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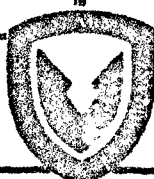
AN EVALUATION OF A FLUOROSILICONE
ELASTOMER USED AS A DYNAMIC SEAL
IN THE LANCE PROPULSION SYSTEM

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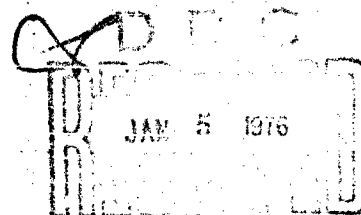
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Poly(trifluoropropyl)methyl siloxane (a fluorosilicone elastomer), the material used as a dynamic seal in the LANCE propulsion unit, was heat-aged for five years at 150° to 160°F. Physical and mechanical properties were monitored through this evaluation and it was found that the elastomer had lost 70% of its tensile strength. Thus, it was evident that this elastomer was temperature-sensitive and should be monitored when used in critical applications.		

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1. Background

This program was initiated in the latter part of 1969 to determine the stability of the fluorosilicone elastomer used as a seal in the LANCE engine. The LANCE concept relies on the propulsion system for its effectiveness. The military characteristics of the LANCE system dictate that the system must be storable for a minimum of five years under environmental conditions which may produce temperature extremes from -65° to 155°F . In addition, the system must operate effectively between the temperature limits of -40° and 140°F . The organic elastomeric materials that serve as functional components, such as static or dynamic seals and hoses are especially susceptible to attack and subsequent deterioration.

During the development of the LANCE system, only the components and materials with proven performance and storage life were used. Because of this, many of the design features evolved from concepts tested in other programs. The LANCE is unique among weapon systems because it uses components that require elastomeric seals in contact with the propellants for dynamic and static applications.

To provide a continuous sealing surface, the seal must be capable of following the changing contour of the tank wall during tank pressurization. This requirement eliminates simple rigid-type seal designs, such as O rings. Figure 1 shows the details of the spring-loaded elastomeric seal which was designed to meet the stated requirement. The dynamic seal consists of an elastomer vulcanized to a radial spring assembly composed of fifty-six projections (Figure 2). During storage one leaf of the three-leaf spring applies pressure to the elastomer to keep it in contact with the tank wall. The other two leaves of the spring are supported by a block and do not apply pressure to the elastomer except in movement of the piston.

Many different types of elastomers were considered and eliminated without evaluation. This could be done by applying the operational criteria of the system; e.g., the vinylidene-fluoride-hexafluoropropylene copolymers are not acceptable at low temperatures. The highly unsaturated diene monomer and comonomer were rejected because they do not withstand the oxidizing effects of the nitric acid. From the operational and environmental criteria it appeared that the silicones, fluorosilicones, and hydrocarbon elastomers are acceptable. After careful evaluation, the elastomer chosen to make the dynamic seal was a fluorosilicone-methyltrifluoropropylsiloxane elastomer.

This elastomer was developed in the 1950's [1]. It has properties that are different from the general silicone elastomers and offers even a greater advantage in its solvent resistance. It shows only slight attack when subjected to most solvents, fuels, and oils over a temperature range beyond the capabilities of any nonfluorosilicone elastomer. The elastomer stock is prepared by combining a reinforcing filler,

usually silica, with a peroxide vulcanizing agent and additives for heat stability. It may be processed by milling, calendering, extruding, or molding.

Fluorosilicone elastomers have excellent solvent resistance, thermal and oxidative stability, and low-temperature flexibility. In one respect, fluorosilicone and conventional dimethylsilicone polymers are at a disadvantage at high temperatures in a confined area. Depolymerization can occur with resultant deterioration of the physical and mechanical properties. The need for reversion-resistant elastomers at elevated temperatures has prompted research in preparation of polymers in which the backbone consists of fluorocarbon units connected by a disiloxane linkage.

2. Experimental Results

a. Test Chamber

The fluorosilicone elastomer was evaluated for degradation by exposing it to a temperature of 150° to 160°F for five years. Samples of the elastomer were stored in a specially designed container (Figure 3). It was designed as a closed system, thereby simulating the stored condition of the LANCE. The load on the elastomer in the container is transmitted through two springs. One spring on the inside is a portion of the spring assembly from the LANCE supporting the elastomer arrangement and the other spring is located externally. This spring was wound to provide a load of 65 pounds when compressed to 37% of its length. After the elastomer is placed in the specimen chamber and the container sealed, a screw in the outer chamber is used to compress the spring to a scored mark on the specimen chamber. It was discovered later that the mark was 1 inch from the top instead of 1.1 inches. This difference in compression gave a slightly less load than was calculated.

The specimen test chamber was designed to accommodate a series of elastomeric discs separated by aluminum discs. This arrangement is shown in Figure 4. A bellows was molded from neoprene to seal the specimen chamber to the chamber case lid. After the test bomb was assembled, a positive pressure of nitrogen surrounded the fluorosilicone elastomer and the outer spring compressed to the mark on the specimen chamber. This simulated the LANCE environment. The bomb was checked for leaks and then placed in an oven maintained between 150° and 160°F.

b. Fluorosilicone Elastomer

The fluorosilicone elastomer used in this evaluation was supplied by the LANCE Project Office in test slabs that measured 6 x 6 x 0.080 inches. Circular test specimen (1.625 inches diameter) were cut from each of the slabs. Thickness and Shore A hardness measurements were taken on the specimens. Five specimens were used in each test fixture and were stacked alternately with aluminum discs. The test

chamber was closed, gaseous nitrogen purged the inner cavity; and the outer spring compressed to the prescribed mark on the specimen chamber. The test bomb was checked for leaks and placed in an oven at 150° to 160°F. After heat aging, the elastomer was removed from the test bomb after 1, 2, 3, 12, 48, and 60 months of exposure. Properties measured were:

- 1) Hardness, Shore A.
- 2) Thickness.
- 3) Tensile strength and elongation.

c. Hardness

Hardness measurements were made using the Shore A durometer, and in accordance with the procedures described in ASTM-D-2240. The requirement for the vulcanized fluorosilicone elastomer as required by the specifications MIS13382 and MIS13384 is 55 ± 5 (MIS13382 - Rubber, Fluorosilicone, Uncatalyzed; MIS13384 - Vulcanization of Fluorosilicone Rubber Dynamic Seal Assembly, Process for). The hardness measurements before exposure to heat-aging were Shore A60. After heat-aging for 48 and 60 months, the hardness increased to a Shore A70. The literature values for hardness after heat aging show a slight increase; however, the samples reported in the literature were heat-aged for 70 hours at 212°, 302°, and 392°F.

d. Thickness

Thickness measurements were made on each stack of elastomer before the heat aging-test using a Randall-Stickney gauge. At the end of the five-year storage period a decrease in thickness of 2% was observed. The change, although small, results from the elastomer taking a set under load and at an elevated temperature. These data do not represent compression set since compression set is obtained by another method.

e. Tensile/Strength and Elongation

Tensile ribbons were cut from the circular specimen with an instrument used to cut low-temperature brittleness specimens. Two tensile ribbons were cut from each disk along a centerline and 1/4 inch wide to each side of the centerline. The samples were measured and pulled in tension on an Instron machine at a rate of 20 inches per minute. The breaking load was recorded on a chart and the tensile strength calculated from the recorded values. Elongation was taken from the gage length.

An evaluation of the test data reveals that at least one test slab was not of the same quality as the other slabs. It had a tensile strength that was 30% lower than the average. This can be observed by

comparing the data presented in Tables 1 through 4. It is also shown in Figure 5 as a control specimen after 6 months storage. The tensile strength for this particular sample was not used in averaging the other control samples. After heating for 4 years, this particular test specimen lost its identity. Because the sample could not be distinguished from the other samples, it is included in the data from the 60 months storage.

The tensile data show that the fluorosilicone elastomer is temperature-sensitive. Data [2] from the literature also show that the fluorosilicone elastomer loses its strength with time and temperature. The loss is much worse when confined in an inclosed tube. At the end of 4 years aging in the closed container the tensile strength had decreased by 50% and at the end of the 5 years, the tensile strength had decreased by 70%. The literature [3] also revealed that some vulcanizates evolve decomposition products which, when contained in a test tube, causes premature degradation. Results obtained from the test tube method of aging will be poorer than those obtained with circulating air ovens. These are shown in Figures 6, 7, and 8 [2,4]. Pierce and Kim [2] have evaluated and reported on the fluorosilicone rubber that was heat aged for 1 year at 392°F. This is shown in Figure 9 [2].

During the examination of the elastomer that had been stored for 5 years, a clear, tacky residue was found on the aluminum disk. This residue was analyzed by a Consolidated Electrodynamics Corporation 21-130 Mass Spectrometer. A sample of the elastomer was also analyzed. Both spectra were very similar except the intensity of the peaks from the residue samples was of a lower magnitude than the solid elastomer.

Samples of the residue, a heat-aged elastomer and an elastomer that was not heat aged, were prepared and analyzed by internal reflection spectroscopy. This technique can be used to produce quantitative and qualitative infrared spectra on solid, liquid, or gas samples. When a material that selectively absorbs radiation is placed in contact with the reflecting surface, the beam will lose energy at those wavelengths where the material absorbs because of an interaction with the penetrating beam. This attenuated radiation, when measured and plotted as a function of wavelength by a spectrophotometer, will give rise to an absorption spectrum characteristic of the material.

The stored, heat-aged fluorosilicone and the sample not heat-aged were placed on the KRS-5 crystal. Figures 10 and 11 are spectra of this material. It is obvious, by comparison, that the materials are identical.

The tacky, clear residue was dissolved in toluene and this solution was placed on a sodium chloride plate. The solvent evaporated, thus leaving a film of the residue to be analyzed. Figure 12 is the spectrum of this material. When compared with the other spectra, it shows the same characteristic pattern of the elastomer, except that the intensity of the peaks is not as great.

3. Conclusions and Recommendations

At the end of the heat-aging study, the fluorosilicone elastomer had lost 70% of its tensile strength. This is indicative of a material that is temperature sensitive. The hardness measurements for the vulcanized stock are 55 ± 5 and 50 ± 5 , respectively, as required by the Government process and material specification and the supplier specification. Hardness measurements during this evaluation increased to Shore A 70 and do not agree with reversion or softening of the elastomer. Without some uncured stock as a standard, it is difficult to conclude that the vulcanized material reverted.

It is recommended that the tanks that have been stored for several years in areas where the temperature is above 110°F be monitored for deterioration of physical properties of the fluorosilicone elastomer.

TABLE 1. THIRTY DAYS EXPOSURE TO 165°F

Thickness before exposure	0.420 in.					
Hardness before exposure	Shore A 60					
Thickness after 30 days exposure	0.422 in.					
Hardness after 30 days exposure	Shore A 60					
	Control	I	II	III	IV	V
Breaking load (lb)	29.5	27	24	Slipped	18.5*	26.5
	29.5	25	23.5	26	16.0	23.0
Tensile strength (psi)	1270	1270	1150		900	1250
	1270	1260	1130	1270	780	1080
Average tensile strength (psi)	1270	1200				

*Not included in average

TABLE 2. SIXTY DAYS EXPOSURE TO 165°F ENVIRONMENT

Thickness before exposure	0.429 in.					
Hardness before exposure	Shore A 60					
Thickness after 60 days exposure	0.429 in.					
Hardness after 60 days exposure	Shore A 60					
	Control	I	II	III	IV	V
Breaking load (lb)	29	21.5	25.5	14*	26	25.5
	26	27	25	15	26.5	26
Tensile strength (psi)	1330	1010	1230	660	1160	1200
	1200	1270	1200	730	1180	1240
Elongation (%)	300	200	300	175	200	300
	250	250	275	175	175	300
Average tensile strength (psi)	1270	1190				

*Not included in average

TABLE 3. SIX MONTHS EXPOSURE TO 165°F ENVIRONMENT

Thickness before exposure	0.419 in.					
Hardness before exposure	Shore A 60					
Thickness after 6 months exposure	0.418 in.					
Hardness after 6 months exposure	Shore A 60					
	Control	I	II	III	IV	V
Breaking load (lb)	19	26	23	12*	27	22
	18	26	26	13	26	24
Tensile strength (psi)	920	1260	1120	570	1270	1070
	880	1260	1260	620	1220	1150
Elongation (%)	250	300	300	150	350	200
	250	300	350	150	300	200
Average tensile strength (psi)	900	1200				

*Not included in average

TABLE 4. ONE YEAR EXPOSURE TO 165°F ENVIRONMENT

Thickness before exposure	0.429 in.					
Hardness before exposure	Shore A 65					
Thickness after 1 year exposure	0.425 in.					
Hardness after 1 year exposure	Shore A 65					
	Control	I	II	III	IV	V
Breaking load (lb)	27.5	22	25.5	26.5	27.5	12*
	26.5	23	25	26	28	12
Tensile strength (psi)	1280	1070	1160	1290	1270	580
	1230	1090	1140	1270	1290	580
Elongation (%)	300	150	150	250	250	150
	300	150	150	300	250	150
Average Tensile strength (psi)	1260	1200				

*Not included in average

TABLE 5. FOUR YEARS EXPOSURE TO 165°F ENVIRONMENT

Thickness before exposure	0.430 in.				
Hardness before exposure	Shore A 60				
Thickness after 4 years exposure	0.425 in.				
Hardness after 4 years exposure	Shore A 70				
	I	II	III	IV	V
Breaking load (lb)	15.5	17.5	8.5*	18.5	15.5
	20	13	8.5	13.5	15.5
Tensile strength (psi)	700	830	410	910	740
	940	620	410	660	740
Elongation (%)	100	175	100	200	150
	150	150	100	150	125
Average tensile strength (psi)	770				

*Not included in average

TABLE 6. FIVE YEARS EXPOSURE TO 165°F ENVIRONMENT

Thickness before exposure	0.420 in.				
Hardness before exposure	Shore A 60				
Thickness after 5 years exposure	0.410 in.				
Hardness after 5 years exposure	Shore A 70				
	I	II	III	IV	V
Breaking load (lb)	11	9	8	8.8	8
	10	10	8.5	5.8	8.8
Tensile strength (psi)	500	450	400	400	400
	500	500	400	300	450
Elongation (%)	150	100	100	100	100
	150	100	100	100	100
Average tensile strength (psi)	430				

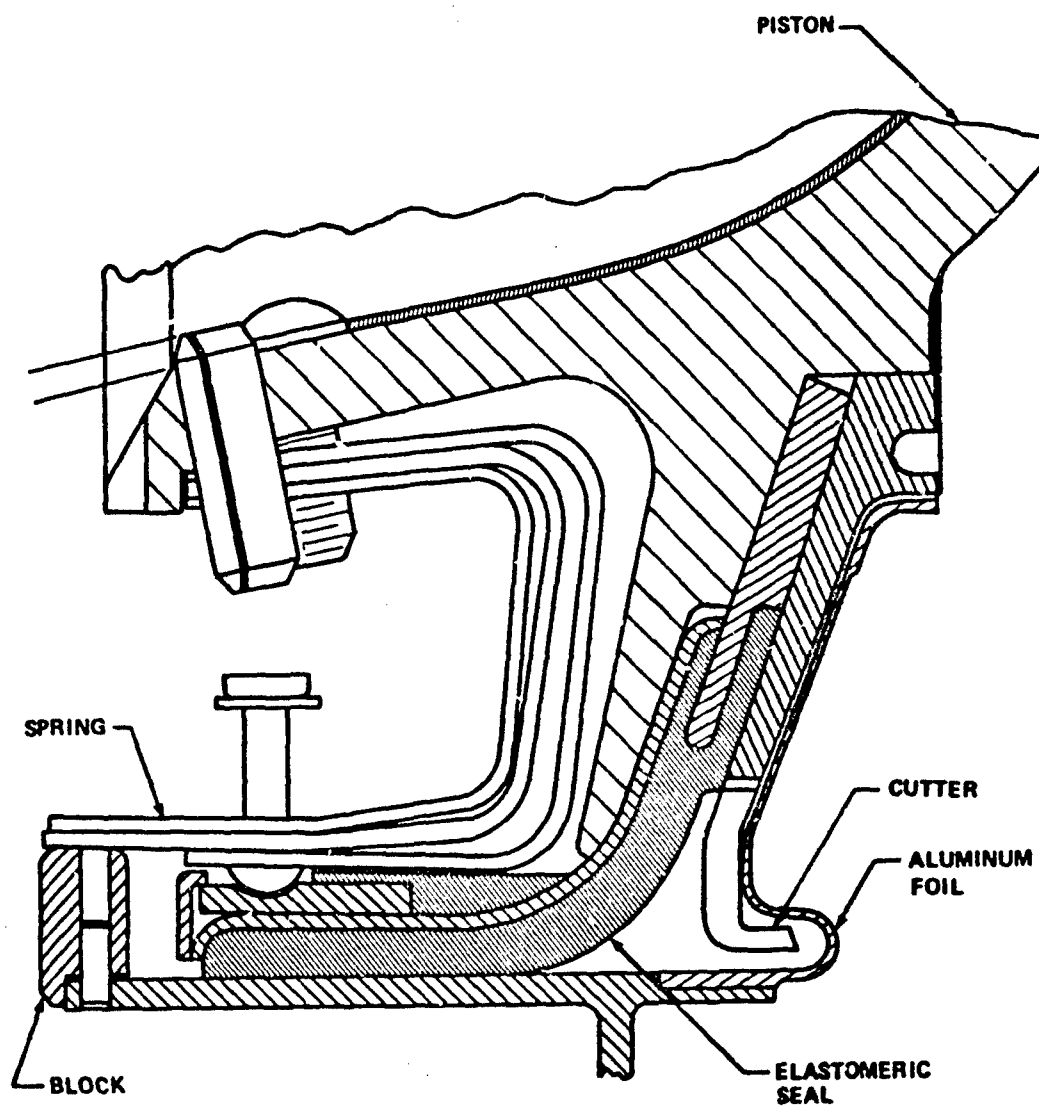


Figure 1. Elastomeric seal design.

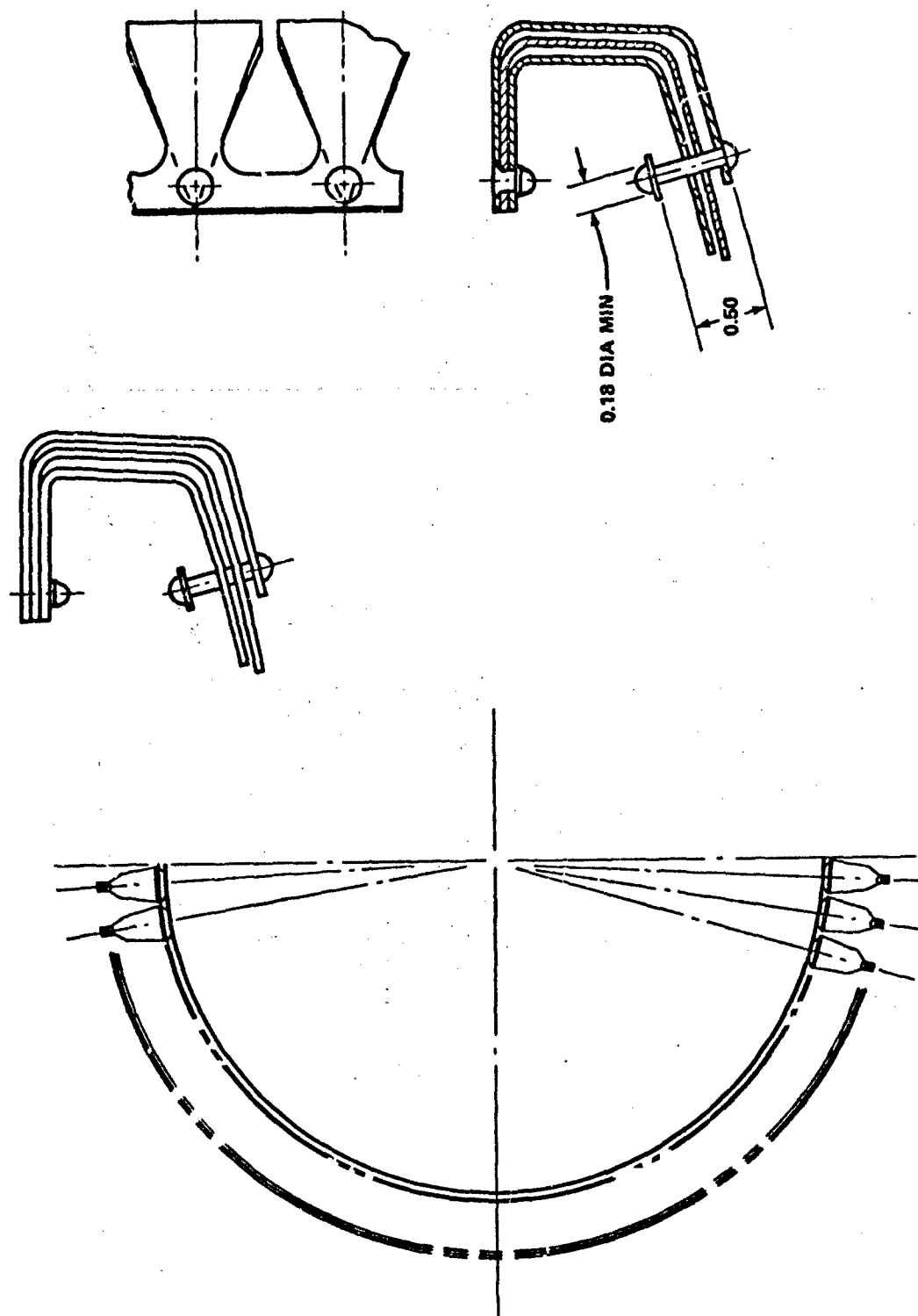


Figure 2. Spring assembly.

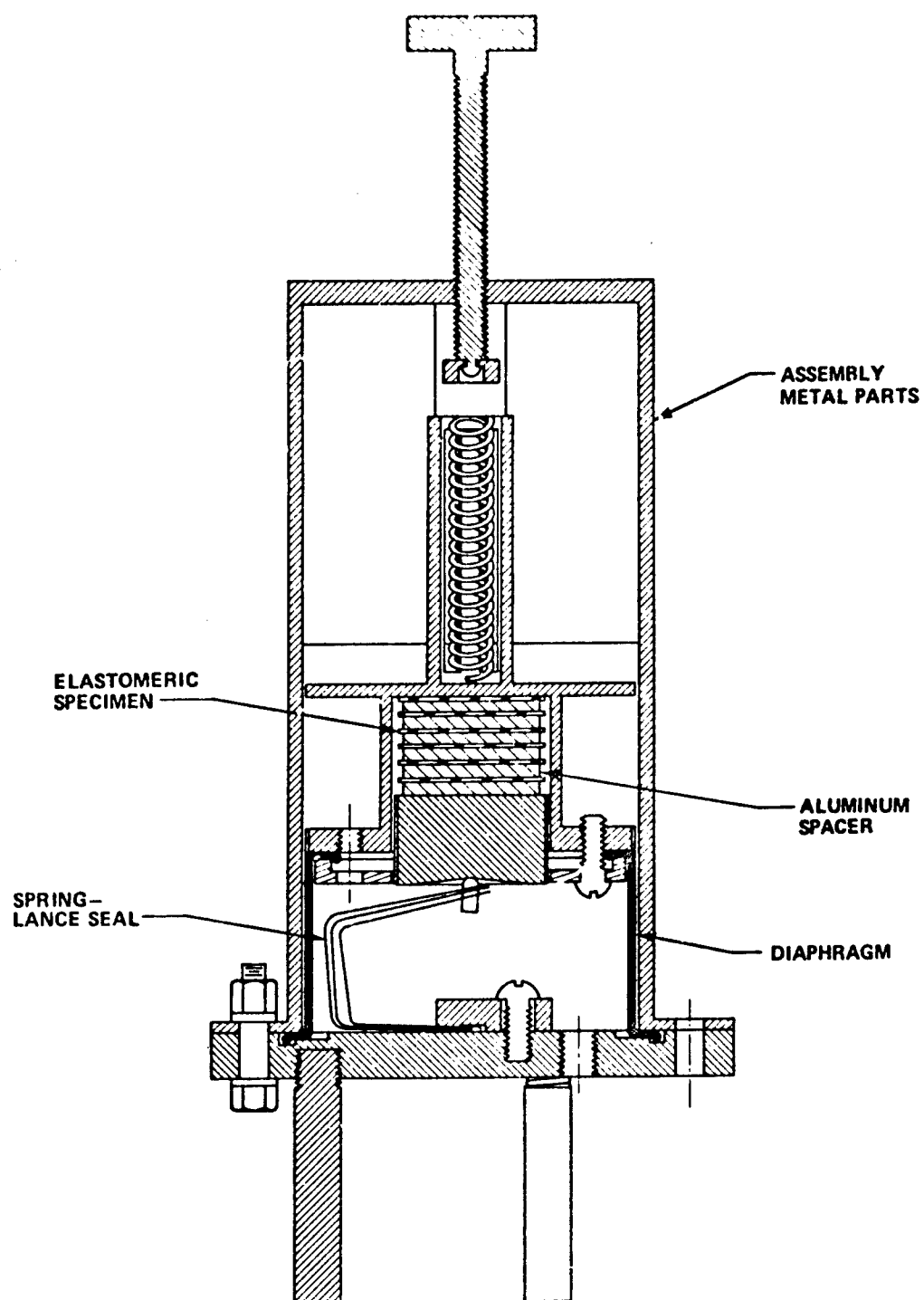


Figure 3. Test bomb assembly.

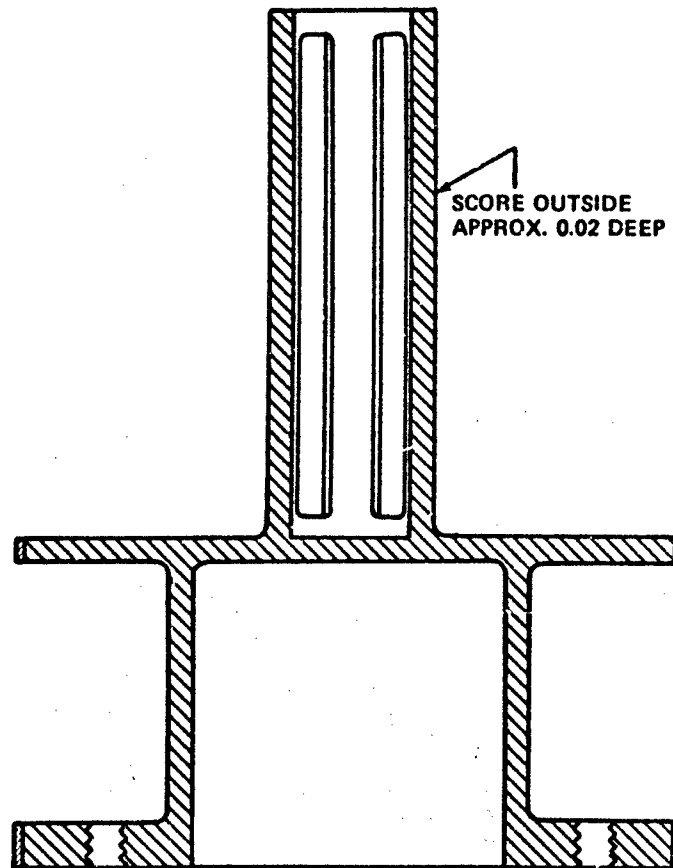


Figure 4. Specimen chamber.

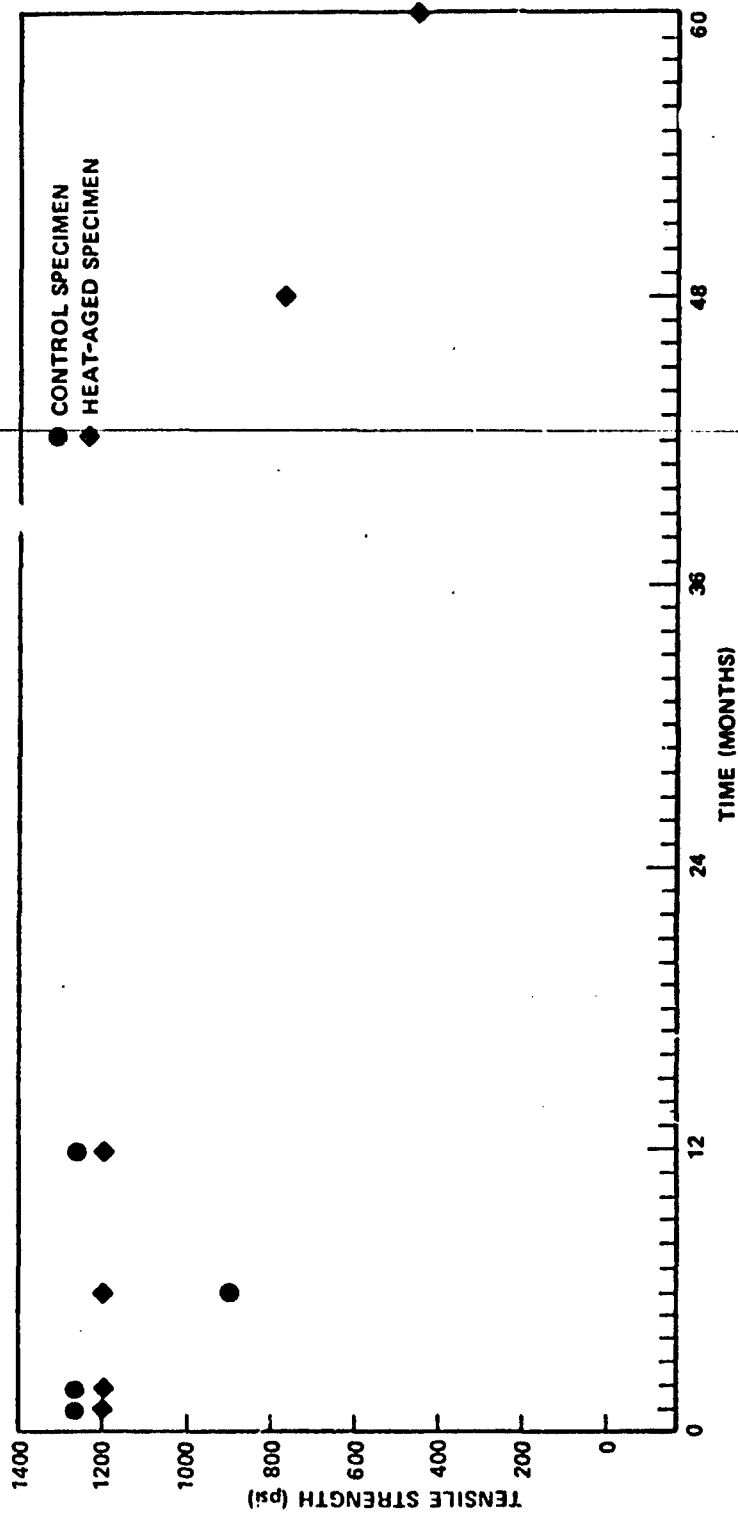


Figure 5. Tensile strength of fluorosilicone elastomer heat-aged at 150° to 160°F.

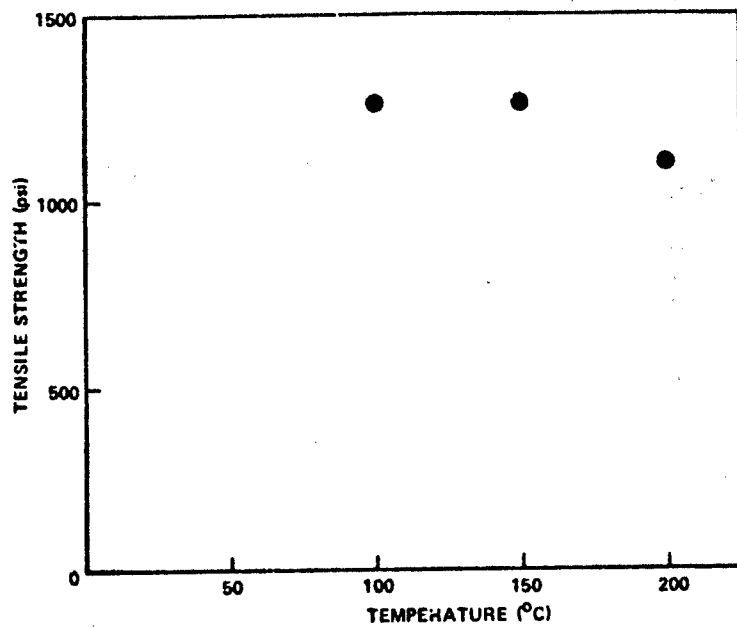


Figure 6. LS 2332U - Heat-aged for 70 hours at temperature, post cured 8 hours at 200°C.

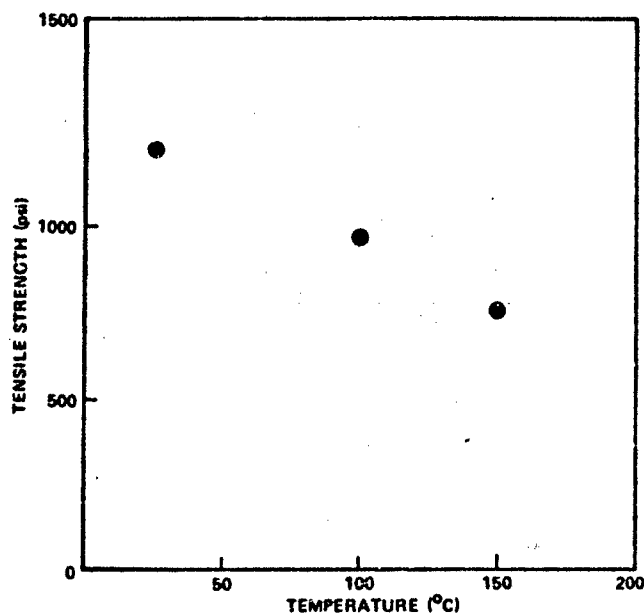


Figure 7. LS 2332U - Conditioned in tester for 15 minutes at temperature, cured 8 hours at 200°C.

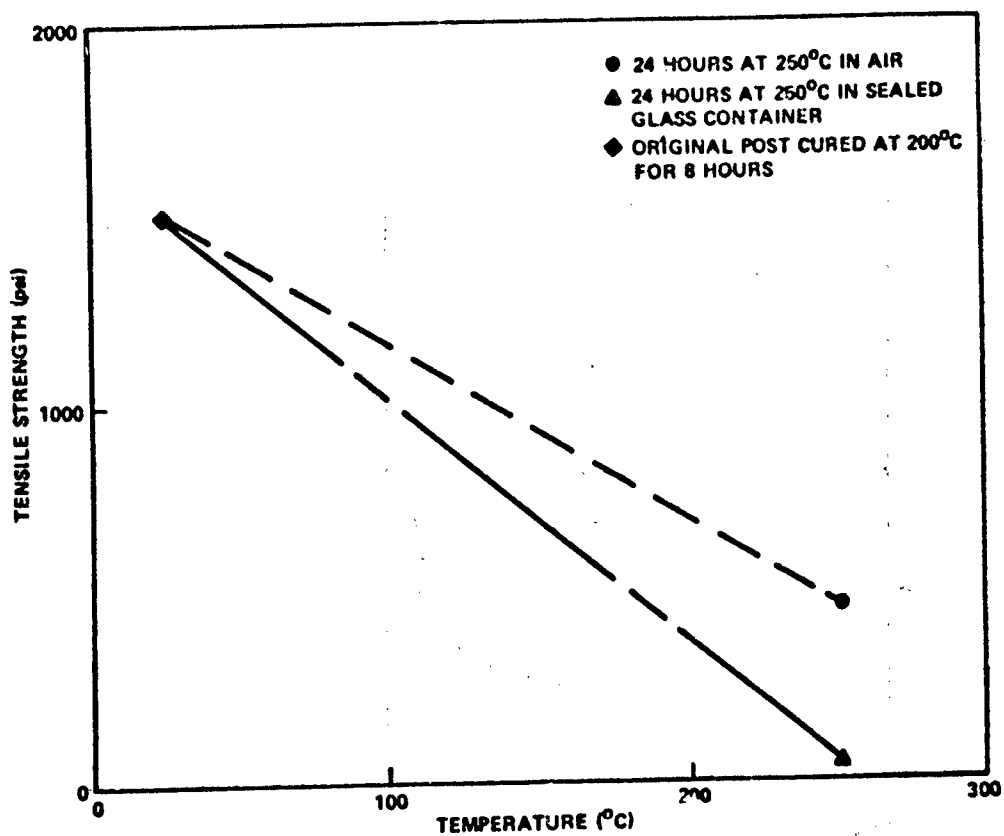


Figure 8. LS - Poly-(3,3,3trifluoropropyl)-methylsiloxane.

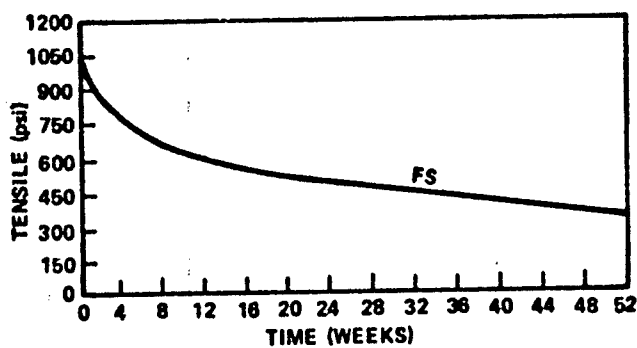
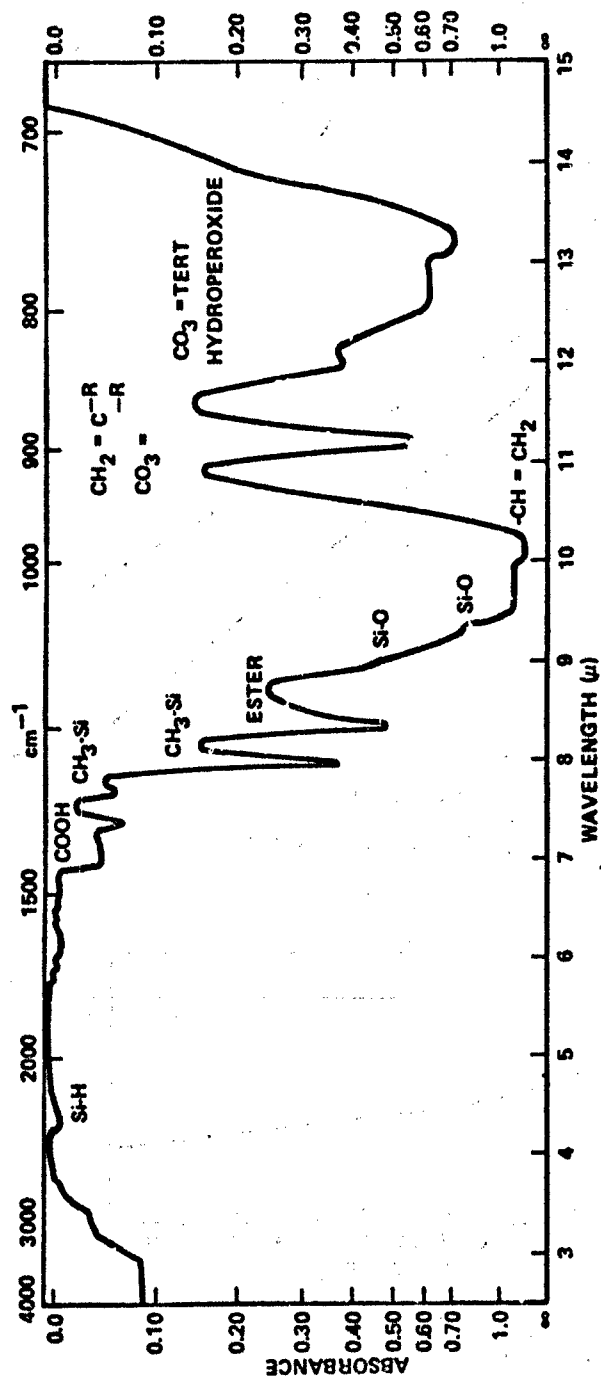


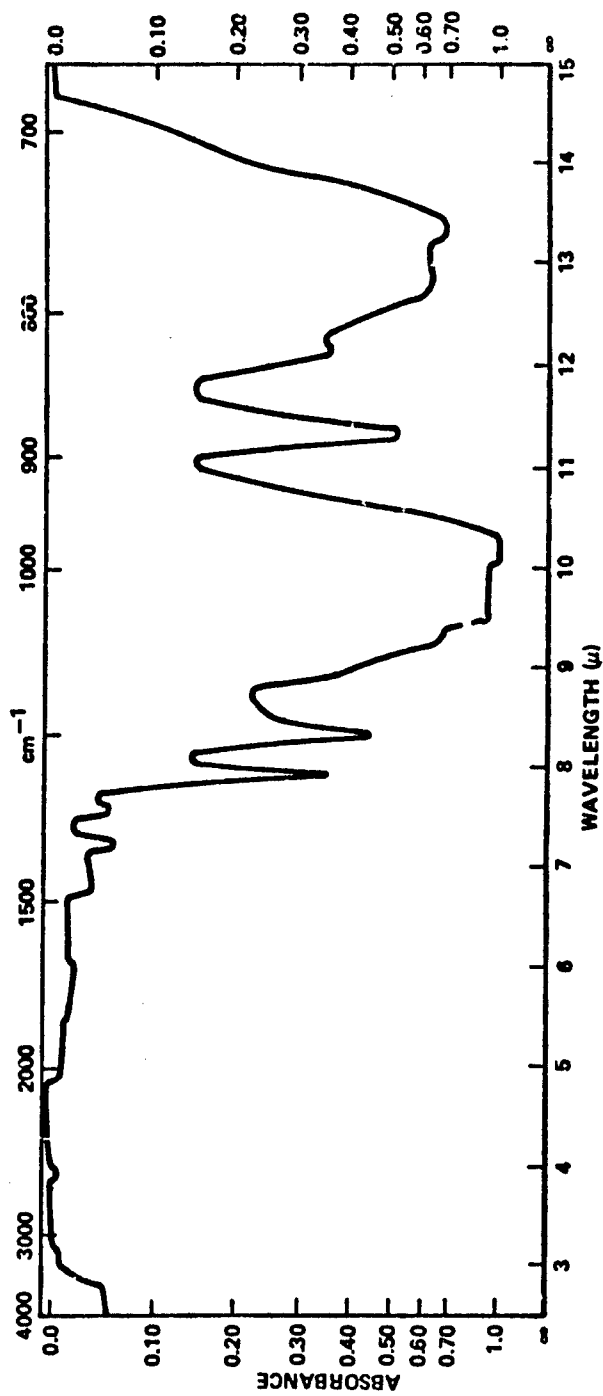
Figure 9. Tensile of a fluorosilicone which has been heat-aged at 392°F for indicated length of time.



SAMPLE: SI-RUBBER, 5-YEAR
STORAGE, SURFACE
CLEANED WITH ϕCH_3
DRIED IN VACUUM
OVEN.

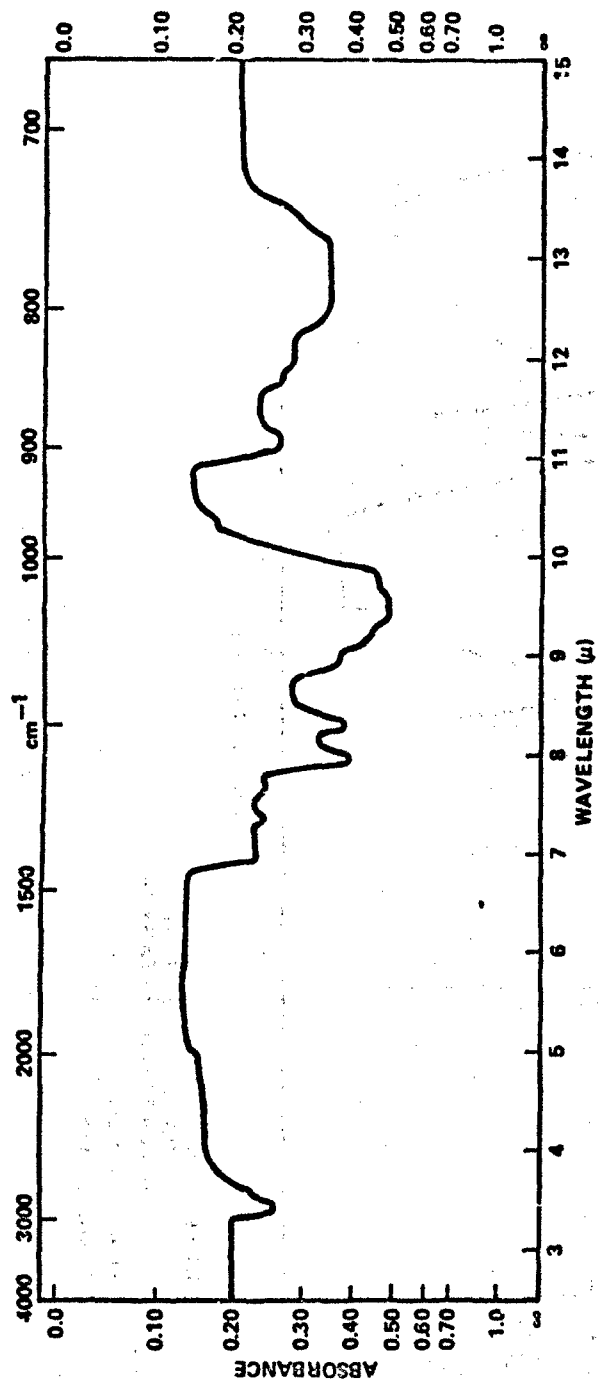
PHASE: SOLID
THICKNESS: ATR

Figure 10. Spectrum of fluorosilicone elastomer stored for 5 hours at 150° to 160°F.



SAMPLE: SI-RUBBER
 DID NOT STORE AT 165
 FOR 5 YEARS. CREAMY TAN.
 PHASE: SOLID
 THICKNESS: ATR

Figure 11. Spectrum of fluorosilicone elastomer.



SAMPLE: SI-RUBBER
 STICKY SURFACE. WASH
 WITH ϕ TO REMOVE
 CH_3
 STICKY MATERIAL.
 PUT ON
 NACI CELL - SAMPLES
 1 AND 2.
 PHASE: SOLID

Figure 12. Spectrum of residue form stored and heat-aged fluorosilicone elastomer.

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