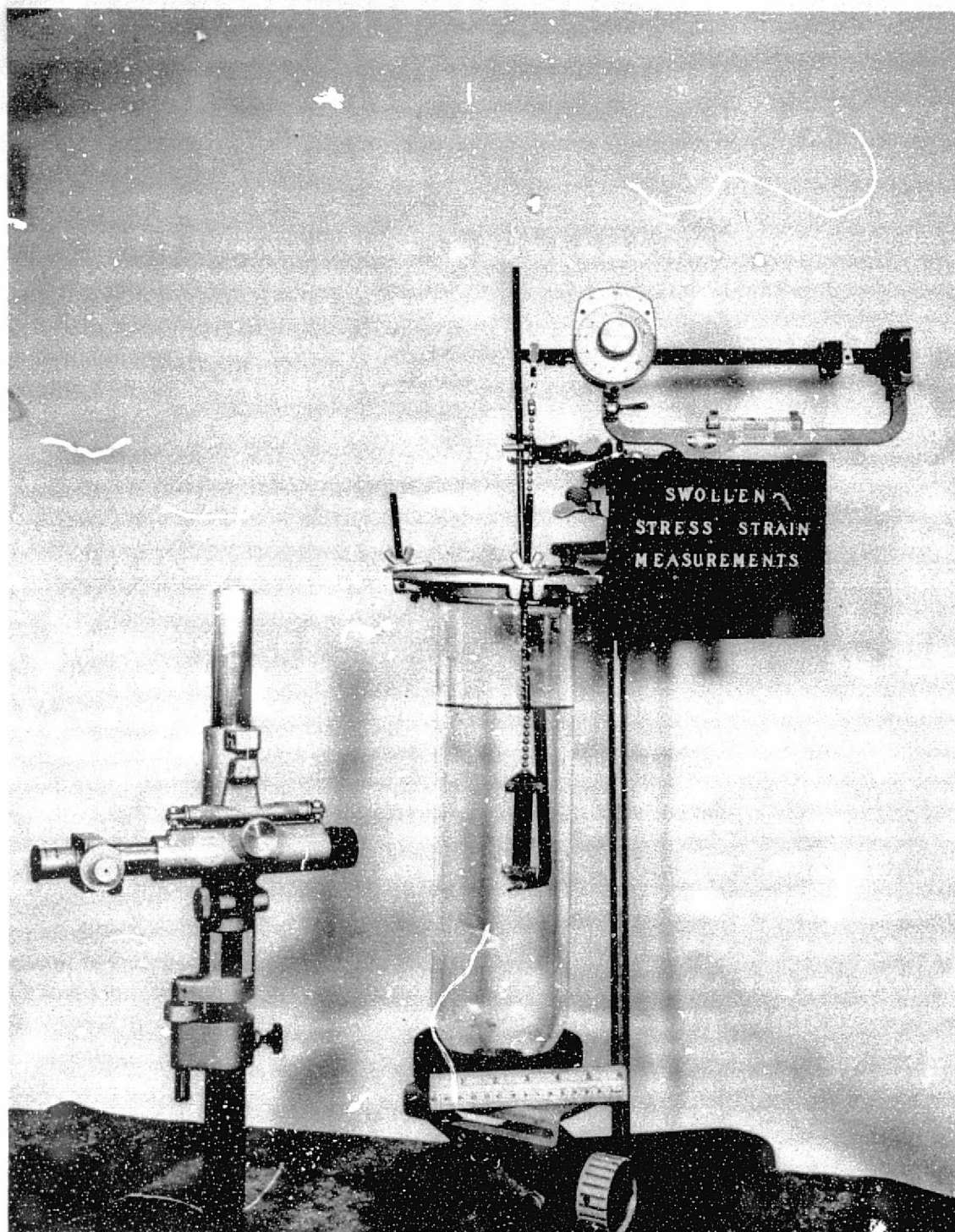
Figure 13.   Apparatus for Swollen Stress-Strain Measurements

Crosslink densities were calculated from the following equations:

$$\nu_{e(0)} = \frac{f/(\Delta l)l_o}{3\,A_o\,RT} \qquad (3a)$$

$$\nu_{e(t)} = \frac{\ln(1 - V_2) + V_2 + V_2^2\,X_1}{V_2^{1/3} - V_2/2} \times \frac{1}{V_s}$$

where,

$$V_2 = \frac{1}{1 + \left(\dfrac{W_s}{W_t}\right)\left(\dfrac{\rho_r}{\rho_s}\right)}$$

$\nu_{e(0)}$ = initial crosslink density, moles/m^3

$\nu_{e(t)}$ = crosslink density at time t, moles/m^3

f = force

A_o = dry stressed area

R = gas constant

T = absolute temperature

Δl = change in length; l_o = dry length

X_1 = polymer-solvent interaction parameter defined by the Flory-Rehner equation

V_2 = volume fraction of rubber in swollen gel

V_s = molar volume of solvent

W_s = weight of swollen gel; W_t = dry weight

ρ_r, ρ_s = densities of rubber and solvent

Results are shown in Table 1; it can be seen that apparent crosslink densities do not decrease precipitously for either the Vitons or Kalrez, but the initial (and final) effective crosslink densities for Viton 10K are very high.

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Material	Unaged $\nu_e(0)$	20 h at 252°C			40 h at 252°C			60 h at 252°C		
		Sol.1	Sol.2	Sol.3	Sol.1	Sol.2	Sol.3	Sol.1	Sol.2	Sol.3
Viton 10	1100	936	1080	942	868	986	858	924	987	868
Viton 10K	3400	4336	4343	-	4585	4522	-	4721	5059	-
Kalrez 3050	520	470	476	473	474	470	461	472	472	470
Kalrez 3065	650	562	564	525	553	551	511	550	550	507

3. Weight-Loss Measurements

The percent weight-loss values for Vitons, Kalrez, and AFLAS 150H
were measured as a function of time of aging at 250°C (482°F) in brine
(solution 1), as shown in Figure 14. (AFLAS 150H, tetrafluoroethylene-
propylene copolymer from Asahi Glass, Yokohama, Japan, was obtained only
in small quantities late in the first year's work and was not tested
extensively. It is available in commercial quantities at a reasonable
price, and a supply of the gum rubber has been ordered.) Weight-loss
increased from less than 1% for AFLAS 150H (after 60 hours at 250°C in
solution 1) to about 17% for Viton 10G. Although lower weight-losses,
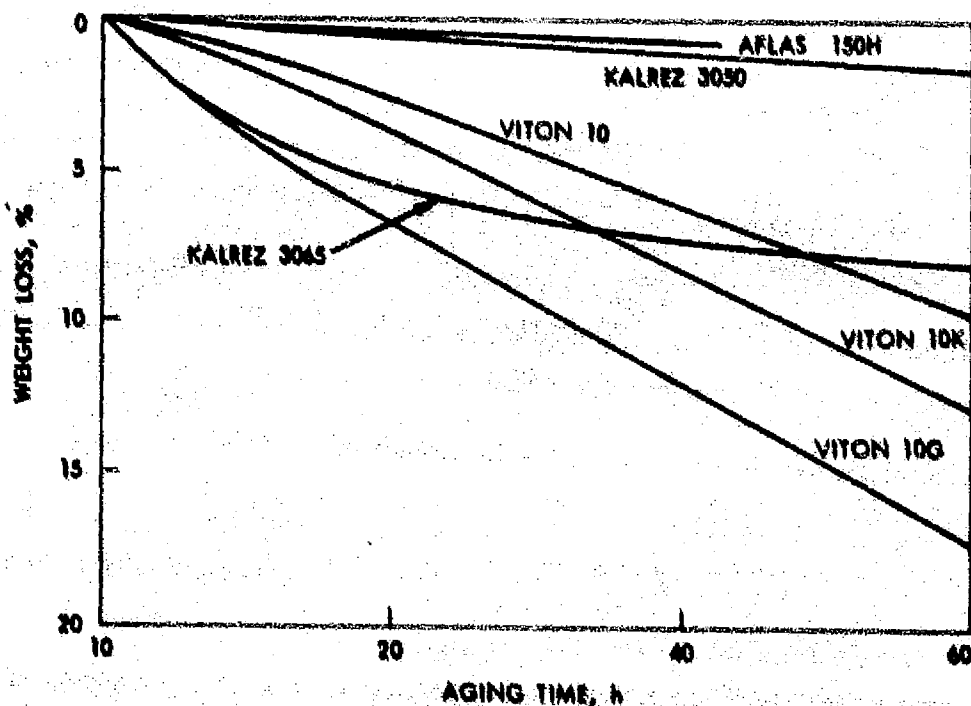
Figure 14. Percent Weight Loss of Fluorinated Elastomers
During Aging at 250°C in Brine (Solution 1)

as for AFLAS 150H and Kalrez 3050, are preferred, it has generally been found that good correlations between elastomer mechanical behavior and weight-loss are difficult to establish. These results do, however, indicate that Kalrez and AFLAS 150 are better than Vitons, and the results are reasonably consistent with other aging data obtained.

4.   Tensile Properties on Aging

Some mechanical properties before and after aging at 252°C (486°F) in solutions 1, 2, and 3 were measured at room temperature and at 260°C (500°F) for Vitons, Kalrez, and AFLAS 150. The data are tabulated in Table 2 and in Figure 15. Some conclusions from these results are

(1)   Initial mechanical properties are probably inadequate to meet the target goal (24 hours at 260°C (500°F)), pressure differential of 10.34 MPa (1500 psi), in a geothermal environment for most applications. Estimated properties required are tensile strengths of about 2.76 MPa (400 psi) and at least 50% elongation measured at 260°C (500°F).

(2)   After 40 hours in solution 3, Kalrez 3065 retains 50% of initial tensile strength and 100% of initial elongation; AFLAS 150H retains 35% of tensile strength and 51% of elongation. Mechanical properties retained by the remaining compositions are generally very low.

Figure 15.   Effect of Aging in Brine (Solution 1) and Deionized Water (Solution 3) on Elastomer Compositions

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Table 2. Mechanical Properties of Aged Elastomers

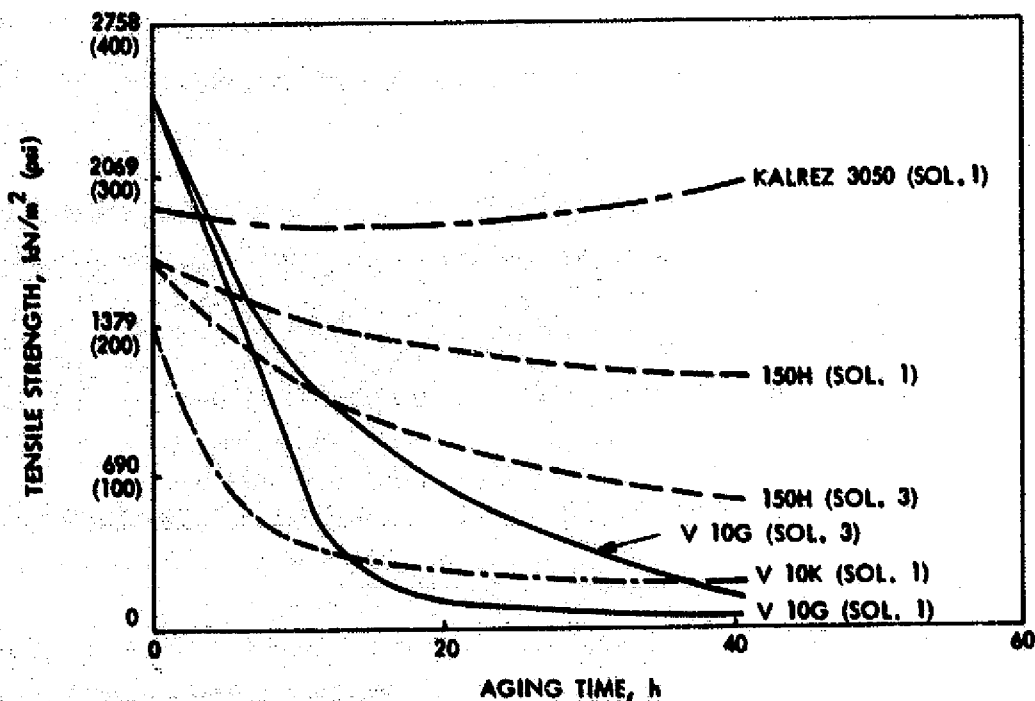| | Tensile Strength, psi, and (Elongation, %) Measured at 260°C (500°F) | | | | | | | | | |
| | Unaged Samples | 20 h at 250°C | | | 40 h at 252°C | | | 60 h at 252°C | | |
		Sol. 1	Sol. 2	Sol. 3	Sol. 1	Sol. 2	Sol. 3	Sol. 1	Sol. 2	Sol. 3
Viton 10	250 1470* (18)	220 860* (27)	256 1100* (21)	101 910* (13.5)	14.5 - (18)	26 - (12)	10 - (#)	10 - (10)	13.5 - (12)	5.4 - (#)
Viton 10K	200 1090* (10)	41 920* (10)	44 850* (#)	- - (-)	30 - (#)	20 - (#)	- - (-)	23.5 - (#)	21 - (#)	- - (-)
Viton 10C	365 - (22)	14 - (14)	- - -	95 - (16)	8 - (9)	20 - (8)	- - -	- - -	- - -	- - -
Kalrez 3050	278 2470* (58)	269 2515* (53)	250 2330* (52)	152 2000* (33)	296 - (64)	298 - (62)	59 - (12)	263 - (56)	257 - (46)	32 - (10)
Kalrez 3065	280* 1840* (32)	187 1780* (57)	211 1680* (56)	138 1400* (36)	202 - (57)	198 - (54)	141 - (37)	195 - (51)	194 - (50)	131 - (35)
AFLAS 150H	246 - (69)	184 - (64)	- - -	120 - (46)	163 - (60)	- - -	85 - (35)	- - -	- - -	- - -

Sol. 1 = 2.5% NaCl + 1000 ppm CO_2; Sol. 2 = 2.5% NaCl + 300 ppm H_2S; Sol. 3 = Deionized Water

* Measured at room temperature

\# Less than 10% elongation at break

- Not measured

(3)   Mechanical properties retained in brine-carbon dioxide and brine-hydrogen sulfide are approximately the same for specific compositions, i.e., the effects of solutions 1 and 2 are similar.

(4)   Except in deionized water, Kalrez 3050 is stable in the test environment for 60 hours.

(5)   Stability of AFLAS 150H is intermediate between Vitons and Kalrez.

(6)   Although Viton 10G has the best initial properties, it degrades more rapidly than the other compositions.

5.   General Conclusions

At present there is no candidate commercial elastomer that would appear to satisfy the target requirements. Kalrez 3050 appears to be the best, but is too expensive. However, it may be applicable for small parts, e.g., O-rings, or packer backup rings. AFLAS 150H may be better than Viton and studies are under way to improve the initial properties while maintaining stability. For many high temperature applications, it appears that it will be necessary to use chemically modified polymers with high second order transition temperatures, or to synthesize new systems that retain high tensile strength and elongation at elevated temperatures.

SECTION IV

SYNTHESIS OF NEW HIGH TEMPERATURE ELASTOMERS

A.   INTRODUCTION

The characteristics of an elastomer for high temperature geothermal applications differ from many other applications in that the operating temperature range can be limited to temperatures above 200°C (392°F). Therefore, the polymeric material can be rigid and nonelastomeric at room temperature and higher, except for certain applications, e.g., many O-ring seals where the seal must be deformed at lower temperatures for ease of assembly, as for most drill bit designs. It was planned to attempt to utilize existing high temperature polymer synthesis procedures and modify the chemical structure of such polymers so that they would be flexible at high temperatures.
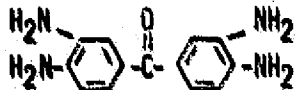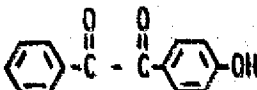
Although these types of polymers are often thermally stable at temperatures exceeding 290°C, they are not elastomeric and some are not hydrolytically stable. Preliminary work showed that polyimides were not as hydrolytically stable as polyphenyliquinoxalines (PPQ). Therefore, it was decided that the latter type would be used for initial synthesis studies. The reaction scheme selected was to prepare a PPQ polymer using excess tetraamine, resulting in terminal diamino groups, followed by reaction of these groups with hydroxybenzil. The resulting polymers would be a PPQ with terminal phenolic hydroxyl groups, to be used as the hard blocks of a block copolymer. A second polymer, such as bromobutyl rubber, would be used as the soft block. After conversion of the hydroxyl groups to the corresponding sodium salt, they can be reacted directly with the halogenated polymer to give the block copolymer. Because PPQ has a Tg above the use temperature, the PPQ segments should act as virtual crosslinks to prevent viscous flow. The soft blocks should support the load and provide elastomeric characteristics. Procedures for preparation of PPQ's have been established and described (Ref. 7).

Although block copolymer systems offer processing advantages, including little or no compounding, the use of thermoplastic molding techniques, and possible assembly at reasonable temperatures, an alternative is to prepare a curable material having a Tg of about 100°C. The latter would involve less synthesis, and could be available at lower cost. Polystyrene has been selected as a candidate base polymer and has been found to be thermally stable at 250°C in brine; however, further work is required to develop a suitable crosslinking system.

B.   DISCUSSION OF RESULTS

The chemical structures of starting materials used in this work are shown in Table 3. Reaction of ODB with TABP gives a PPQ with a second order transition temperature of only 265°C. Therefore, a block copolymer made from these would not be usable near or above this temperature.

Table 3. Intermediates for the Synthesis of PPQ-Alkyl Segment Block Copolymers

Chemical Structure	Name	Abbrev.
	Oxydibenzyl	ODB
	p-bis (phenylglyoxalyl) benzene	PGB
	3,3', 4,4' tetraaminobenzophenone	TABP
	3,3' diaminobenzidene	DAB
	4-hydroxybenzil	HOB

However, these intermediates were the most readily available and preliminary work to establish synthetic methodology and procedures was carried out using ODB and TABP. To obtain a polymer with a Tg substantially higher than the anticipated use temperature, polymers made from PGB and DAB will be prepared. (Some PGB has been procured and recently a source for obtaining DAB has been located, and this intermediate has been ordered.) A series of PPQ's was made, varying excess TABP from zero to 14 mole %. The polymer made with 2.7 mol % excess TABP could be cast as a tough, flexible thin film, indicating that the reaction conditions and methods were satisfactory and that reasonably high molecular weight PPQ polymers could be readily prepared. The measured Tg of this polymer was 265°C by differential scanning calorimetry (DSC) using the DuPont 900 Thermoanalyzer. Compositions and some molecular weight results for some of these polymers are shown in Table 4.

In this work, the purity of all these intermediates is of primary importance, since the polymer-forming reactions must proceed to nearly 100% yield. In most cases, it has been found that recrystallization of

Table 4. Hard Block Polymers Prepared From ODB and TABP

ODB   TABP
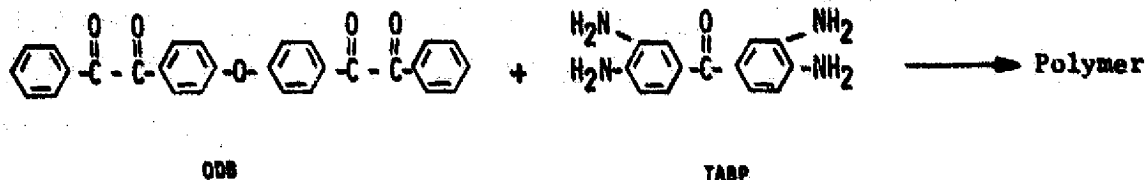
Polymer No.	% Excess TABP	M_w (GPC)	M_n (VPO)	Calc. M.W.	Remarks
1	0	-	-	-	Powdery
3	2	-	-	-	Bendable film
4	2.7	30,000	8,500	-	Tough, creasable film, T_g 265°C
11	2.7	22,500	-	-	Scaleup of 4
7	5	-	-	-	Hard, sticky film
5	7.6	-	-	-	Brittle film
101	14	9,000	3,009	5,000	Brittle film, colorimeter end group analysis 0.02, -0.05 wt % NH_2
101R	14	-	2,140	5,000	Brittle film, colorimeter end group analysis 0.02, -0.05 wt % NH_2.
102	10	-	2,956	7,000	Brittle film, colorimeter end group analysis 0.02, -0.05 wt % NH_2.

intermediates is required before use. Although hydroxybenzil (HOB) is commercially available, it has not been possible to purify it to the extent desired. Therefore, work is in progress to synthesize it at JPL, by condensation of benzaldehyde with anisaldehyde, followed by oxidation and demethylation. Reaction of commercial HOB (10% excess) with polymer 101 (cf. Table 4) resulted in a prepolymer with phenolic functionality corresponding to an M_n of ~10,000. The vapor pressure osmometer molecular weight was ~3,000, indicating incomplete reaction. Since this HOB was obviously of very low purity, no further experiments to obtain phenolic functionality were planned before pure HOB could be prepared.

Since there are many prepolymers available that contain hydroxyl functional groups, some work was done to attempt to convert hydroxyl groups to chlorides or tosylates. These prepolymers could then be used for the soft blocks in copolymers. Results are shown in Table 5. It was found that the chloride-terminated Telagen could be reacted with bisphenol A (as a model reaction) to obtain a polymer, indicating that the desired formation of the PPQ block copolymer should proceed satisfactorily.

Table 5. Preparation of Soft Block Prepolymers (X ∿ Polymer ∿ X) by Conversion of Hydroxy-Terminated Prepolymers

Polymer	X (End Group)	Yield, %	End Group Analysis, % of Theoretical
Poly (Ethylene Oxide) *	Chloride	50	65
Poly (Ethylene Oxide) *	Tosylate	40	Low
Telagen S **	Chloride	80 - 90	78
Telagen S **	Tosylate	∿ 90	Unreactive (?)

*   Hydroxy-terminated, M.W. 1500.

** Saturated hydrocarbon, M.W. 1980,
    Hydroxyl functionality M.W. 1.84. (This is an
    experimental prepolymer prepared by General
    Tire and Rubber.)

It can be concluded that synthesis of the desired block copolymers is feasible. However, with respect to required mechanical behavior at high temperatures in a geothermal environment, the effects of variations in the chain lengths of hard and soft blocks cannot be established until those types of polymers have been synthesized. Preliminary analysis suggests that soft block lengths of the order of 10,000 may be required. Further work will be done to define segment length requirements for different potential block components. In any event, it is anticipated that nearly complete reaction of the soft block segments with PPQ's will be required and that the soft block molecular weight is critical and should be relatively high to obtain good mechanical properties. Also, saturated hydrocarbon soft blocks, such as Telagen or butyl rubber, may not be sufficiently stable. If not, it will be necessary to prepare more stable soft blocks. These could include polystyrene, polyphenyl ethers or fluorinated prepolymers. (The polystyrene-PPQ polymer would be extremely rigid at room temperature, but polystyrene has a heat distortion temperature in the vicinity of 100°C (212°F), and is normally molded at temperatures above 160°C (320°F).)

C. EXPERIMENTAL

1. Recrystallization of Intermediates

To dry ethanol (300 ml) was added 4,4'-oxydibenzil (10 g, m.p. 101-107°C, lit. 106.4-106.5°C). Recrystallization gave a 58% yield, m.p. 106.5-107.5°C; 77.46% C, 4.19% H (calculated 77.41% C, 4.18% H).

A solution of 3,3', 4,4'-tetraaminobenzophenone (10 g) in 100 ml dimethylformamide was prepared under nitrogen and heated almost to boiling; 200 ml of boiling water was added, and the solution was decolorized with carbon. After crystallization, the product was removed by filtration, washed with water and dried in a vacuum. The yield was 62%, m.p. 215°C (lit. 218°C); 64.6% C, 5.94% H, 21.66% N (calculated 64.44% C, 5.82% H, 23.13% N).

Repeated attempts to recrystallize 4-hydroxybenzil from 10:1 methanol:water to obtain a pure product were unsuccessful. Yields were 22% or less, m.p. 117-119°C (lit. 129-130°C); 75% C, 4.59% H (calculated 74.3% C, 4.42% H).

2. Polymerization to Prepare PPQ's

TABP and ODB were dissolved separately in m-cresol to make 20 w/v % solutions. The TABP solution was added to the stirred ODB solution at room temperature over a period of about 15 minutes, and the mixture stirred for 18-24 hours. The polymer was precipitated by the addition of methanol, washed with hot methanol, and dried. For high molecular weight polymer, films could be cast from 20 w/v % solutions.

3. Reaction of HOB with PPQ

PPQ 101 (2.2739 g) and 4-hydroxybenzil (0.2261 g) were added to 20 ml of m-cresol and stirred overnight. The polymer was isolated as indicated above. Analysis showed 0.2 mg/g phenolic hydroxyl, corresponding to a molecular weight of ~10,000, if the polymer is assumed to be difunctional. This molecular weight is too high by a factor of two or more based on the value measured by vapor pressure osmometry, indicating incomplete reaction, probably because the HOB was not pure.

SECTION V

CONCLUSIONS

Current elastomeric materials, even in the absence of hydrolytic, oxidative, or other types of breakdown, undergo a reversible loss of 85-90% of their room temperature properties when heated to 260°C. If a seal or packer can be designed to operate successfully using an elastomer having 200 psi tensile strength, 50% elongation, and compression set estimated at 60%, it could be made and would probably operate for at least 50-100 hours at 250-260°C in brine.

Under operating conditions, tensile strength and elongation of elastomers are inversely related to the difference between Tg and the temperature at which the elastomer must perform. For the case of a suitable NBR, in a petroleum application, the difference between Tg and maximum operating temperature is of the order of 150°C. If it is necessary to operate at 250°C with elastomer properties similar to NBR at 150°C, an elastomer is needed with a Tg of about 100°C. Work on development of such an elastomer (based on polystyrene) is currently in progress.

It does not appear at present that formulation changes using available gumstocks are likely to provide a material that will prove to be satisfactory in the long term. This area has been well explored, and discovery of a new formulation or ingredient that will solve the problem is not likely.

In addition, it is not safe to assume that developments in the petroleum area will apply to geothermal problems, since the environments are not the same. Furthermore, a material suitable for geothermal use is not likely to find much application outside the geothermal area, and would face an uncertain market. Development of materials for specific applications that depart significantly from established use is a slow process, requiring long-term commitment to achieve success. For geothermal applications at high temperatures, it appears that it will be necessary to chemically modify existing polymers with high Tg's, or to synthesize new polymers with satisfactory mechanical properties at elevated temperatures.

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APPENDIX A

MANUFACTURER'S NAME

Trade Name	Manufacturer
AFLAS	Asahi Glass Co., Yokohama, Japan
Calidria HPO	Union Carbide Corp.
Chemigum	Goodyear Tire and Rubber Co.
DIAK 7	Dupont Co.
Fluorel	3-M Co.
Freon TF	Dupont Co.
FR-N	Firestone Tire and Rubber Co.
Herclor	Hercules, Inc.
Hycar	B. F. Goodrich Co.
Hydrin	B. F. Goodrich Co.
Kalrez	Dupont Co.
Kevlar	Dupont Co.
Litharge	NL Industries, Inc.
Luperox 130-XL	Lucidol Division, Pennwalt Corp.
Lustrex	Monsanto Co.
NORYL	General Electric Co.
Paracril	Uniroyal, Inc.
Pelletex NS	R. T. Vanderbilt Co.
PNF-200	Firestone Tire and Rubber Co.
Tefzel	Dupont Co.
Telegen S	General Tire and Rubber Co.
Thermax	R. T. Vanderbilt Co.
U-Car-Sil	Union Carbide Corp.
UC A-172	Union Carbide Corp.
Vespel	Dupont Co.
Viton	Dupont Co.
VPA #2	Dupont Co.

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APPENDIX B

SUMMARY REPORT FROM DRESSER INDUSTRIES, INC.

HIGH TEMPERATURE ELASTOMERS
IN THE OIL FIELD - A REVIEW

With the current push to develop all available sources of energy, the industry has found itself in a difficult situation: Deeper and deeper holes yield higher and higher temperatures and, almost correspondingly, higher and higher pressures. Unfortunately, the equipment on which we depend for taming these environments almost universally depends on some type of elastomeric product.

Up until now it has been assumed that more and more severe environments can be handled with the same or similar equipment. We have had good success thus far because a large majority of wells are completed at temperatures below 300°F and at pressures below 6000 psi, differential--conventional elastomers work well in these cases. However, at temperatures between 210°F and 300°F a very basic degradation of conventional elastomeric properties takes place, which cannot be reversed by compounding or molding techniques. This degradation, then causes a corresponding loss in performance of oil tools. Figure 1 shows this effect. Steady state pressure holding capability of oil field elastomers, when used in the relatively large extrusion clearances of an oil field retrievable packer, show drastic decreases with temperature; thus, as shown in Figure 1, at temperatures above 300°F often it is necessary to convert to a non-resilient asbestos braid sealing material.

Although there are times when the performance predicted in Figure 1 is exceeded, it must be noted that these are exceptional cases. For instance, in permanent installations (eg., drillable packers), an elastomer seal may have various backups, such as heavy mud, expanding metal plates, or in a case where the elastomer seal is totally static, the rubber itself hardens and becomes its own backup against extrusion.

In dynamic systems, or in the case of retrievable packers, where the tools must be resettable, oil field elastomers are severely limited above 300°F. (Performance in these installations more nearly follows Figure 1.) Because of this, over the years a trend has developed to avoid installations which require dynamic systems. This has, in fact, improved reliability (and has misled many oil company people into believing rubber is capable of more than it is). Unfortunately, this trend is now being reversed because the increasing demand for energy improves the economics of operating in such harsh environments.

To maintain our present position of leadership in high performance oil field packing elements, we regularly survey the industry for new developments which affect our product lines. We have, therefore, compiled a list of suitable products which could be expected to have a certain degree of usefulness in our business.

In the range of 75°F to 300°F, the most commonly used elastomer in the oil field is nitrile rubber. This elastomer consists of two monomers co-polymerized to give acrylonitrile-butadiene (NBR). The versatility of the elastomer offers a wide latitude in compound design and processing. In service, the NBR compounds show excellent oil

resistance and moderately high tensile strengths of 3000 to 5000 psi. Because increasing temperature weakens rubber rapidly, these initially high values are essential for maintaining reasonable good physical strength at elevated temperature. This effect can be seen in Figure 2, which shows how increasing temperature affects the physical properties of rubber. (A complete discussion of Figure 2 will be included later.)

Our present use of Hycar (B. F. Goodrich) NBR elastomers in high temperature (to 300°F) packing elements came as a result of vigorous testing with these and other nitrile polymers, as well as other specialty elastomers. Other nitrile polymers which have been tested and have in some way shown to be inferior are: Chemigum (Goodyear), FR-N (Firestone), and Paracril (Uniroyal). A common problem with these brands is failure to retain physical properties at elevated temperatures.

Elastomers which are about equivalent to nitriles and are at times judged somewhat better are the epichlorohydrins (ECO) -- Hydrin (Goodrich) and Herclor (Hercules). These types have an operating temperature maximum of 275°F, and may be compounded to give vulcanizates comparable to heat resistant nitriles. Tests have shown ECO compound packer rubbers can perform as well as NBR parts. ECO, however, generally exhibits lower elongation values, higher compression set and slightly lower tensile strengths. These compounds present processing difficulties such as mill sticking and molding.

Chlorinated polyethylene (CPE) elastomers have shown very little promise as high performance elastomers due to lower physical properties and poor chemical resistance.

Because of its excellent thermal stability, some attempts have been made to prepare silicone (SI) compounds for use as high temperature seals. We have not, however, been able to obtain sufficient physical properties at elevated temperatures to suit our needs. Silicones are rated as high as 550°F, but are noted for high gas permeation and poor resistance to oils.

Fluorocarbons (FKM), such as Viton (DuPont) and Fluorel (3-M), have shown much promise as high performance elastomers. They exhibit operating temperature ranges between -40 and 500°F. FKM compounds characteristically exhibit high tensile strength and relatively low elongation, tear resistance and steam resistance. Because of these properties, fluorocarbons must be considered the best high temperature elastomers available. Fluorocarbon compounds in high performance configurations are considered difficult to mold by conventional means and are at best inconsistent. Steam resistance, however, remains their primary drawback.

Several new products have recently been introduced which show relative amounts of promise and which should bear further investigation. These are DuPont's ethylene-acrylic elastomers and their "Kalrez" perfluoroelastomer, Firestone's PNF-200, and Union Carbide's "U-Car-Sil." We have tested the first three of these products in varying amounts with mixed results.

Ethylene-acrylic elastomers exhibit thermal stability somewhere between that of NBR and Viton, and may be easily compounded. Relatively high physical properties may be obtained at room temperature, but decline rapidly with elevated temperatures. Aging properties are much better than NBR. Oil swell seems to be a problem, but changes in compounding could possibly lower this to an acceptable value.

The perfluoroelastomer "Kalrez" has excellent thermal stability up to 550°F and has been tested in one of our thermal expansion joints with excellent results. Although we believe that "Kalrez" has good chance for success in hot oil field environments, we have not pursued study of this product due to its extreme cost ($2000/lb.) and that special molding equipment is required. (Only molded parts are available at this time.)

PNF-200 compounds show low physical strength at room temperature as well as at elevated temperatures, although high temperature aging is good at 400°F. The compounded elastomer exhibits mill sticking, which makes processing difficult. Its high cost ($100/lb.), combined with poor results to date, has caused us to go slow with this elastomer. PNF-200 is still under development and improvements are expected.

"U-Car-Sil" is a 600°F carborane-siloxane elastomer which is characterized by low tensile strengths that would make it unsuitable as a high performance elastomer. Its high cost ($2000/lb.) prevents us from testing this product.

Figures 2 and 3 are envelope cures representing optimum properties of oil field rubber. Data from 100°F to 300°F are for NBR compounds, 300°F to 400°F is for fluoroelastomers, and 400°F to 600°F is the estimated properties of some of the more exotic materials. Data at 300°F represent the current state of the art for high pressure (6000 - 10,000 psi) holding capability in large gap installations.

As can be seen, physical properties decrease so rapidly that at 500°F, only 25% of the strength at 300°F is available. Also, as shown in Figure 4, cost increases one hundredfold. As previously mentioned, methods are available for improved pressure holding, but these use semi-elastomeric, non-resilient materials which severely limit usefulness and reliability. It is felt that a reasonable goal is for an elastomeric product to be developed which has sufficient physical properties at 500°F to hold 6000 psi on an oil field packer; i.e., 1500 psi tensile and 1000 psi modulus (at 100%). At the same time, costs must be reduced by an order of magnitude.

Figure 5 shows a schematic of the test well facility utilized by Guiberson for testing oil well packers at elevated pressures and temperatures. Within this system there is the capability to test almost any type of elastomeric product used in oil wells, including O-rings, packer rubbers, V-packings, and packer cups. The high pressure pumps and hot oil system give us a test capability of 550°F (700°F with special preparations), 20,000 psi, and ± 100,000 lbs. mechanical load.
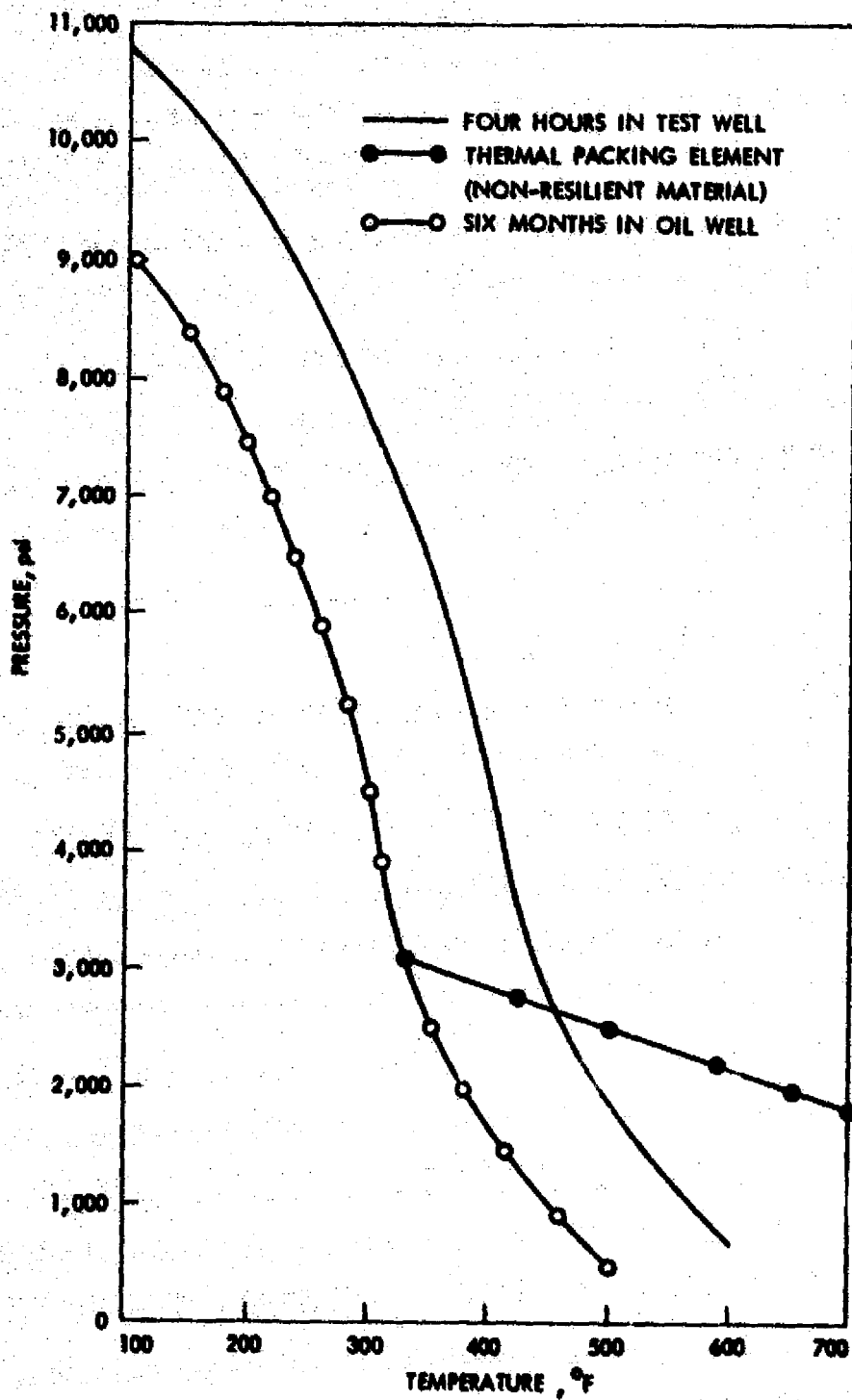
MB JETT: 10-12-76

Figure 1. Differential Pressure Capability
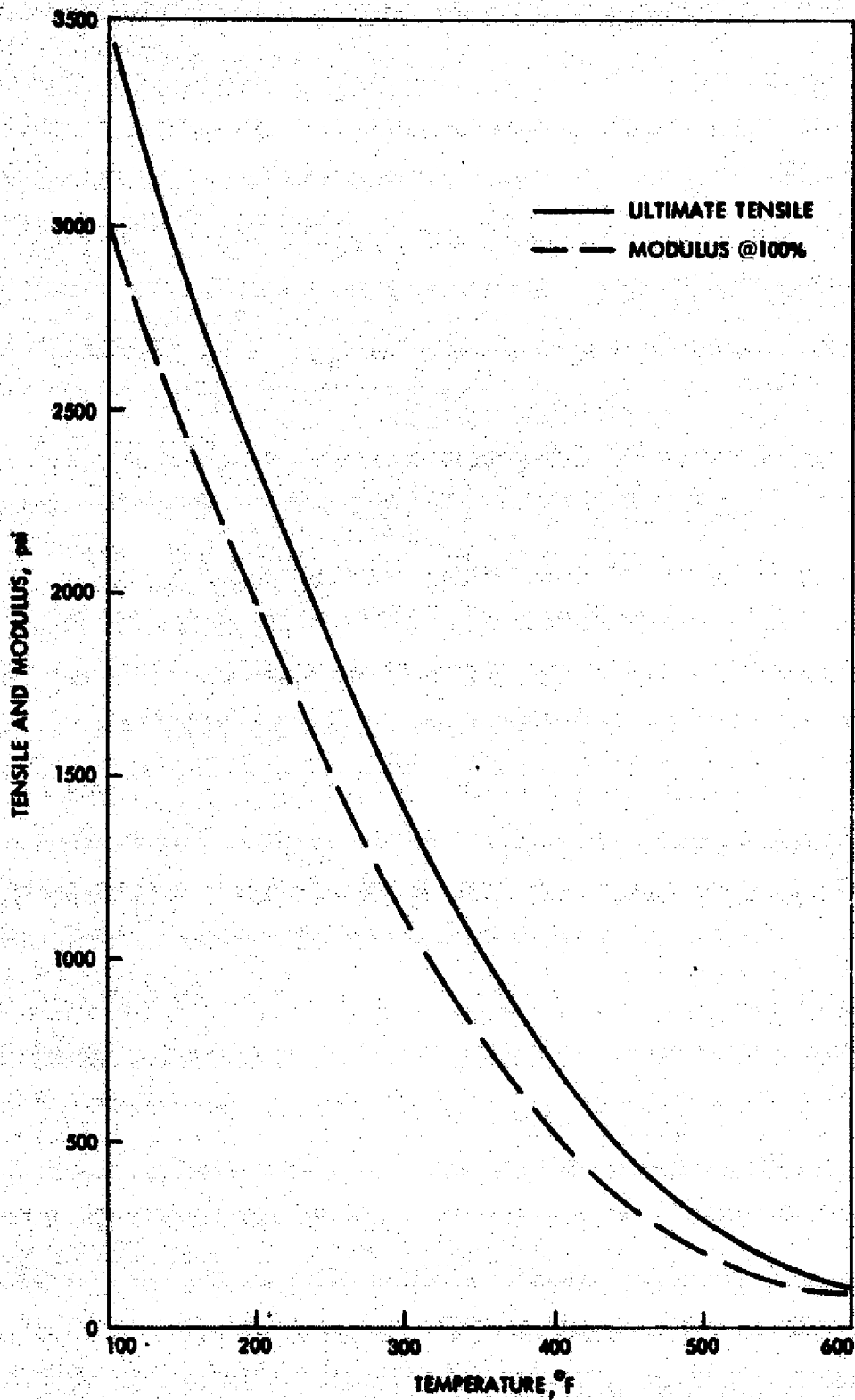of Oilfield Packers
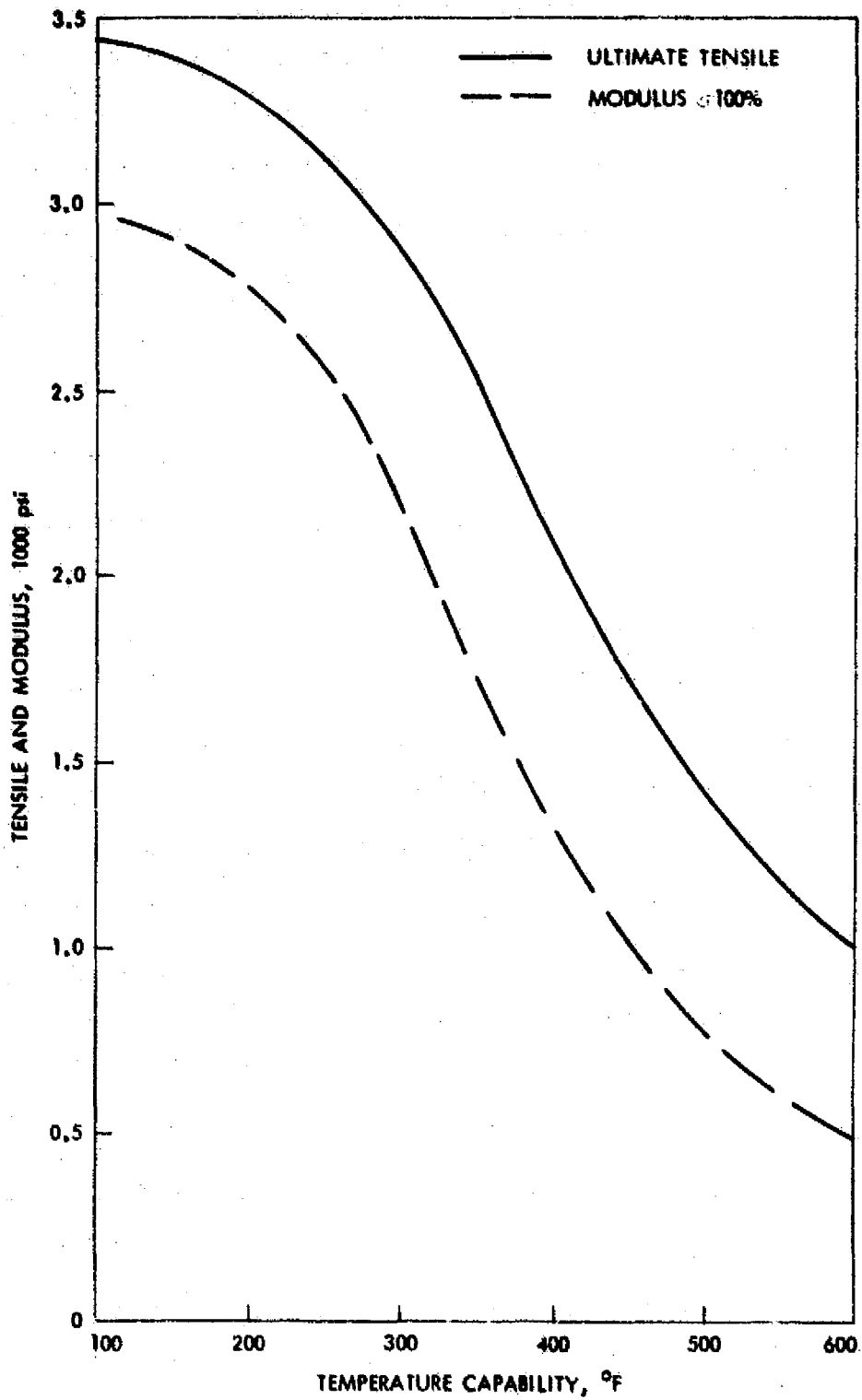
Figure 2. Optimum Properties of
Oilfield Rubber

Figure 3. Room Temperature Properties
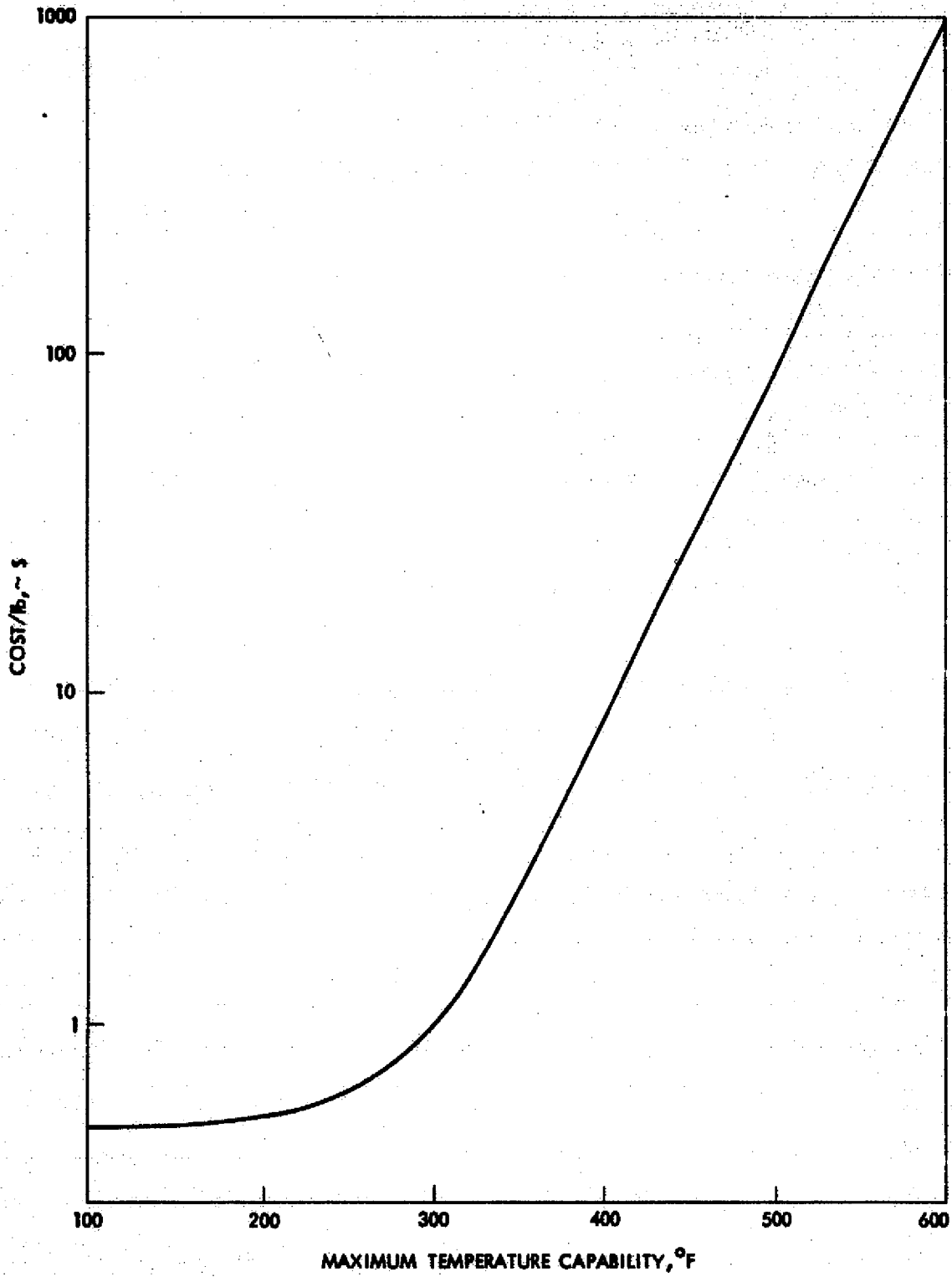of High Temperature Elastomers

Figure 4.   High Temperature Elastomers
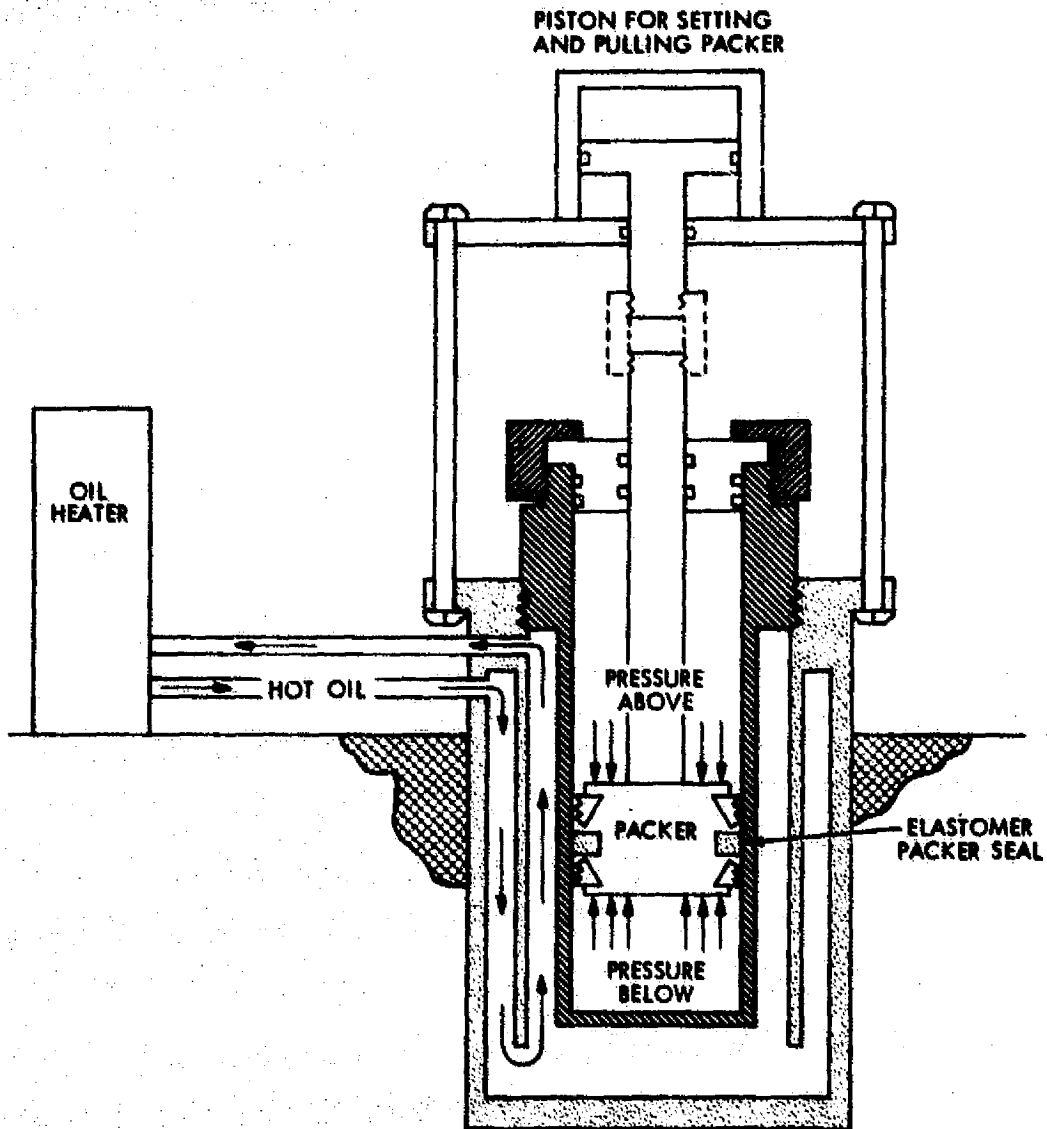Cost Comparison

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Figure 5.   Piston for Setting and
Pulling Packer - Lab Test
Well

Attendees
High Temperature Elastomer Meeting
Guiberson Division
Dallas

10-19-76

Name	Company	Tele. No.
Brewer, J. E.	Dresser Atlas Division Dresser Ind., Inc.	(713) 784-6456
Brown, Mack	Dresser Ideco Dresser Industries, Inc.	(713) 835-3731
Caddell, Mike	Patent Dept., Dresser Industries, Inc.	(214) 745-8881
Ellis, Gary D.	Guiberson Division Dresser Ind., Inc.	(713) 784-8303
Gordon, Paul G.	Jet Propulsion Lab	(213) 354-3559
Hier, Allyn R.	P&M Manufacturing Div., Dresser Ind.	(214) 421-4101
Ingham, John D.	Jet Propulsion Lab	(213) 354-4401
Jett, M. B. (Dub)	Guiberson Division Dresser Ind., Inc.	(214) 421-4101
Mueller, Wm. A.	Jet Propulsion Lab	(213) 354-2420
Phillips, Victor	Dresser Swaco Dresser Industries, Inc.	(713) 784-6324
Williamson, R. L.	Security Division Dresser Industries, Inc.	(214) 330-5156
Woodson, Jimmy	Guiberson Division Dresser Ind., Inc.	(214) 421-4101

DRESSER ATLAS PRESSURE TEST PITS

Pressure Pit #1:   No Feed-Thrus

        450°F (Max.)   20,000 psi (Max.)
        Inside Height: 12"
        Inside Diameter: 4.5"

Pressure Pit #2:   10 Feed-Thrus

        400°F (Max.)   20,000 psi (Max.)
        Inside Height: 36"
        Inside Diameter: 4.5"

Pressure Pit #3:   10 Feed-Thrus

        300°F (Max.)   20,000 psi (Max.)
        Inside Height: 8 ft.
        Inside Diameter: 4.0"

Pressure Pit #4:   No Feed-Thrus

        Ambient Temperature 20,000 psi (Max.)
        Inside Height: 16 ft.
        Inside Diameter: 5.0"

Pressure Pit #5:   10 Feed-Thrus

        400°F (Max.)   25,000 psi (Max.)
        Inside Height: 24 ft., 9 in.
        Inside Diameter: 6.0"

Pressure Pit #6:   2 Feed-Thrus

        600°F   40,000 psi
        Inside Height: 48"
        Inside Diameter: 6.0"

Pressure Pit #7:   30 Feed-Thrus   (Gas Only)

        350°F (Max.)   40,000 psi
        Inside Height: 14"
        Inside Diameter: 4.0"

Pressure Pit #8:   (Gas Only)

        350°F (Max.)   6,000 psi (Max.)
        Inside Height: 13"
        Inside Diameter: 2.5"

Pressure Pit #9:   (Steam Only)

        600°F (Max.)   1,500 psi (Max.)
        Inside Height: 29.5 ft.
        Inside Diameter: 4.5"