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FUNDAMENTALS OF NONCURING SEALANTS FOR AIRCRAFT FUEL TANKS

ELASTOMERS AND COATINGS BRANCH
NONMETALLIC MATERIALS DIVISION

DECEMBER 1977

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The need for efficient space utilization in military aircraft has led to the use of wing and fuselage cavities as fuel tanks. Of the three methods of sealing these cavities (filleting, faying, and channel), channel sealants are the least understood and have the most contrast between behavior and requirements. Potential failure mechanisms were identified against the thermal, chemical, and physical aspects of the fuel tank environment. Thermal degradation, low temperature embrittlement, thermal expansion, and viscosity reduction were mechanisms

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20. Abstract (Continued)

associated with the -54°C to +177°C temperature range. Hydrolysis, oxidation, closed system reversion, and crosslinking were associated with the chemical aspect. Fuel swelling of the sealant, extraction by fuel, system pressure, vibration, shear, and adhesion/cohesion were associated with the physical aspect.

Selected polymers with a wide variety of formulating ingredients were evaluated as channel sealants in a laboratory-sized test apparatus to confirm the suspected failure mechanisms. The results have been digested as engineering principles that govern the behavior of channel sealants. Application of these principles resulted in some immediate benefits and a basis for long range sealant development. For example, the addition of vulcanized elastomer particles to commercial and experimental sealants prevented gap extrusion and increased the time to failure in laboratory sealant testers by a factor of four (4). The selection of highly fluorinated polymers such as the poly (fluoroalkoxy phosphazene) (PNF) extended life by reducing fuel swell. When combined with Lithium Aluminum Silicate to reduce thermal expansion about 50%, the PNF sealant did not fail at four (4) times the life of state-of-the-art materials over the -54°C to +177°C temperature range. Development plans include the construction of an improved laboratory-sized sealant tester and continued application of the engineering principles to the synthesis and formulating of broad temperature range, long service life channel sealants.

FOREWORD

This report was prepared by the Elastomers and Coatings Branch under Internal Work Documentation Unit No. 24210106, "Seals and Sealants," with Warren R. Griffin (AFML/MBE) as Project Engineer.

This effort was conducted at the Air Force Materials Laboratory in support of the using commands where channel sealed aircraft are maintained and operated. This report covers work performed over the two year period from January 1975 to January 1977.

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SECTION I

INTRODUCTION

Most military aircraft use the irregularly shaped internal cavities of wings and fuselage to carry fuel. The channel or groove injection method of sealing these structures has the desirable feature of external repair via reinjection which can be accomplished with relatively few manhours per leak repair and can be performed in thin winged aircraft where internal access is too limited for internal repairs. Difficulty has come in several forms: (1) the high cost of manpower and materials, (2) the increased frequency of leaks, and (3) leaks in inaccessible areas. The cost of specialized labor alone is sufficient justification to provide longer life materials, but in addition, channel sealants are not performing as well as anticipated. Frequent leaks require that materials and qualified repair personnel be stationed at each aircraft base. Inaccessibility of areas next to engines, cockpit, and electronic bays requires costly time consuming removal of equipment before repairs can be made. A reliable, longer service life sealant is needed that would reduce operational and maintenance costs as well as reduce hazardous fuel leakage. The research toward improved sealants requires an understanding of the sealing action in an aircraft environment, the modes of failure, and the properties of elastomeric materials.

Integral fuel tanks utilize the aircraft structure (i.e. the skin and structural members) for fuel containment as opposed to bladder cells or external tanks which are separate fuel containers within or attached to the airframe. The skin and frame must be sealed at every joint and fastener by a flexible material to provide a permanent barrier to fuel leakage. Fuel resistant elastomers such as the polysulfides, fluorosilicones, polyesters, cyanosilicones, and nitrile-butadiene types have been used as sealants with varying degrees of success.

Integral fuel tank sealants can be divided into three types: (1) filleting, (2) faying, and (3) channel. Filleting sealants are viscous liquid polymer mixes applied by spatula or caulking gun. They are extruded over seams, into joint corners, over fasteners, and around other tank intrusions such as hydraulic lines and electrical conduits. Most vulcanize to a tough rubber-like product in a few days at room temperature. Repair is made by physically removing the fillet, often with the aid of solvent and desealing solutions, and reapplying a fillet of the same or compatible material. Repairs become difficult in inaccessible areas. Faying surface sealants are filleting type materials which are applied between skin and structural members during assembly. The bond line is thin because the mating parts are fastened together after applying the liquid elastomeric compound, often thinned with a solvent. Most are room temperature vulcanizing products that reach full state of vulcanization in a few days. Faying surface sealants are not repairable without disassembly of the skin and frame. Channel sealants are nonvulcanizing mastics that are injected into grooves formed in the structure-skin joints. The sealants can be prepacked into grooves as the aircraft is assembled or injected after assembly. Repair is easily effected by injecting new sealant into a port on the skin of the aircraft as old sealant is pushed out an adjacent port.

While any one of these sealing methods can be used alone, many aircraft use two or all three to insure reliability. In addition, a vulcanizing type of channel sealant is now being used that may not be repairable by the usual reinjection procedure. The discussion here is limited to noncuring channel sealant types used as the primary seal for integral fuel tanks. The objective of this work is to understand more fully the fuel tank environment, the mechanisms causing the observed failure modes of channel sealants, and the engineering principles that will lead to longer life channel sealants.

SECTION II

FUEL TANK ENVIRONMENTS

A channel sealant must prevent seepage of fuel through structural joints. To do so it must have an elastomeric flexibility, adhere to the metal with a tacky type adhesion, resist being pushed or extracted from the joint by fuel, and retain these properties over the required temperature range. The pressure to inject sealant originally or to repair leaks must be within the limit allowed for particular structures. The time between repairs should be 3-5 years. While reasonably easy to define, the properties that allow the ease of repair are in contradiction to the long life requirement of the fuel barrier (i.e. easy to inject, will remain in place indefinitely during use, yet is easily reinjected when repairs are necessary). The channel sealants presently in use are formulated for a balance of properties that provide a compromise between permanence and repairability. In order to shift the compromise toward longer life, an understanding of the fuel tank environment is important.

1. Thermal

The majority of military aircraft operate over geographical and speed ranges such that fuel tanks have a general thermal environment of -54°C to +180°C. Lower temperatures occur on the ground in arctic climates. Parked aircraft can easily experience the -54°C temperature. Wind gusts under these conditions support the requirement of -54°C flexibility. The high temperature environment results from aerodynamic friction and heat sources such as hydraulic fluid coolers in the fuel, engines, and hot exhaust gases.

2. Chemical

The chemical environment consists of hot air, fuel, fuel vapor, metal, and water. Hot air contacting the external walls of fuel tanks has interaction with the sealant at the narrow joint in the skin. The oxygen in the air that replaces fuel must also be considered. The fuel consists chiefly of aliphatic and aromatic hydrocarbons which are relatively inert chemically. However, J-P fuel contains over 300 individual components.[1] The most chemically active are sulfides, pyridines, and water. The sulfides are simulated in test fuels by adding 1% tertiary butyl disulfide and .015% tertiary butyl mercaptan. The pyridines present are high pH chemicals and join water and metal to provide a hydrolyzing environment. Jet fuel absorbs about 70 parts/million of water at 21°C and the absorption increases with temperature and aromatic content of the fuel. This "dissolved" water is available for hydrolysis throughout the fuel tank. The metal of the fuel tank is not inert. It is often prevented from corroding by an acrylonitrile/butadiene copolymer or urethane coating. Yet, in joint areas, fasteners, etc., metal ions are available to provide an environment for confined heat reversion of vulnerable sealants. Fuel additives are part of the fuel tank environment. The most significant is the anti-icing additive.

A small percent (.015%) of ethylene glycol monomethyl ether is used in the fuel by the Air Force to prevent separated water from freezing. In the water sump areas, the concentration of the additive has been measured at 40% in the water sample.[2]

3. Physical

Pressure, vibration, shear, fuel swell, extraction of sealant, and the effects of sloshing fuel are involved in the physical "mechanical" environment. The pressure in a fuel tank arises from the weight of fuel (to which must be added "g" forces in flight) and 2-5 psi system pressurization. The pressure in the channel can become several hundred psi from thermal expansion, fuel swell, and sometimes thermal degradation of the sealant. Vibration is on the order of 145-160 dB and the frequency depends upon aircraft type, location on the aircraft, and mission requirements. Generally, the peak power is dissipated in the 600 to 1,200 Hz region within a broad range of 30 to over 10,000 Hz. Measured as "g" forces, 2g's at 30 Hz will damage structural panels. A slosh and vibration test of 15 RPM ±15° tilt and 30 Hz is used to qualify structural designs for resistance to vibration damage. Shear is similar to vibration but at a slower rate and usually greater amplitude or movement. Wing flexing, joint strains, etc. fall into this category.

Swelling in the 4 to 30% range is normal for fuel resistant elastomers. The increased volume builds pressure within the channel.

The variation in aromatic content of the fuel changes the amount of swell and can be a source of early failure. The extraction of low molecular weight polymer by fuel may counteract the swell but more often the extraction of sealant depletes the volume in the channel and leaks soon develop.

Sloshing fuel can physically erode sealant from the faying area by a shearing effect.

SECTION III

MECHANISMS OF FAILURE

A prerequisite to the designing of an improved sealant is understanding why the present ones fail. The physical and mechanical properties of channel sealants that have failed on operational aircraft and laboratory evaluation apparatus can be observed and measured. These modes of failure appear, in Table I, as gap extrusion, reversion, mud cracking, extraction by fuel, or often a combination of these. While the observed changes in sealants lead to categorizing the modes of failure, no real cause and effect relationship can be developed between the environment and the failure of specific sealants. A deeper examination of the sealant-environment interaction leads to mechanisms (causes) of failure such as thermal expansion, thermal degradation, and viscosity changes related to temperature effects; hydrolysis, oxidation, closed system reversion, and crosslinking in the chemical area; and fuel swell, polymer extraction, vibration and shear induced viscosity changes, adhesion/cohesion, and system pressure in the physical area. These mechanisms can be related to specific polymer types, sealant formulations, and the fuel tank environment. From this point of reference, the causes of sealant failures can be established and research directed toward eliminating the thermal, chemical, or physical vulnerability of the sealant.

TABLE I

FAILURE MODES OF CHANNEL SEALANTS ON OPERATIONAL AIRCRAFT [3]

SEALANT	AIRCRAFT	FAILURE MODE
Polysulfide	F-4, A-7	Gap extrusion
Fluorosilicone	F-15	Gap extrusion, reversion
	Early F-111	Gap extrusion into tank area
Cyanosilicone	A-6, F-14	Gap extrusion, mud cracking* corrosion
Polyester	F-111	Gap extrusion, fuel extraction, reversion

*Mud cracking is a descriptive term for degradation into a stiff paste accompanied by shrinkage and has been observed only during laboratory tests.

1. Thermal

a. Thermal Expansion

Thermal expansion is a mechanism of failure that is more serious as the temperature range of the environment broadens and is a property of all elastomeric materials. Vulcanized elastomers show less volumetric expansion as filler content is increased and as crosslink density is increased. The coefficient range is $10 \times 10^{-4}/°C$ for gum vulcanizates to $0.5 \times 10^{-4}/°C$ for vulcanizates with selected fibrous carbon reinforcement. Channel sealants are uncrosslinked mastics. Therefore, the only means available to reduce the expansion is the dilution with low expansion ingredients. The dilution effect is not linear and, in the amounts usually employed for channel sealants, the thermal expansion remains a major problem.

Table II shows the volumetric (cubical) expansion of some common elastomers in the linear range from their respective glass transition temperature (Tg) to room temperature. These are formulated vulcanized elastomers that have found general use. The range does not vary greatly. The most significant point is the difference between the elastomers and aluminum metal - listed last as a comparison. The mathematics to determine the change in groove volume as the expansion of the aluminum takes place is complicated and not significant since the elastomers expand ten (10) times the rate of the aluminum metal.

TABLE II

VOLUMETRIC EXPANSION OF ELASTOMERIC POLYMERS*[4]

POLYMER	β, Tg to 25°C
Hexafluoropropylene/ Vinylidene fluoride (with carbon black and amine cure)	3.9×10^{-4}
Butadiene/Acrylonitrile	4.5×10^{-4}
Chlorobutadiene	3.9×10^{-4}
Cyanosilicone	6.0×10^{-4}
Fluorosilicone	7.5×10^{-4}
Polysulfide	4.5×10^{-4}
Urethane	6.0×10^{-4}
Acrylate	6.6×10^{-4}
Cis 1-4 poly butadiene	5.1×10^{-4}
Cis 1-4 poly butadiene, 10 pts. plasticizer, Lithafrax 50 pts.	4.5×10^{-4}
Aluminum Metal Alclad 17ST	$.66 \times 10^{-4}$

*Crosslinked (60-80 Shore A)

The maximum thermal expansion allowed by a proposed Navy specification on channel sealants was set at $9.5 \times 10^{-4}/°C$. A better perspective can be gained if one considers the percent volume change. Figure 1 shows graphically the volume change of a sealant with $9.5 \times 10^{-4}/°C$ expansion coefficient. The change for a temperature span of -54°C to +177°C amounts to a change in volume of 22%. Considering only room temperature to +177°C, the expansion amounts to 15%. Most channel sealed aircraft have no provision for the dissipation of the forces developed by this expanding sealant. Elastomeric polymers are compressible to about 6%. However, the pressures required are in the range of 10,000 psi. A converse way of viewing compressibility is the pressure developed by an expanding sealant. Figure 2 shows the force developed[5] by a fluorosilicone Mil-S-3116 O-ring (1.5" ID 0.210" cross section) as it was contacted with type III test fuel and heated to 85°C (160°F). The O-ring was confined in a groove with only 5% space to expand. The force developed upon heating increased sharply to about 6,500 pounds. The decay after 300 hours can be explained as extrusion of the elastomer through the narrow gap in the apparatus. The point of interest is the magnitude of the force developed by the approximately 4.7 lineal inches of elastomer confined in a groove.

Figure 3 shows the way voids are formed in the channel by thermal expansion and contraction. The experimental fluorosilicone, lightly crosslinkable, channel sealant was cycled from room temperature

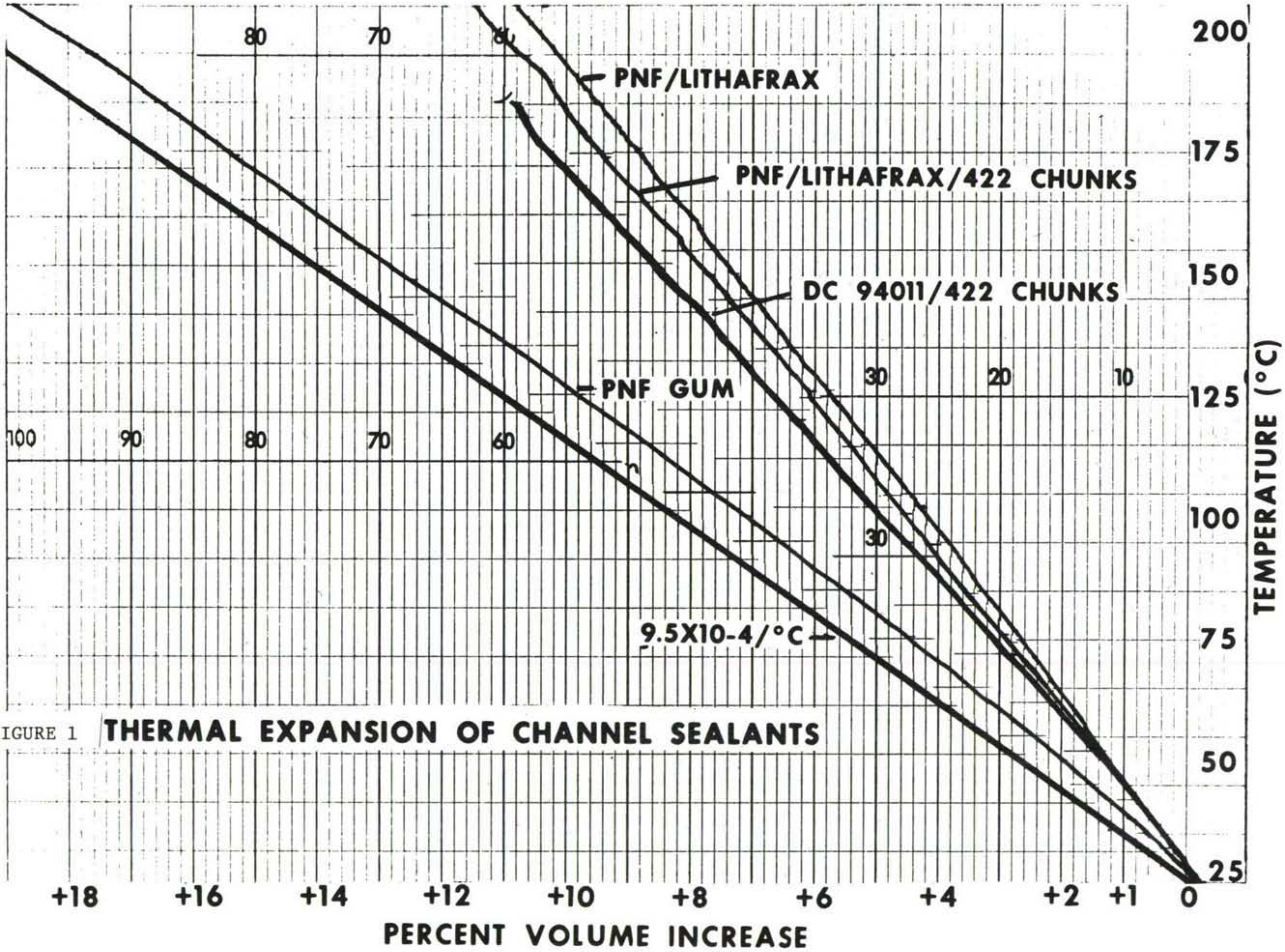
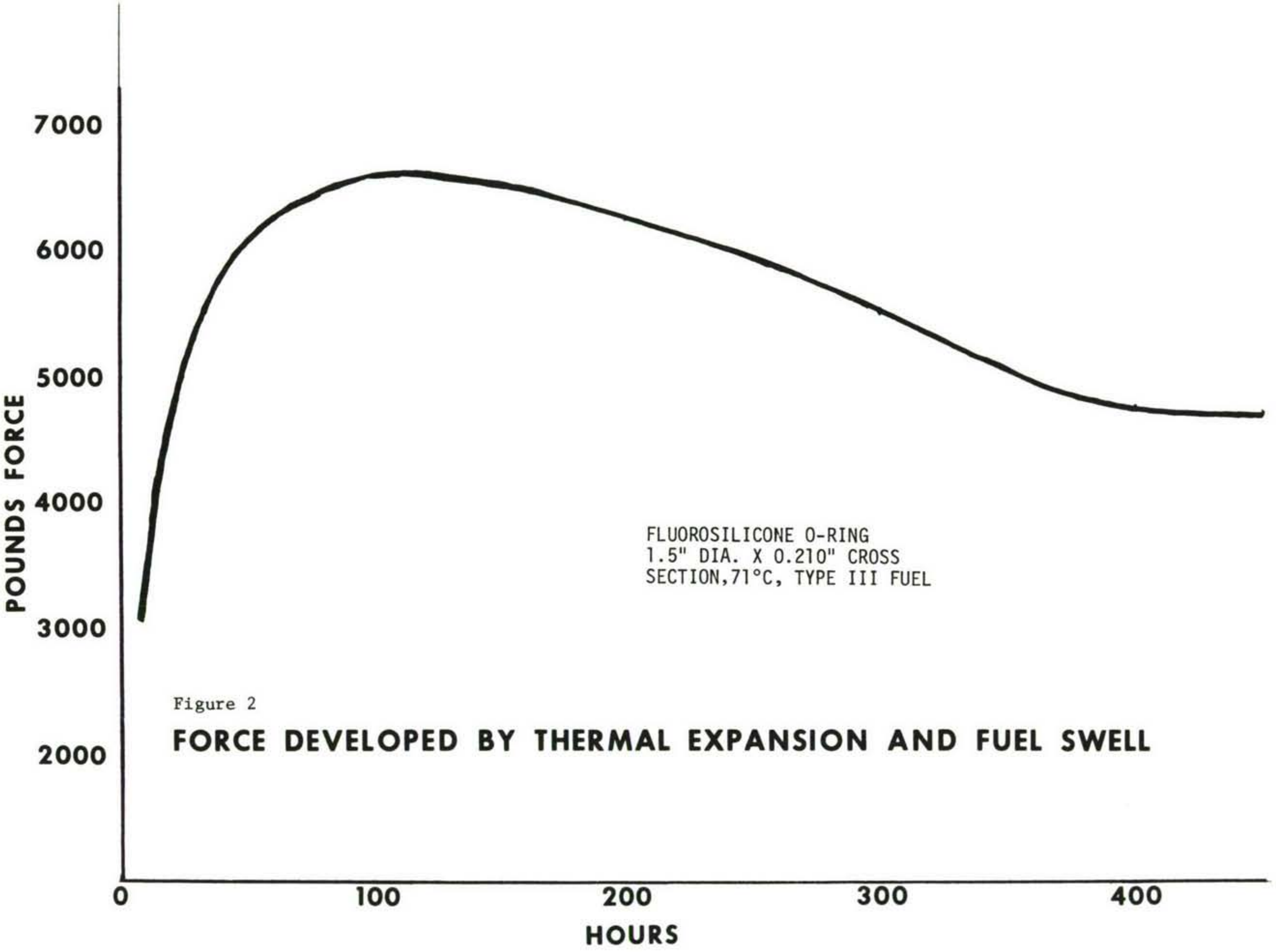


FIGURE 1 THERMAL EXPANSION OF CHANNEL SEALANTS



FLUOROSILICONE O-RING
1.5" DIA. X 0.210" CROSS
SECTION,71°C, TYPE III FUEL

Figure 2

FORCE DEVELOPED BY THERMAL EXPANSION AND FUEL SWELL

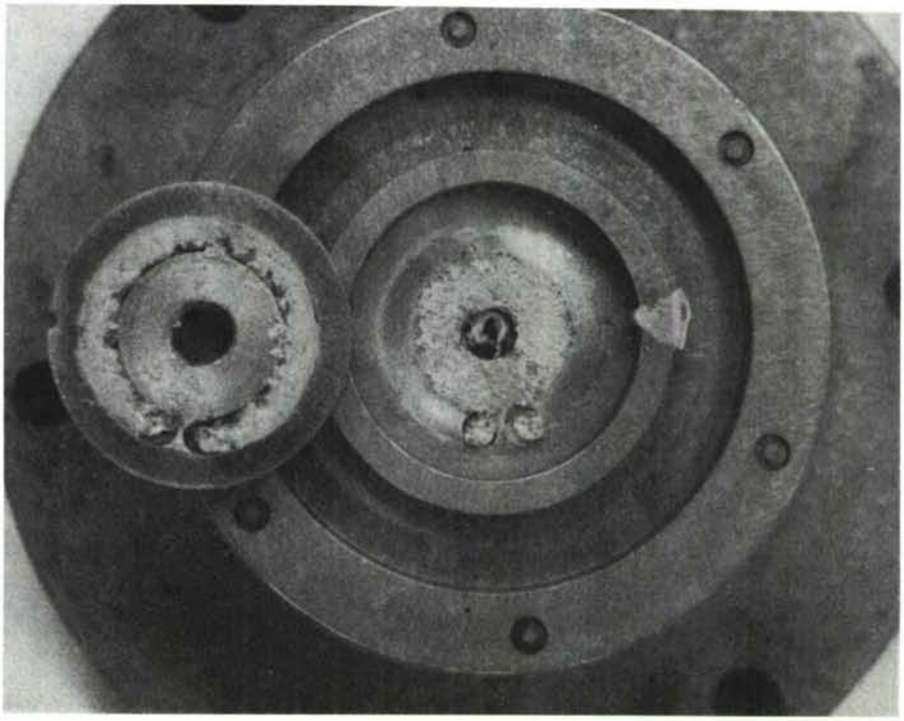


Figure 3 THERMAL EXPANSION/CONTRACTION FAILURE MECHANISM, SEALANT FORMULATION #11

to 160°C (320°F). After 11 cycles, failure occurred because each expansion forced sealant across the faying surface to the fuel area. Finally, insufficient sealant remained in the channel to provide a fuel barrier. Fuel from the center of the apparatus seeped across the sealant groove to the leak collection channel surrounding the circular sealant groove.

A simple way to measure volumetric expansion is to place a known volume of sealant in a cavity which is closed except for a small opening where the sealant can expand out, but not return when cooled. The volume (weight divided by density) extruded divided by the original volume and the temperature range gives the cubical expansion coefficient of the sealant.

An apparatus has been designed by the author at the Air Force Materials Laboratory where the volumetric expansion of mastics can be charted over the elastomeric range. Figure 1 is a recording of volume versus temperature for the commercial fluorosilicone channel sealant (DC 94011) containing 20 parts of vulcanized fluorosilicone particles. The allowed 9.5×10^{-4}/°C expansion is also shown for reference. In the same figure are curves for fluoroalkoxy phosphazene (PNF) formulations. Of particular note is the change of expansion for pure PNF 200 polymer from a volume increase of 18% over the 25 to 180°C range to an increase of 10% when a low expansion filler was added. This was done with a 100 part loading of lithium aluminum silicate (expansion coefficient of 0.002×10^{-4}/°C). The dilution effect of 50% does not reduce the expansion by 50% but the change is significant.

b. Thermal Degradation

Three aspects of thermal degradation of elastomers are important. There is degradation that causes crosslinking with and without gas formation. There is degradation that causes chain scission. And, finally, there is degradation from polymer to monomeric units (unzipping) or low boiling rearrangement products. None of these aspects are tolerable in a channel sealant. The tendency to crosslink or thermoset will defeat the repair by not allowing new sealant to push out the old. Chain scission reduces the viscosity allowing gap extrusion. The gas evolution from crosslinking or unzipping depletes the amount of sealant in the groove, creates voids, and generally adds to the internal pressure generated by thermal expansion. Fortunately, the temperature range of -54°C to +177°C does not pose a serious thermal problem for most fuel-resistant elastomers. The polysulfides which will thermally crosslink in the range of +120°C to +140°C should be carefully selected and used in fuel tanks that do not exceed +100°C. The cyanosilicone sealants are vulnerable to crosslinking in the +150°C to +160°C range and should be limited to areas where the temperature does not exceed +120°C to +130°C. The cyanosilicones have a hydrolysis problem that also results in crosslinking. The combination creates repairability problems for cyanosilicone sealants. Poly(urethanes) in general are not thermally stable above +177°C, but a properly designed channel sealant is possible. The same can be said of the poly(fluoroalkoxy phosphazenes) (PNF). Other candidate elastomers such as liquid NBR, neoprenes, polyesters, fluorocarbons, epichlorohydrin, chlorinated hydrocarbons, and hybrid fluorocarbon/fluorosilicones must be carefully examined for use over the full temperature range and for other areas of vulnerability.

c. Viscosity Reduction

Viscosity changes are caused by fuel swell, fuel extraction of lower molecular weight polymer, and thermal degradation; but there is an overriding natural phenomena of viscosity reduction with increasing temperature. This vis-temp slope is steep for high polymers because of inter-chain attractions and proximity to the second order transition temperature (Tg). The normal use range of elastomers is in the visco-elastic region between the Tg and +150°C to +200°C. The higher the temperature, the more energetic the polymer chain movements and the more like a liquid is the polymer behavior. As the polymer cools, the viscous contribution increases especially fast in the region 50°C above the Tg. This effect[6] is illustrated in Figure 4. The vis-temp slope of dimethyl silicone with a Tg of -120°C is much flatter in the +100°C to +180°C range than the FCS 210 hybrid series with a Tg range of -28°C to -40°C. The increase in viscosity is smooth, predictable, and relatively insensitive to changes of polymer structure within a series. It is also apparent that the viscosity selected by injectability requirements (room temperature) may be very temperature sensitive and be too stiff for field repairs. In addition to the lowering of viscosity by fuel swell and thermal degradation, the normal temperature effect will be aggravated by pressure build up from swelling, thermal expansion, etc. to make gap extrusion the apparent failure mode.

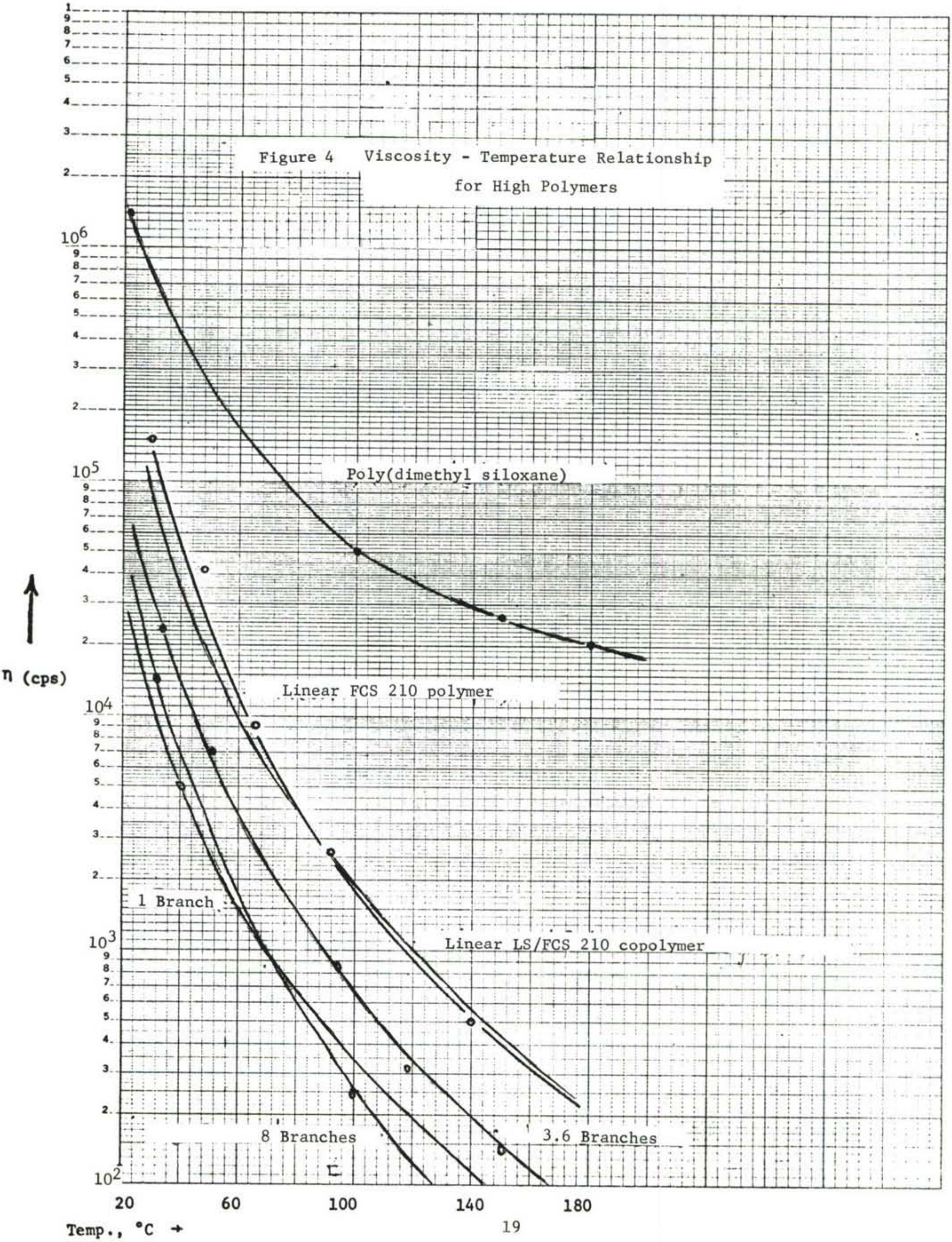


Figure 4 Viscosity - Temperature Relationship for High Polymers

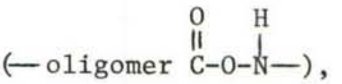
2. Chemical

a. Hydrolysis

Hydrolysis attack on polymer structures can cause chain scission as well as form new chemical structures that destroy the useful properties. The most common examples of chain scission are polyesters and polyester based urethanes.[7] Generally, the result of hydrolysis is a lower viscosity product. If the hydrolysis products tend to be solids and possibly crystalline, the sealant could harden and resist reinjection. Reinjection also becomes difficult with the cyanosilicones and acrylates where the backbone chain remains and the hydrolysis occurs on the side chains. This feature has caused some deception in the performance of cyanosilicone as a channel sealant.[8] In this case, hydrolysis causes continuous swelling because the nitrile functionality is lost as the hydrolysis progresses. The tendency to crosslink prevents loss of sealant. This sounds good as long as the sealant can be replaced before complete hardening takes place.

Water in many forms is available to hydrolyze a vulnerable sealant. The largest sources are the fuel and moisture that condense from the air drawn in to replace the fuel as it is consumed. The average JP fuels absorb 70 parts per million water at room temperature and the amount increases with aromatic content of the fuel and temperature. Cooling causes the absorbed water to precipitate. Anti-icing additives are added to prevent this liquid water from freezing at low temperatures. This gives a water ethylene glycol monomethyl ether environment for the tank bottoms. Moisture is able to penetrate the faying surfaces as gas (vapor). Moisture arriving from this source is just as damaging as that of the tank bottoms. Water absorbed into the sealant from any source becomes a reactant at the elevated temperatures and any sealant sensitive to hydrolysis will be destroyed in a short time.

The polyester based sealant that was used for sealing most F-111 aircraft also contains imide structures that are prone to hydrolysis. Even though the reason for early failure of this sealant in some of the aircraft has been traced to improper storage of the sealant, the system was vulnerable and hydrolysis to a flowing liquid was to be expected in time. Aircraft are usually kept in service longer than anticipated. A fuel tank sealant must be very resistant to hydrolysis in order to stretch the period between sealing and resealing.

Polyesters, specific urethanes  $(\text{—oligomer }\overset{\overset{O}{\|}}{C}\text{-O-}\overset{\overset{H}{|}}{N}\text{—})$, polyamides, epoxy-amine systems, fluorocarbon triazines, cyanoethy(methyl) siloxane, and acrylates should be avoided in fuel tank sealant development. A very good means of evaluating the hydrolytic stability of aircraft materials has been established. The controlled humidity and heat of environmental chambers operating at 95% relative humidity and 93°C

(200°F) provide approximately 500 times the rate of tropical climate hydrolysis. The survival of a sealant after 28 days shows hydrolytic stability beyond the anticipated life of the aircraft. The measurements to indicate damage are viscosity change of channel sealant or simple hardness measurements on vulcanized products that contain the same polymer structure.

Water also contributes to the reversion of fluorosilicone in that it makes metallic ions available to initiate the closed system reversion discussed below.

b. Oxidation

Air contacts channel sealants only at the faying surface joints. The hot air from outside the aircraft could cause the sealant in faying surfaces to become brittle and may allow fuel to escape more easily. In general, however, oxidation is not a cause of channel sealant failure. Most fuel resistant materials are also good in hot air environments and the presence of oxidizable fuel vapors helps reduce the severity of the environment. The considerations of thermal stability and chemical resistance screen out those that are very vulnerable to oxidation.

c. Closed System Reversion

This particular type of reversion was mentioned in the discussion on hydrolysis. The most documented example is the poly 3,3,3-trifluoropropyl(methyl)siloxane. Ionic species available in parts per million from the polymer/sealant manufacturing process or from the aircraft metals cause a catalytic rearrangement of the siloxane backbone to a preferred lower energy cyclic such as the cyclic tetramer. The reduction of sealant viscosity interacts with the thermal expansion, fuel swell, and fuel extraction effects to cause a slow but progressive failure of the sealed tank. Normal exposure to humid environments such as the screening test for hydrolytic stability will not evaluate the resistance to this kind of reversion. A good property to measure for reversion is the modulus of a vulcanized product of the same polymer structure (tensile strength and hardness decrease while elongation increases). A gram or two can be wrapped in aluminum foil, to help hold in the degradation products, and heated in a small half pint paint can. A blank of known reverting material is a good check on the sealed condition of the can. Since the degradation is of the polymer chain, solvent extraction of the sealant followed by analysis of the solution by GPC (gel permeation chromatography) may give a more accurate measure of the extent of reversion. A simple weight loss of the sealant upon heating in an oven will also indicate if volatile oligomers have been formed during the closed system heating. Polymers that are prone to form cyclics include the fluorosilicones, fluoroalkoxy phosphazenes, polyethers, polyesters, and certain polyurethanes.

d. Crosslinking

This form of chemical degradation was mentioned under thermal stability and hydrolysis. An additional factor to consider is the chemical environment posed by the near constant supply of reactive trace ingredients that can provide considerable attack on a vulnerable sealant. Among the 300 plus differing components of JP-4 are sulfides, pyridines, unsaturated hydrocarbons, and a host of other chemicals picked up from the storage and transport of fuel. The best test method is liquid fuel exposure at elevated temperatures with frequent change of fuel - possible continuous flow.

3. Physical

a. Swell

All elastomers absorb fuel to varying degrees. Absorbed fuel takes space occupied by polymer chains and the combined volume must increase. The extent of the increase depends upon how strongly the polymer molecules attract fuel and how constrained the elastomer is by network crosslinks or by the container. Refer back to Figure 2 where the combination of heat and pressure caused high forces to exist on a confined O-ring. Since a channel sealant is a noncrosslinked mastic, the tendency to build pressure from thermal expansion and fuel swell is related to the tightness of the container. Figure 5 shows fluorosilicone channel sealant that has expanded and forced itself through the faying surface and fluorosilicone fillet of an F-111A saddle tank.

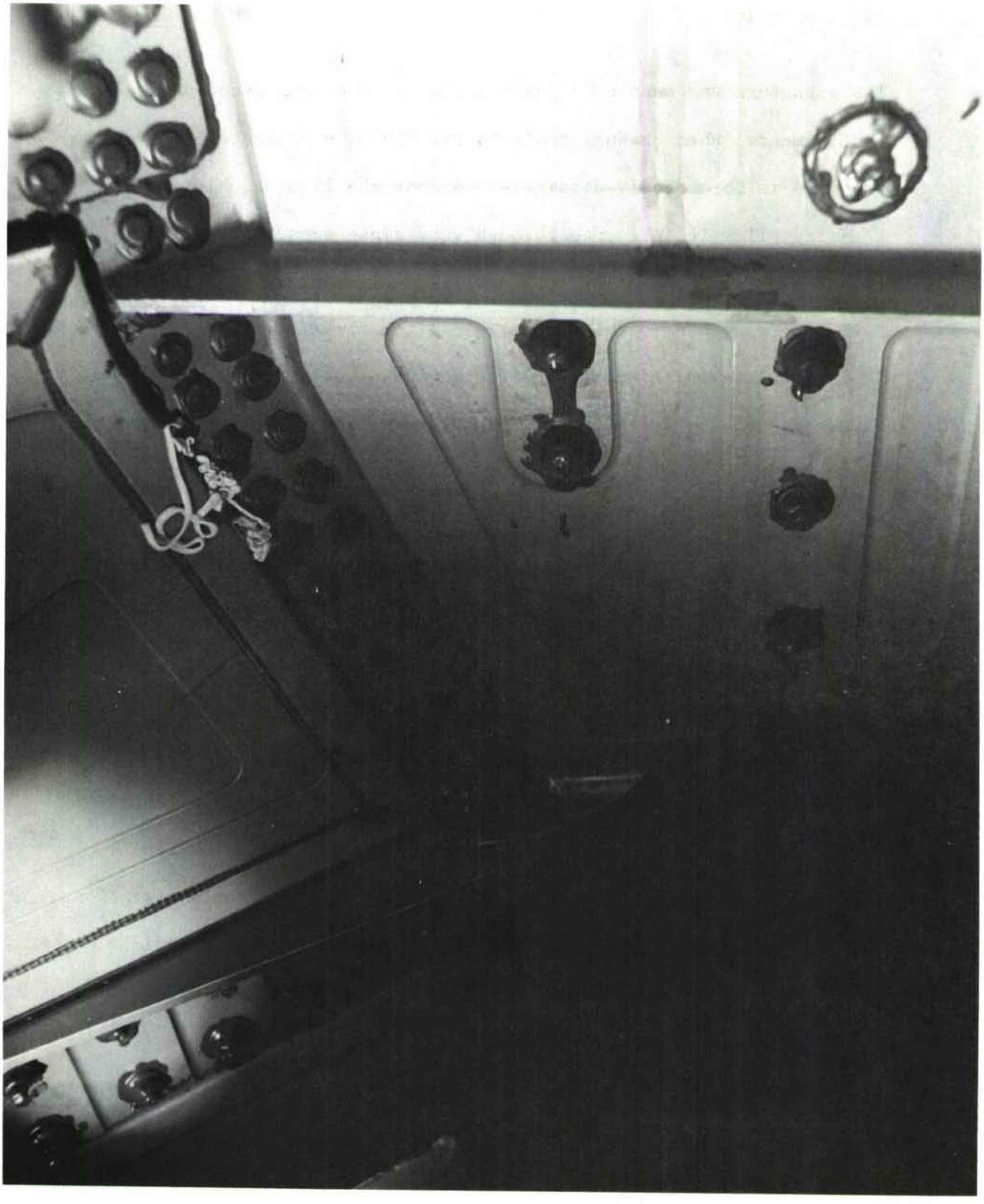


Figure 5 Gap Extrusion in an F-111 Saddle Tank

The structure was unable to prevent the sealant from escaping its confinement. When channel sealants are the only sealants used, the pressure is more easily dissipated because the liquid qualities of a mastic allow it to escape through very close gaps. A possible case to indicate the relatively low residual pressure existing within a channel was observed when some F-15 aircraft were refueled with JP-8 as a less volatile replacement for JP-4 fuel. Wings sealed with fluorosilicone began to leak. A laboratory measurement of the differences in swell of the sealant showed the JP-4 to have 2% greater swell.[9] The 2% reduction in fuel swell with JP-8 appears to have contributed to the failure by causing negative pressure in the channel.

b. Fuel Extraction

When elastomers swell in fuel, it is an indication of solubility. A lower molecular weight polymer in channel sealants is more easily dissolved, especially by hot fuel. In addition, the swelled mastic has a lower viscosity allowing polymer chain migration and fuel extraction to occur more easily. Thermal or hydrolytic degradation that causes chain scission provides additional fuel soluble products. Most fuel resistant polymers that are free from low molecular weight products are not extracted by fuel. The problems that have occurred can be traced to reversion or hydrolysis. A good screening method is the exposure of a weighed bead of sealant on a panel to fuel at temperature. The difference between the original weight and the weight remaining after driving off the fuel by heating is a measure of the amount extracted. The more fuel resistant the polymer the less extraction will take place. Other extractable agents in the formulation must also be eliminated such as plasticizers, antioxidants, inhibitors, etc. The sealant in the channel is protected from the direct contact with the fuel. However, the sealant in the gap is exposed to the fuel and extraction will proceed if the sealant is vulnerable.

c. Vibration

Elastomeric polymers are good dampers for vibration, especially in the 30-50°C temperature range just above the glassy region.[10 & 11] When sound or vibration is absorbed, or attenuated, heat is developed in the polymer. This slight temperature rise is controlled by thermal conduction to the aircraft structure. A portion of the temperature effects of expansion and viscosity change can result from the vibration. Another feature which has not received sufficient study is the effect of vibration on the thixotropic (shear thinning) nature of most channel sealants. This desirable rheological feature of low viscosity during injection (high shear rate) and lack of flow when the injection is complete (negligible shear rate) may be nullified during flight by vibrational energy. Viscosity measurements of channel sealants, while simultaneously being heated and vibrated at 30 to 10,000 cycles and 160 dB, need to be obtained.

d. Shear

Bending and twisting movements during flight are of lower frequency than normally associated with sound vibrations. Joint openings in the range of .003" to .005" cause shear stress on the mastic which can result in chain scission and lowering of viscosity. More likely the shear causes a pumping, pushing action that aggravates adhesion and "works" the sealant through the faying surfaces. Some polymers such as urethanes and polysulfides are prone toward chain scission under stress. Measurements on a dynamic test apparatus should include shear as an important part of the environment.

e. Adhesion/Cohesion

Adhesion is molecular attraction between surfaces of materials in contact. For channel sealants, the attraction is between the metal of the grooved structure (including the possibility of corrosion protection coatings) and the elastomeric sealant. Adhesion of the sealant to the groove prevents fuel from migrating by capillary action. If the fuel wets the surface, displacing the sealant, the fuel quickly seeps across the joint. Note the rapid failure of sealants numbers 15, 16, and 17 of Table III in the Appendix. The smooth surface of the sealant shown in Figure 6 indicates the nonsticking qualities of the formulations. The silica filler of these formulations was treated with a hybrid silicone monomer to enhance fuel resistance and provide compatibility with the hybrid silicone polymer. Apparently this treatment also reduced the adhesion to an unacceptable level. Further

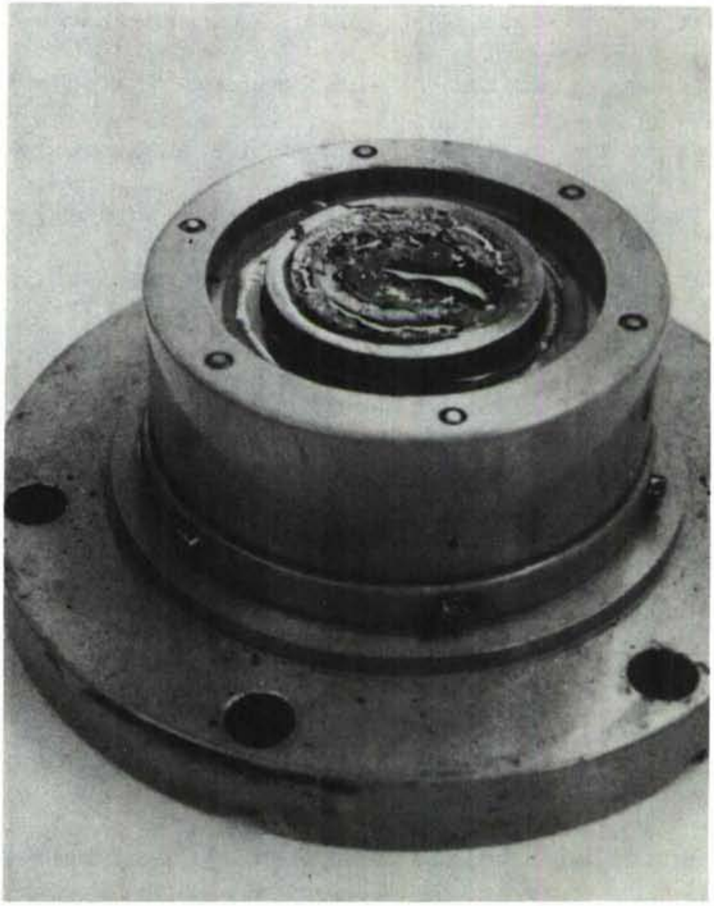


Figure 6 Adhesion to Metal Failure Mechanism, Formulation #16

analysis is necessary to establish the actual cause of adhesive failure because the polymer was of significantly increased molecular weight (259,000 weight average) and was end blocked with trimethyl silyl groups.

Most uncrosslinked viscous elastomers adhere to metals and coatings; some more than others. Laboratory evaluations of peel adhesion for channel sealant is a good screening method. Another is the examination of static and dynamic test specimens that have been cycled in thermal-chemical-physical modes. The thin molecular layer that adheres to the surface of the groove must not be displaced by fuel and, in turn, the sealant must be able to displace fuel and other contaminants when reinjected to repair a leak.

Cohesion is achieved when the molecular structure of the sealant unifies into one mass. The relatively low molecular weight elastomeric base of mastics has the sticky quality that provides good cohesion. It is a molecular mixing phenomenon that knits the product into one mass. This quality is important for providing a uniform-flawless barrier to the fuel. In addition, cracks or breaks that occur in the sealant from shrinkage (cold exposure) or unusual flexing of the structure must reseal to a flawless fuel barrier.

f. System Pressure

Integral fuel tanks are pressurized during flight with 2 to 5 psig air to insure positive delivery in sumps. The weight of fuel can contribute significantly to the system pressure. The main F-111 fuselage tank is about 5 feet high. Full of fuel, the pressure on the bottom amounts to an additional 2 psi. Aircraft maneuvers at 6g's amount to about 12 psi. Systems are often pressurized at 20 psi before takeoff to check for leaks. This gentle but constant pressure, pushing the sealant to the outside of the aircraft, must be countered with more than the viscous resistance of a mastic. Uncrosslinked polymers are fluids by definition, i.e., a free molecule above its melt temperature. Therefore, a gentle pressure will eventually move the mastic. This unrestricted flow through structural gaps allows thermal expansion and fuel swell to push and pull the channel sealant. It is surprising that channel sealants can seal an aircraft for even a few missions. McDonnell-Douglas Corporation patented the addition of spherical beads to channel sealants to prevent gap extrusion by causing a log jam effect at the gaps. The diameter of these spheres are from 400 to 18 mesh (0.0015" to 0.0394"). While these cause a slowing of the escape of mastic under pressure, the spherical beads do not distort to seal the gap. When continuous pressure was applied during the heating and cooling cycles, more rapid and consistent failure times were observed. The significance of this pressure can be seen in the case of formulation number 13 where the polymer component of the sealant was swollen and pushed from the filler portion causing sudden fuel release to the leak side.

SECTION IV

APPLICATION OF ENGINEERING PRINCIPLES

Correlation of base polymer, formulation, and fuel tank environment with specific channel sealant failure mechanisms has yielded engineering principles for channel sealant development. The principles involved can be discussed in three areas: (1) polymer selection, (2) sealant formulation, and (3) compensation for inherent limitations.

1. Base Polymer Selection

The thermal environment of -54°C to +177°C eliminates many elastomeric polymers before other considerations further reduce the candidates. Rubber-like flexibility at -54°C is a goal that is not often met with synthetic elastomers. Often, when other requirements are met by a specific polymer, the low temperature flexibility is accepted if the intended application does not normally experience -54°C or if the temporary brittle condition can be tolerated. High temperature oxidation or chemical activity cause many fuel resistant elastomers to crosslink (harden), chain scission (soften), or eliminate gasses (sponge).

Base polymers considered for -54°C to +177°C include the following:

a. Urethanes - carefully selected

b. Fluorosilicones

c. FASIL

d. PNF 200 (modified)

e. Fluorocarbon-fluorosilicone hybrids

The polysulfides and cyanosilicones tend to crosslink at temperatures below +177°C and would not be repairable by reinjection.

At +232°C the candidates are further reduced to a few experimental polymers. Suitable polymers for the -54°C to +232°C range may include variations of the following:

a. Improved FASIL

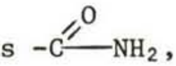
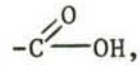
b. Fluoroethers

c. Fluoroether triazines

Thermal stability screening of candidate base polymers is easily done by isothermal weight loss techniques and measuring changes in viscosity. Since few elastomeric polymers remain unchanged over long term aging, polymers that slowly revert (undergo chain scission) at the maximum use temperature will assure repairability; especially if accidently overheated. Certain polyurethanes, fluorosilicones, and PNF elastomers have this desirable feature. Antioxidants and crosslink inhibitors can be added to formulations to control, or delay, the crosslinking that normally would lead to a nonrepairable condition. Careful consideration of fuel extraction and active life of the agent will add to the reliability of such systems.

A channel sealant polymer must have inherent thermo-chemical stability since little can be added to the formulations for permanent protection of the polymer. Candidate base polymers that pass the thermal and chemical screening must be selected, or modified, to have suitable visco-elastic properties for injection, adhesion/cohesion, reinjection, etc. The chemical environment of the fuel tanks is not severe, but the renewed source of active agents from refueling imposes the need for a high level of chemical resistance. A test, at the high temperature anticipated, with continuous fuel flow would allow a check on the vulnerability of candidate base polymers. Separate tests conducted for hydrolytic and confined heat reversion would screen out the remainder of the unsuitable base polymers.

Water is everywhere in the fuel tank system. Complete resistance to chemical attack by water is very important. Most elastomeric polymers that are vulnerable to hydrolysis degrade to lower molecular weight products and fail by flowing from the channel or fuel extraction; a few become chalky and give problems on reinjection for repairs. Neither crosslinking or chain scission can be tolerated. The polysulfides, fluorocarbons, fluoroalkoxy phosphazenes, polyether-urea type urethanes, acrylonitrile/butadiene, chlorinated hydrocarbons, and hybrid fluorosilicones are among the fuel resistant polymers that are very resistant to hydrolysis. Closed system reversion is associated with fluorosilicone sealants but care must be exercised with all polymers. The initiators of such reversion appear to be water and ionic species such as metal ions, amine salts, etc. The rate of chain scission, as determined by confined heat tests, is slow and predictable. In some respects, this can become a desirable feature that will insure repairability. For example, the length of time for significant effects of reversion can be controlled in the FASIL and hybrid versions of the fluorosilicones. An acceptable service life may be achievable. Candidate polymers for a channel sealant should pass +200°C (+402°F) confined heating for seven days with essentially no change in viscosity. This is an accelerated test and could be complicated by marginal thermal stability of some polymers. As the temperature is reduced, the time to revert will be longer. A rather unique method of extending the life of the fluorosilicone based channel sealant is the addition of a carefully controlled number of crosslinking sites which would be activated by a temperature sensitive peroxide. The lightly crosslinked product would have a very long reversion time and yet would become reinjectable for repair.

The properties of cohesion and adhesion are characteristic of the polymer morphology and chemistry. The tacky type of cohesion and adhesion are derived from broad molecular weight distribution and branching in the polymer. Low molecular weight polymers which have this tackiness are often added to the dry, higher molecular weight product to provide the desired level of viscosity with tackiness. Adhesion to metal surfaces in the presence of fuel is important and can be achieved by polymer terminations such as  $-\overset{O}{\overset{\|}{C}}-NH_2$,  $-\overset{O}{\overset{\|}{C}}-OH$, $-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{OH}$, or chelatable ligands. Cohesion is natural in most elastomeric polymers. Others can be made to have this property by grafting of monomers and the addition of mutually dissolved polymer chains. The problem of fuel extraction of lower molecular weight polymers should not be overlooked. A gel permeation chromatograph (GPC) of the polymer can be used to show the molecular weight distribution of the polymer used for a channel sealant base. Polymers of a broad molecular weight distribution are more likely to have the best balance of viscosity and cohesion for channel sealant formulations. The quantitative values for adhesion and cohesion are difficult to specify. It is important that separated panels exhibit 100% cohesive failure after fuel soak. Conceivably the cohesive strength could be high enough to cause adhesive failure. Whether the adhesion should be increased or cohesion decreased to cause the desired failure mode depends upon other properties such as viscosity level, reinjection rate, the thermal effects upon cohesion and adhesion, etc.

Channel sealant base polymers must be very resistant to the swelling action of fuel. Swelling above about 5% causes serious changes in viscosity, builds up pressure within the channels, and very often creates voids in the polymer due to high fuel pick up at elevated temperatures that will not stay absorbed in the sealant at lower temperatures. High fuel swell will cause a loss of many of the desirable properties that were carefully balanced in the mastic before injection. Highly fluorinated polymers are required for sealants of this low level of fuel swell.

Elastomeric polymers have a high rate of viscosity change with temperature changes, especially near the second-order transition temperature (Tg). There is some evidence that a highly branched polymer with gel-like characteristics will have less change with temperature than linear polymers at the same molecular weight. Star shaped-radial polymers are possible candidates for lower viscosity change. Considerable more research is needed on the viscosity-polymer structure area to establish the relationship of branching to the vis-temp slope. The effect of temperature change on viscosity can be easily measured by simple apparatus such as the extrusion plastometer of Figure 7 where a 7/8" diameter piston moving at 0.1"/min. forces sealant through a .059" orifice. A more versatile version is made by Instron and others. More complex and versatile yet are the Rheometric Spectrometer and Brabender Plastographs that vary the shear, shear rate, and temperature at programmed rates. The viscosity behavior of the polymers will be modified greatly by formulating, but the general level of viscosity of the pure polymer and the response to temperature changes are important to the proper formulating approach. Another observation suggests that very low Tg polymers in the range of -100°C and below will have a flatter viscosity-temperature curve in the -54°C to +177°C or +232°C range than those with a higher Tg.

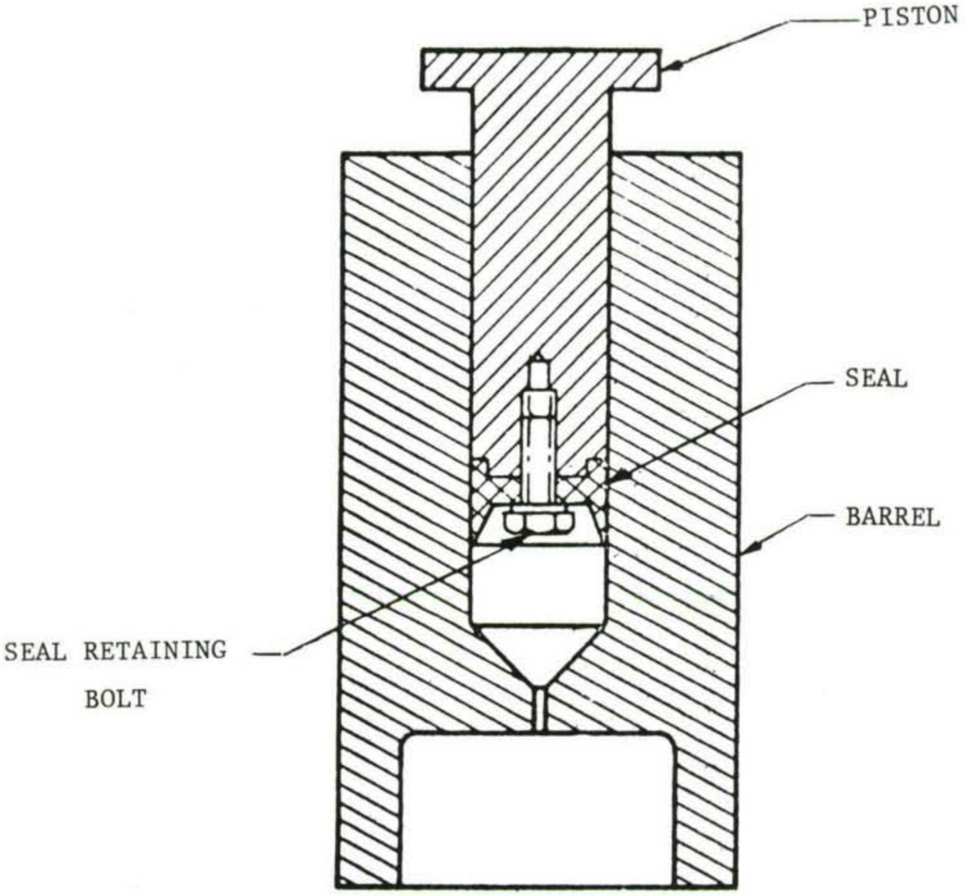


Figure 7 Extrusion Plastometer, Cross Sectional View

2. Formulation of Base Polymer

The most important formulating ingredient, and often the only one added to the polymer, is inert filler. The word inert is not wholly correct since the filler has a modifying effect upon the viscosity. Also, the implication of one filler is not accurate because a combination of inorganic and organic particles and fibers can be used to give the desired bulk viscosity, shear flow characteristics, and gap plugging properties.

Control of the level of viscosity with various fillers is commonplace. The final selection is usually controlled by cost and availability. In the case of channel sealants, viscosity control is desired during high shear injection at temperatures of 0 to +40°C and during operation over the -54°C to +177°C (or +232°C) range. A mixture of electrically conductive carbon black, high surface silica, and diatomateous earth when combined with a base polymer produces a sealant with less change in viscosity with temperature than when a single type of filler is used to obtain the same level of viscosity. A reasonable explanation, that is being supported by evaluations in progress, is as follows. The plate-like electrically conductive carbon black has high affinity for the polymer molecules at low temperatures but weakens as the temperature increases. The high surface silica has high affinity for the polymer molecules at low temperatures and adds the quality of thixotropy (shear thinning) which persists even at elevated temperatures. The large plate-like structure of the diatomateous earth and many irregularities and holes provide traps for flailing polymer molecules at elevated temperatures and appear to retard the change of viscosity at high temperatures. Figure 8 illustrates the control over viscosity change obtainable with proper filler selection.

Another feature of inert fillers is low thermal expansion. High thermal expansion, like high fuel swell, is a source of pressure buildup in the channels. At high temperatures where the force is great and the viscosity somewhat lower, the sealant is extruded through close fitting gaps. At low temperatures, the polymer shrinks causing voids. The life of a channel sealant is related directly to the number and extent of thermal expansion-contraction cycles. Very low (near zero) thermal expansion coefficient fillers such as Lithafrax have excellent potential of reducing the thermal expansion of the formulated sealant to half that of the base polymer.

Other agents added to the base polymer must be carefully selected. Fibrous Teflon or asbestos gives qualities of gap filling and gel-like bulk to the sealant. Antioxidants, tackifiers, and other inhibitors must be very carefully selected to avoid being extracted by fuel.

3. Compensation for Inherent Limitations

Selection of base polymers and innovative formulating techniques will provide improved channel sealants. In addition, the insight into how channel sealants behave will allow tailoring a sealant to a specific

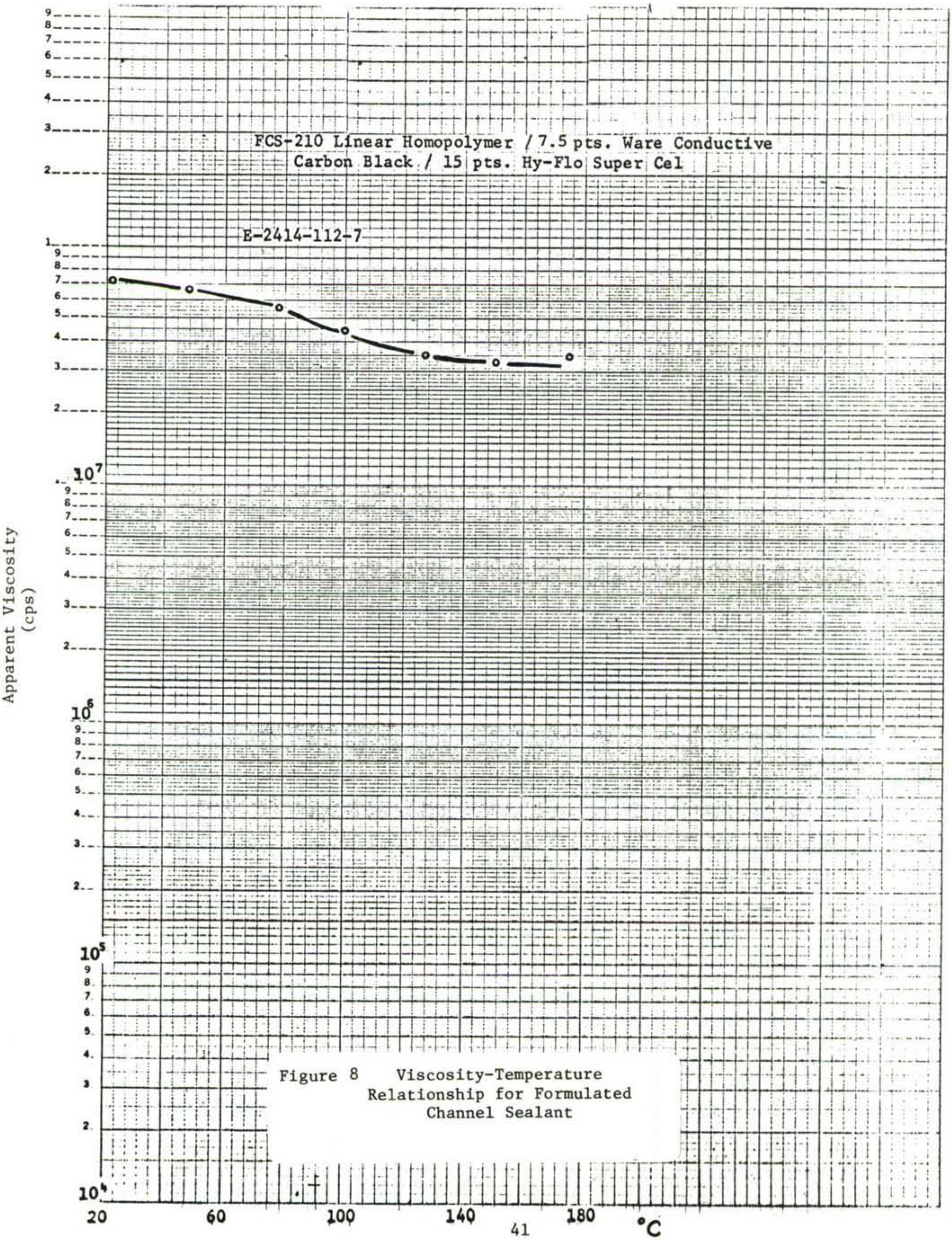


Figure 8 Viscosity-Temperature Relationship for Formulated Channel Sealant

aircraft or to the wings versus the fuselage. Yet, there remain some inherent limitations where the very nature of the noncuring elastomeric sealant precludes the elimination of some failure mechanisms. One of two alternatives can be chosen. The sealant may be used and the inherent limitation allowed to determine the life of the sealant or - a mechanical compensation in the form of devices or aircraft design can be used to regulate the failure mechanism. Three such failure mechanisms appear to be in this category of inherent limitations. They are viscosity change with temperature change, flow characteristics of uncrosslinked polymers, and thermal expansion-contraction.

The change of viscosity of a liquid with temperature changes is an inherent property of uncrosslinked polymers. The injectable requirement of a channel sealant dictates an uncrosslinked, flowable nature of the sealant. As described under the preceding discussion on formulating techniques, the proper choice of filler material can influence the vis-temp slope. Highly branched, gel-like polymers also appear to have less change of viscosity with temperature. The trends of these compensating techniques need to be investigated more thoroughly. Initial results indicate that the vis-temp effect can be compensated to a point where it can be eliminated as a failure mechanism.

The second apparent limitation is also a result of the liquid nature of uncrosslinked polymers. It is the flow of sealant through relatively close structural gaps. The time to flow depends upon viscosity and pressure. The final formulated level of viscosity is directly related to the injection rate which is also related to allowable pressures and shear-flow behavior. The rates of injection are usually a matter of getting the job done in a reasonable length of time. But, consider the distribution of pressures shown in Figure 9. The 8 mil gap in the reinjection test rigs gives the pressure distribution pattern. At the injection port the structure experiences the tip pressure of the gun. At the exit the pressure is essentially zero. This pressure differential is higher with higher viscosity sealants. (It is important to inject the next section of channel from the previous exit port or there will be a section of channel with poorly sealed faying surfaces). The level of injection pressure is limited to that which the aircraft structure can withstand. Usual tip pressures are kept under 3,000 psi for thin skinned aircraft like the F-4 and F-111 but can be as high as 6,000 psi for the F-16 wings. Therefore, a sealant that cannot be used on an F-4 because the viscosity is too high for practical injection times may be very satisfactory for the F-16 wing where a higher pressure can be used. One obvious compensation is to increase the viscosity to the maximum allowable in order to extend the time to flow. Another means to prevent flow through gaps is to incorporate gap pluggers into the sealant. A patent by Robert E. Rosner[12] issued to McDonnell Douglas in 1971 describes the use of styrene-divinyl benzene beads as gap pluggers. The log-jam

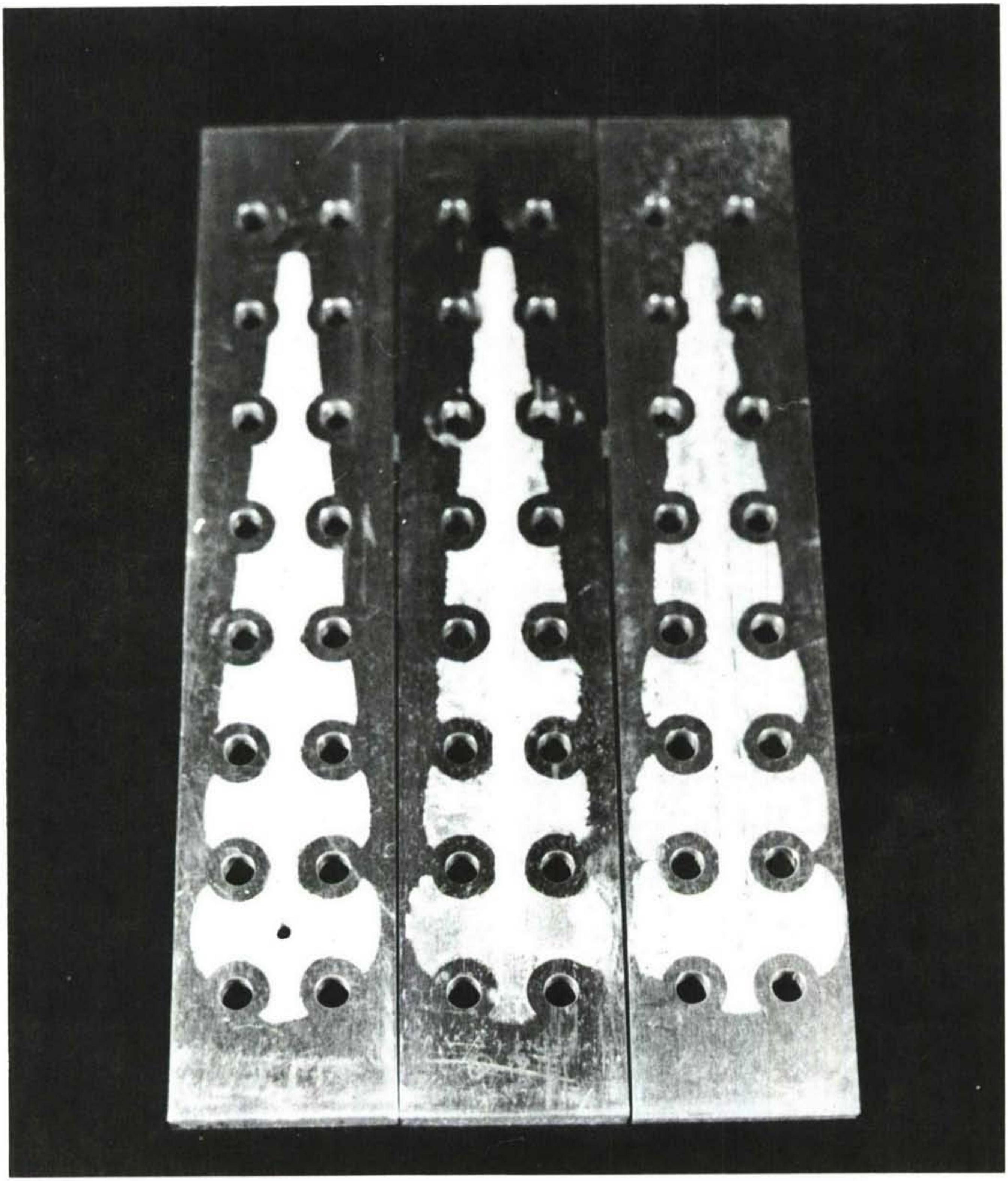


Figure 9 Pressure-Flow Distribution Pattern

effect of the varying sizes of beads greatly increases the resistance to flow at the gap. The long term effects are not as beneficial as the short term effects during injection. The spheres do not distort to seal the crack and the long term effects of pressure cause flow to a point where it becomes the failure mechanisms that cause repairs to be scheduled. Particles that distort under pressure would add sealing to the log-jam effect.

Fluorosilicone particles with sharp angular faces in the 0.012" to 0.040" range were prepared from vulcanized sheets of 88 Shore A durometer. Figure 10 shows an 80X photograph of the particles. Figure 11 shows how the particles seal the faying surfaces. The use of a sealant with particles to seal the 6 to 15 mil gap in the test apparatus described in the appendix is able to extend the sealant life to four times the state-of-the-art. This alone extends the duration of maintenance to an acceptable level. The 25% fuel swell of the fluorosilicone channel sealants still causes considerable pressure to develop, or attempt to develop, within the channel. A sealant with very low fuel swell would have less pressure build up, less viscosity change, and less tendency to extrude through remaining gaps. Addition of 10 to 100 parts by weight on polymer of the fluorosilicone particles has provided gap plugging qualities and the irregular, angular faces of the particles provide a squeegee action that effectively cleans the channel of old sealant during reinjection. The force to extrude 100 part loadings versus 20

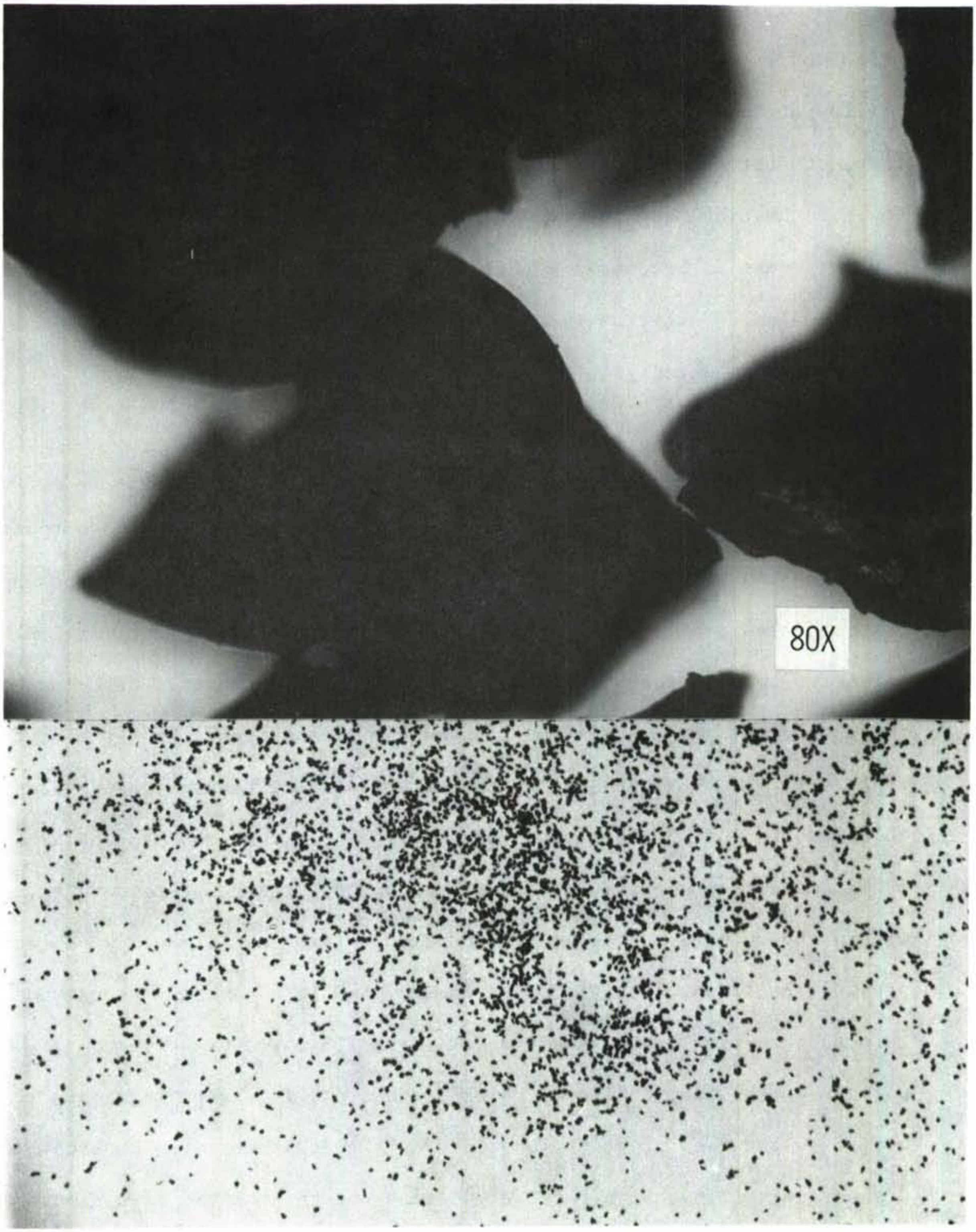


Figure 10 Fluorosilicone Vulcanized Particles

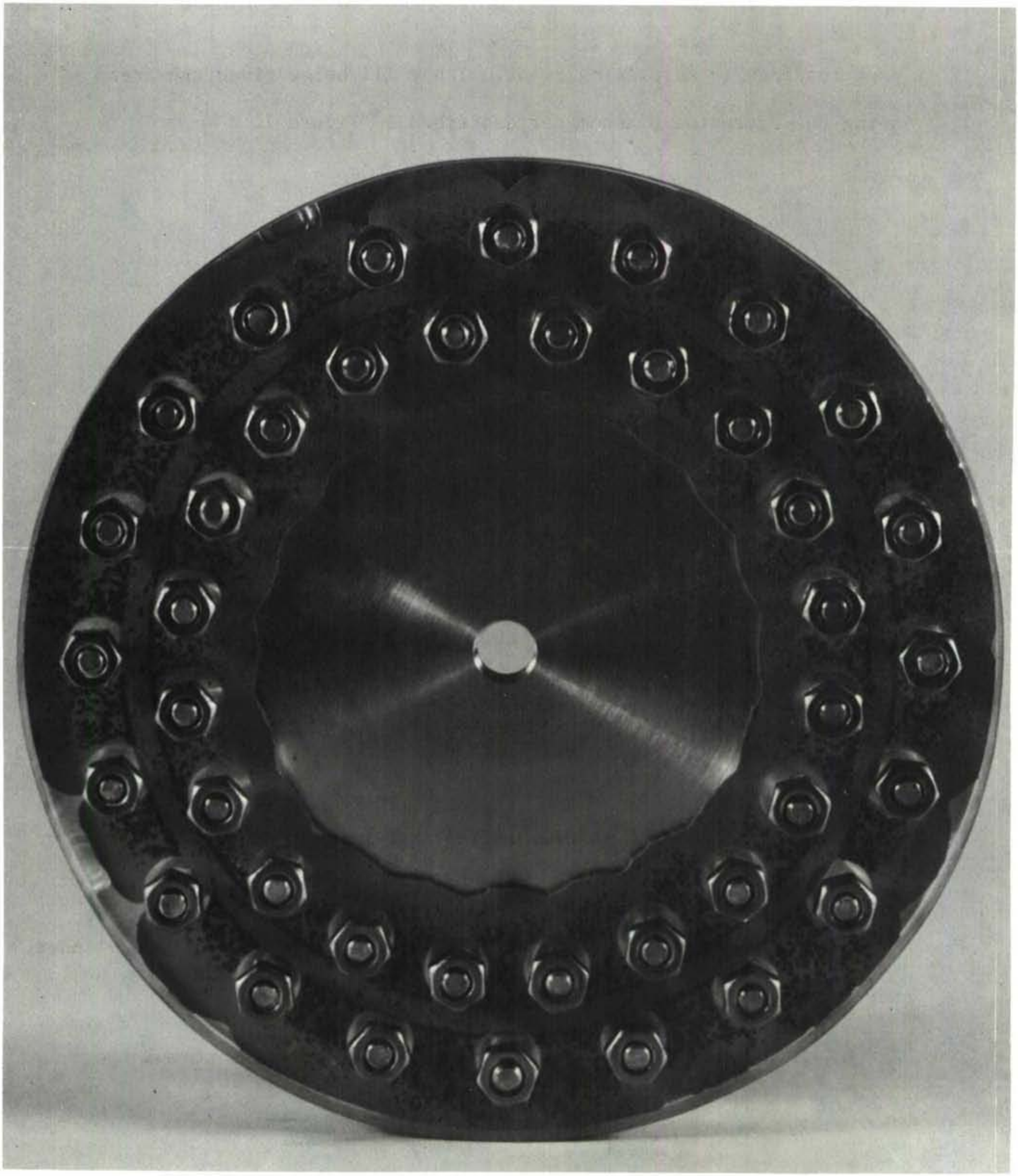


Figure 11 Faying Surface Sealing by Vulcanized Particles

part loadings is surprisingly low. Table III below gives the trend using the extrusion plastometer described in Figure 7.

TABLE III

EXTRUSION FORCE AT 0.1"/MIN. PISTON RATE VERSUS PARTICLE LOADING IN DC 94011

Loadings, parts per 100 of sealant	0	20	40	60	80	100
Force, pounds	273	327	382	460	507	542

The particles should have the following features:

a. Be of the same type base polymer or compatible from an adhesion-chemical perspective.

b. Be in the 0.01" to 0.06" size range with about even distribution of the sizes.

c. Have at least two flat faces for squeegee action (right cylinder, hexahedron, or tetrahedron).

d. Have a concentration of at least 20 parts on the formulated sealant.

e. Have properties optimized for high tensile strength-high modulus with about 100% elongation and high tear strength.

The manner of gap sealing by distortion does not require that a distribution of particle sizes be present. Methods of manufacture of particles that are more uniform size should perform as well as a 0.01" to 0.06" size distribution. An indication of gap sealing potential was observed while gathering the data for Table III. The decay of back pressure was recorded with the crosshead stopped. The lower levels of loading with vulcanized particles allowed rapid decay to friction levels of the piston. Above 40 parts loading the residual back pressure after 30 minutes increased from 20 pounds at 40 parts loading to 50-55 pounds at the 80 and 100 part loadings. The rate of decay was essentially zero after 30 minutes indicating that the particles had log-jammed to seal the .059" hole. The extention of sealant service time is greatly increased with vulcanized elastomer particles as anti-extrusion agents.

The third limitation is thermal expansion-contraction. As discussed under failure mechanisms, polymers expand about 10 times the rate of metals and about 18 times that of inorganic mineral fillers. Fillers are important ingredients for viscosity control and, therefore, can serve two purposes. For example, a fluoroalkoxy phosphazene sealant was prepared from commercial PNF 200 by mill mixing equal parts

Lithafrax* with the polymer and subjecting the mix to +400°F for four hours in an oven. The molecular weight of the polymer was reduced by random scission producing a viscous sealant that could be injected. Vulcanized particles were blended in (20 parts to 100 of mix) and the sealant tester sealed for +177°C (+350°F) to -54°C (-65°F) cycling. The sealant passed the 20 cycle endurance test and was opened for inspection. Figure 12 shows some effects of thermal expansion-contraction on the sealant but it was still capable of sealing many more cycles. The reduction of the thermal expansion rate of PNF 200 by the addition of the Lithafrax was shown in Figure 1 during the discussion on failure mechanisms.

Thermal expansion is an inherent property of all elastomers and only a partial reduction can be made in the volume increase by filler selection. Other means to compensate for thermal expansion must be used. Aircraft could be constructed with spring loaded reservoirs of sealant. In this way the expansion would force sealant back to the reservoirs and when contraction takes place the channel would again receive the sealant rather than form voids or draw in fuel. Such a reservoir system would be a costly retrofit on present aircraft. However, Figure 13 shows a concept where each injection port would become a pressure active reservoir. The metal bellows open to the atmosphere on the inside would exert a spring force upon the sealant

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*Trade name for Lithium Aluminum Silicate by Carborundum Co.

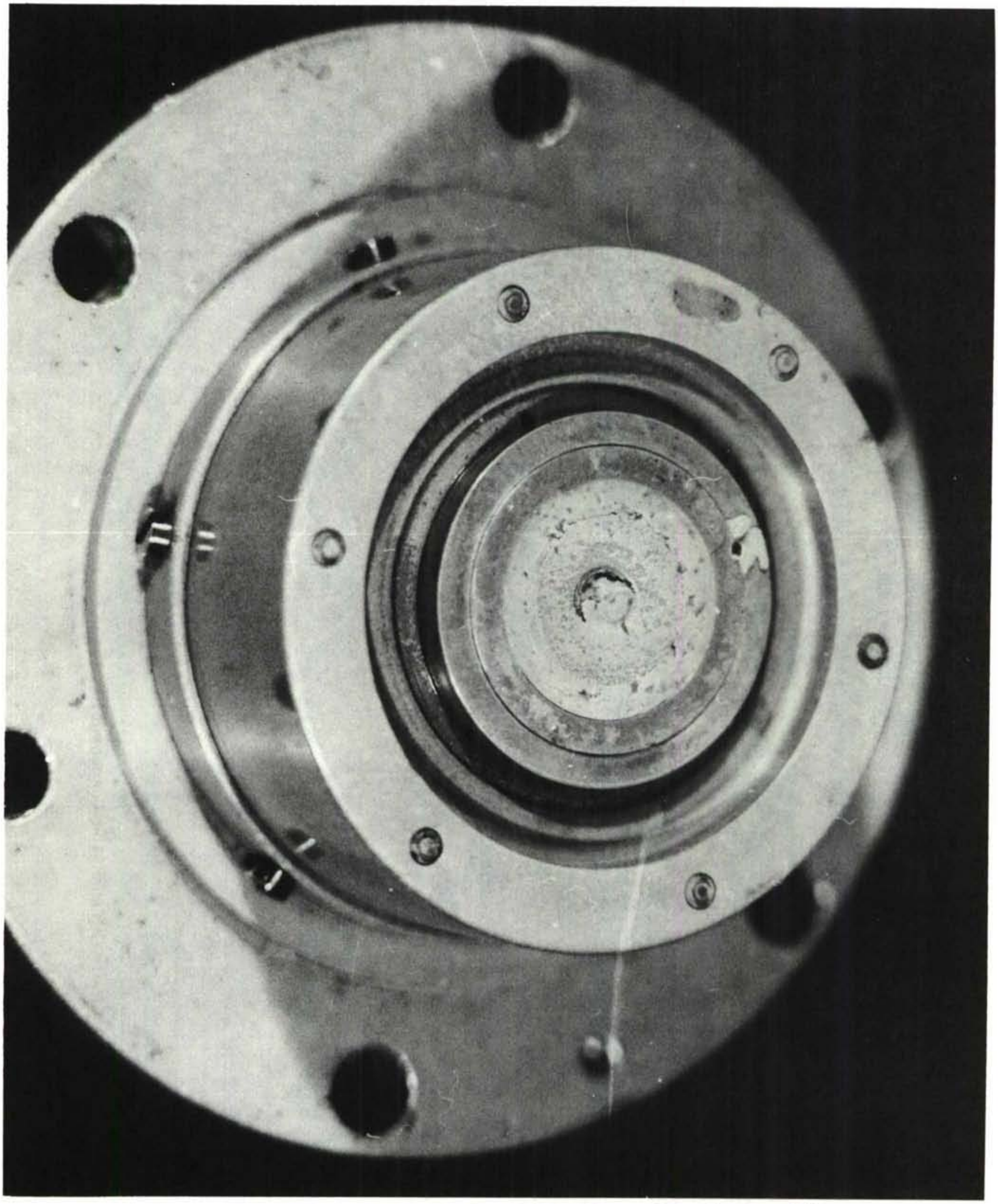


Figure 12 Unfailed PNF 200 Channel Sealant, Formulation #26

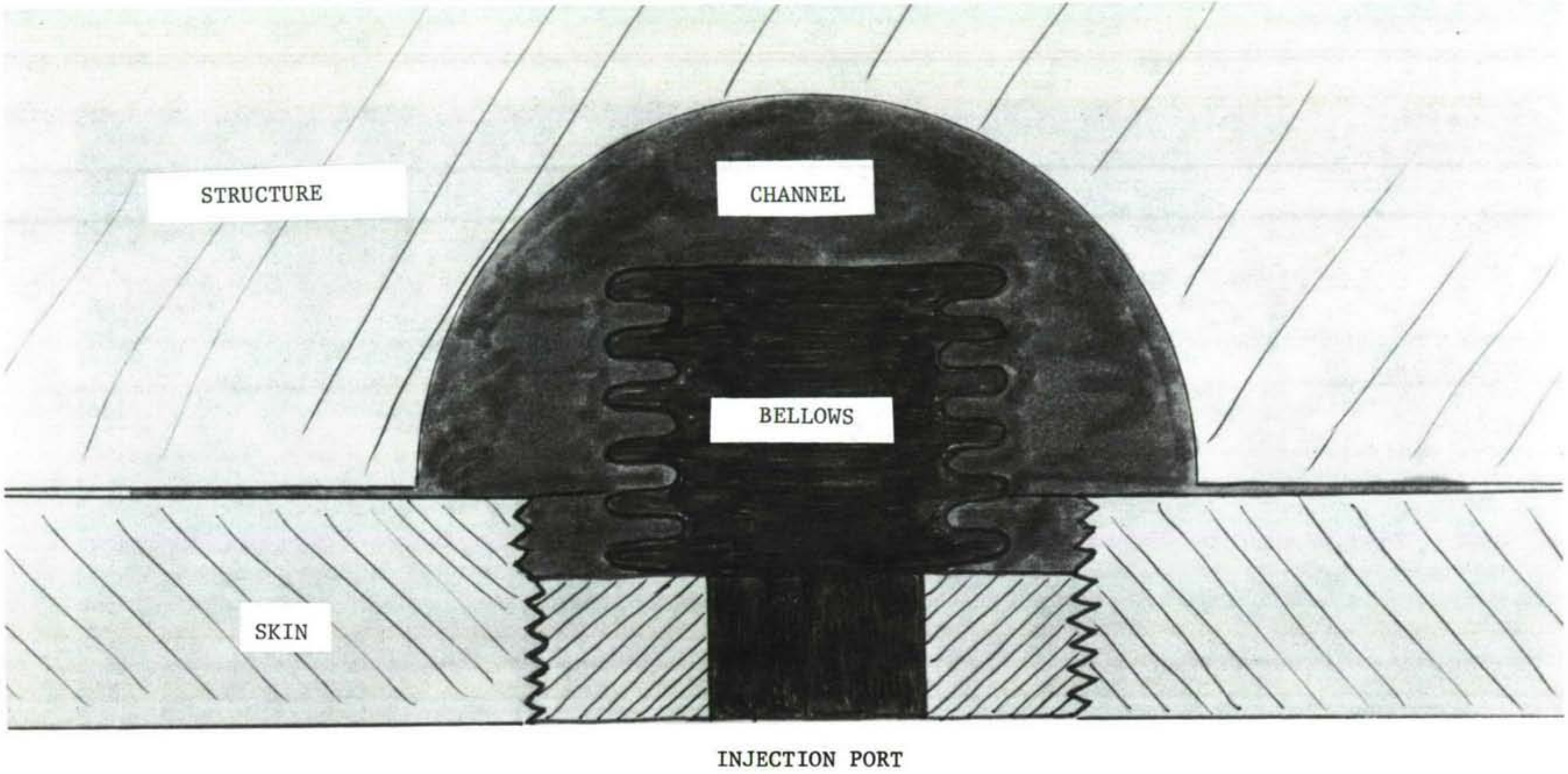


Figure 13 Thermal Expansion Compensation

yet allow for expansion. In addition, a non-destructive check on the level of sealant in the channel could be made by monitoring the depth of the bellows end. A calculation of the sealant volume in the section of channel, the thermal expansion coefficient, and temperature range would give the size of the bellows required. The bellows should be selected with spring constants such that a 30 to 50 psi pressure is developed. This range of pressure was derived from observing the flow of DC 94011 fluorosilicone sealant from an open exit port of a reinjection fixture with 6" between the entrance and exit ports. A pressure of 15 psi was applied by constant air pressure on the reservoir of a Grover 223 injection gun. The tip pressure would be 1.86 times the air line pressure. No sealant was extruded over a 60 day period at room temperature. A pressure of 30 psi on the reservoir caused the sealant to slowly flow from the port in seven days time. Thus, the range of 30 to 50 psi would return the sealant to the groove and yet not continuously force it past gaps in the faying surfaces. Thermal expansion compensation by means of a miniature gas filled bellows, small enough to be considered an injected particle, is being considered. Such means of compensating for the high potential pressure developed by thermal expansion could significantly extend the service life of sealants.

SECTION V

CONCLUSIONS

Channel sealants have been formulated that are not vulnerable to thermal degradation and do not have gross changes in viscosity over the -54°C to +180°C temperature range. However, the thermal expansion/contraction can only be reduced about 50% from that of pure gum elastomer by dilution with low expansion fillers. The volume change from thermal expansion over the -54°C to +180°C range amounts to about 15% with the best formulations to date. Aircraft modifications, such as expansion chambers, are required in this area.

The chemical stability of channel sealants has been a source of problems in the past. Careful selection of base polymers can circumvent hydrolysis, confined heat reversion, and hardening from crosslinking chemicals and oxidation.

The physical environmental effects upon sealants have not received sufficient study to determine if vibration, shear, and fuel sloshing are a problem. The area of fuel swell and fuel extraction can be controlled by the selection of very fuel resistant base polymers such as the fluorocarbons and the fluoroalkoxy phosphazenes (PNF).

Adhesion to channel walls has been established as a requirement. The release of the sealant from the surface of the channel by fuel allows the fuel to seep by capillary action. The absolute and relative levels of cohesion and adhesion have not been established and require further study.

The most common failure mode for channel sealants is gap extrusion. The mechanisms that cause gap extrusion are pressure build-up in the channel from thermal expansion, fuel swell, internal tank pressures, and, to a lesser extent, joint flexing and gas formation from polymer degradation. The mechanisms that allow higher than tolerable gap extrusion rates are hydrolysis, confined heat reversion, viscosity reduction with increasing temperatures, viscosity reduction by fuel swell, and, to an unknown extent, loss of viscosity due to thixotropic effects at high frequency noise levels.

A gap extrusion preventative developed by the Air Force Materials Laboratory is a 10 to 100 part-on-mastic loading of high strength, high modulus fluorosilicone particles. The particles were prepared by wet chopping 0.040" molded sheets to a 0.012" to 0.040" size range. The addition of 20 parts to commercial channel sealants (no beads added) has consistently extended the time to failure in the laboratory sealant tester by a factor of four (4). The injection pressure as measured by the extrusion plastometer increases from 325 for 20 part loadings to 542 for 100 part loadings.

Application of the engineering principles that have resulted from investigating the mechanisms of failure versus the fuel tank environment has provided a sound scientific basis for the development of improved channel sealants.

APPENDIX

DESCRIPTION OF SEALANT TESTER

The sealant tester is a modified apparatus that was designed to sense the sealing pressure developed by O-rings as a function of heating and fluid contact. Figure 14 shows a cross section. The central area was bored to receive a washer that had a semicircular groove on each side. Injection and exit ports were drilled through the body to allow sealant to be injected to the washer. Sealant moves halfway around the upper groove, enters the lower groove through a hole, and, after traveling the reverse direction for the full circle of the lower groove, enters the upper groove to fill the half circular groove remaining and then exits. The grooved washer has a 0.006" clearance in the bored area when the tester is assembled (this clearance was later increased to 0.015"). The edges of the washer have about 0.001" clearance at the sides. Two distinct leak paths are possible. The first is across the upper groove and down the edge of the washer. The second is across the lower groove and is the most direct leak path. Usually the lower groove is a closer fit because the injection pressure tends to force the washer against the lower surface. The assembled tester is placed in a -54°C (-65°F) to +177°C (+350°F) environmental chamber with a leak line and fuel pressure line leading to a leak collector and

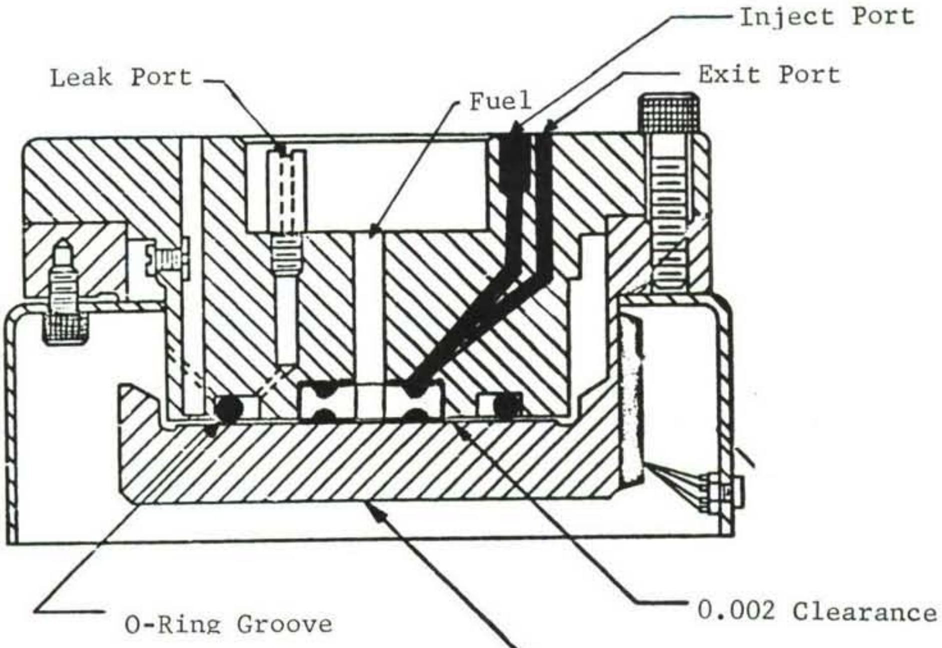


Figure 14 Laboratory Sealant Tester, Cross Sectional View

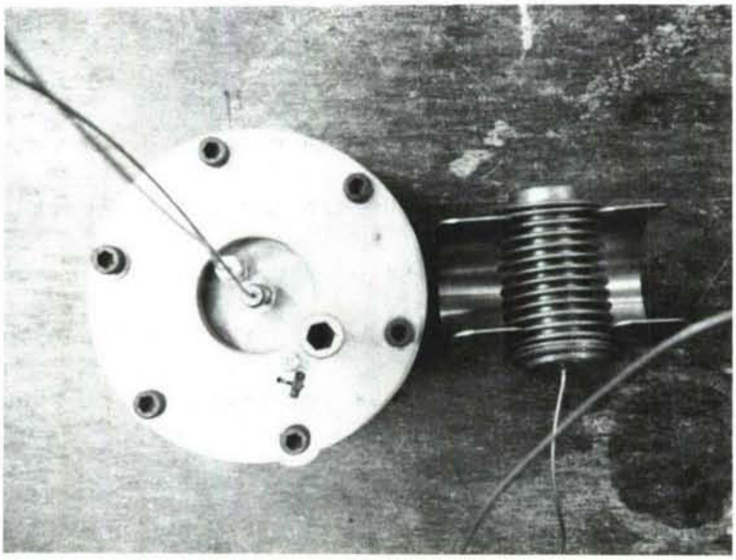


Figure 15 Laboratory Sealant Tester with Bellows Set for Zero psig Fuel Pressure

pressurized fuel source, respectively. Figure 15 shows the tester at zero fuel pressure with the spring clamp restraining the bellows. Figure 16 shows the spring clamp on the outside of the bellows to develop 20 psig on the fuel line. A 0-100 psi gauge in the fuel line was used to sense the pressure and give early leak detection. Figure 17 shows the disassembled apparatus after a sealant has been tested. The clear sealant allows the detail of the parts to show.

The basic test procedure evolved during this research is listed step-wise below:

1. Clean tester with acetone, allow to dry, and assemble with a size 325 Viton O-ring in the leak chamber.
2. Load brass injector and inject sealant with slow, smooth application of pressure using a hand operated arbor press. Estimated injection pressure between 1,000 and 2,000 psi.
3. Seal injection and exit ports with threaded plugs.
4. Clear any sealant extruded across the gap into the fuel area with a flat point 1/4" drill.
5. Fill fuel area with JP-4.
6. Load bellows and line by causing the bellows spring to expand the volume of the bellows while fuel line end is in JP-4 fuel.
7. Attach fuel line to tester with no air bubbles in system.
8. Pressure check overnight (16 hours) by placing the spring on the outside of the bellows, developing 20 psi gauge pressure. If pressure drops, reset by bellows spring to 20 psig. If pressure continues to drop, disassemble and inspect for cause.

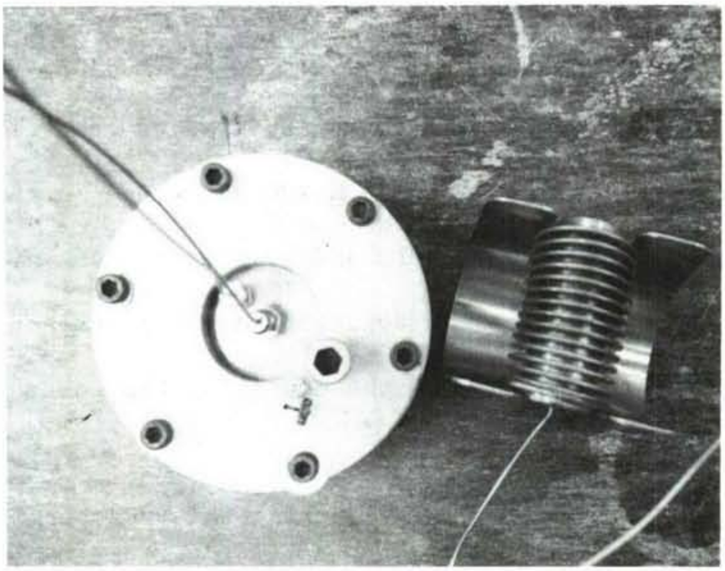


Figure 16 Laboratory Sealant Tester With Bellows Clamp Set for 20 psig Fuel Pressure

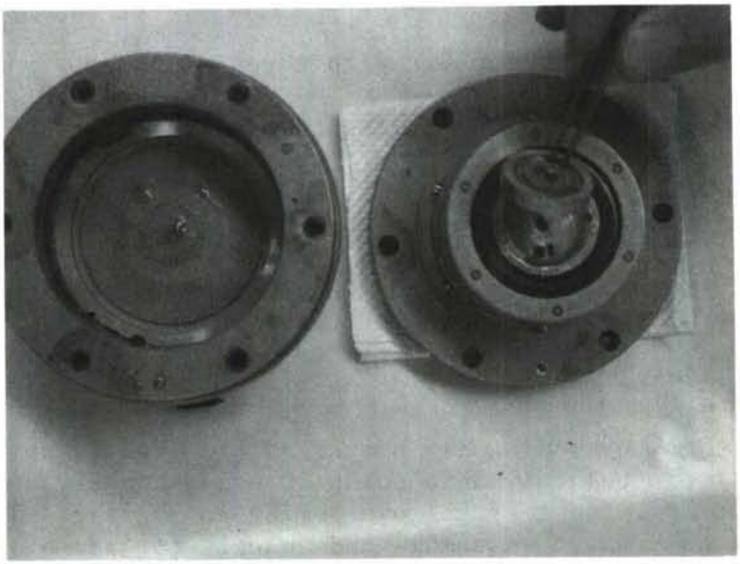


Figure 17 Disassembled Laboratory Sealant Tester - After Evaluating FCS 210 Gel, Formulation #8

9. After passing the 16 hour leak check, place tester in air circulating chamber and heat to the test temperature with 20 psig fuel pressure. The basic cycle consists of 8 hours at 177°C (350°F) and 16 hours (overnight) at -54°C (-65°F). The heat cycle includes about 1 hour heat up time and the cool down takes about 1 hour out of the 16 hour low temperature part of the cycle. The 24 hour heat-cool cycle is repeated to failure. The pressure is reduced to 0 to 1 psig and the temperature maintained at RT over weekends.

Variations of the basic procedure are listed below:

Modification A

Basic except -
Heat to 160°C (320°F)
Cool to room temperature
14 psi gauge continuous pressure

Modification B

Basic except -
Heat to 160°C (320°F)
Cool to room temperature
20 psi gauge during heat cycle only
0 psi gauge during cool down and weekends

Modification C

Basic except -
Heat to 232°C (450°F)

TABLE IV

FAILURE MECHANISMS OF COMMERCIAL AND EXPERIMENTAL SEALANTS(1) DETERMINED WITH SEALANT TESTER

NO.	SEALANT FORMULATION	TEST PROCEDURE	CYCLES TO FAILURE	MECHANISM OF FAILURE
1	DC 94031 Fluorosilicone(2)/ plastic beads	Mod A (160°C-RT)	Failed during fifth heat cycle.	Viscosity reduction by fuel swell and reversion, thermal expansion/contraction.
2	LS(2) 77-135 Plastic beads, lightly crosslinkable	Mod A (160°C-RT)	Failed during fifth cycle.	Viscosity reduction by fuel swell and reversion, aggravated by thermal expansion/contraction.
3	LS 77-135 Plastic beads, lightly crosslinkable	Mod A Except reinjection of that above.	Failed during fifth cycle.	"
4	LS 77-135 Same as above except 0.5 parts Vulcup R(3)	Mod A Except reinjection of that above.	Failed during fifth cycle.	Thermal expansion before crosslinking set the compound at expanded state. Cooling caused contraction. Still crosslinked, thermal expansion/contraction caused failure.

(1) The experimental sealants designated with DC FCS 210 indicate the base sealant formulation was prepared by Dow Corning Corp. under an Air Force Materials Laboratory contract. The beads and LS 422 vulcanized particles were added by AFML prior to testing.

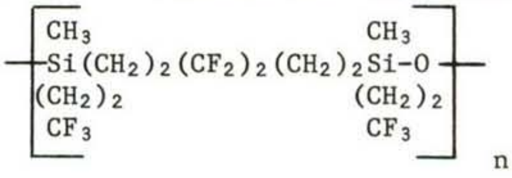
(2) Dow Corning Corp. trade name for poly (3,3,3-trifluoropropyl(methyl)siloxane.

(3) Hercules Inc. trade name for αα´-bis(t-butylperoxy)diisopropyl benzene.

TABLE IV (Cont'd)

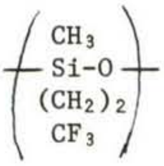
NO.	SEALANT FORMULATION	TEST PROCEDURE	CYCLES TO FAILURE	MECHANISM OF FAILURE
5	LS 77-135 Sponged with chunk benzoyl peroxide. (Figure 19)	Mod A (160°C-RT)	Failed during weekend cool down after completed two cycles.	Compression set of sponged cured sealant. Shrinkage from set stage, when cooled; allowed fuel to seep through voids.
6	LS 2249U With vulcanized hybrid FCS 210(4) particles.	Mod A (160°C-RT)	Failed during weekend cool down after completed three cycles.	Thermal expansion/contraction caused extrusion into fuel area. Particles prevented any extrusion across gap to leak side.
7	FCS 210/LS Copolymer(5) Branched by free radical action in solvent. 20 parts fumed silica 2 parts iron oxide	Mod A (160°C-RT)	No leak after five cycles.	Extruded gel into leak chamber. Pressure on fuel forced sealant from groove.
8	FCS 210/LS Copolymer gel (Figures 20 & 21)	Mod A (160°C-RT)	No leak after five cycles.	Swelled into fuel area, pushed fuel back to inlet. Eventual failure by saturation swelling, intolerable fuel swell.

(4) Dow Corning designation for fluorocarbon fluorosilicone hybrid polymer.



$$-\!\left[\begin{array}{lcr} CH_3 & & CH_3 \\ Si & (CH_2)_2(CF_2)_2(CH_2)_2 & Si-O \\ (CH_2)_2 & & (CH_2)_2 \\ CF_3 & & CF_3 \end{array}\right]_n\!-$$

(5) FCS 210/LS copolymer is FCS 210 above copolymerized with



$$-\!\left(\begin{array}{c} CH_3 \\ Si-O \\ (CH_2)_2 \\ CF_3 \end{array}\right)\!-$$

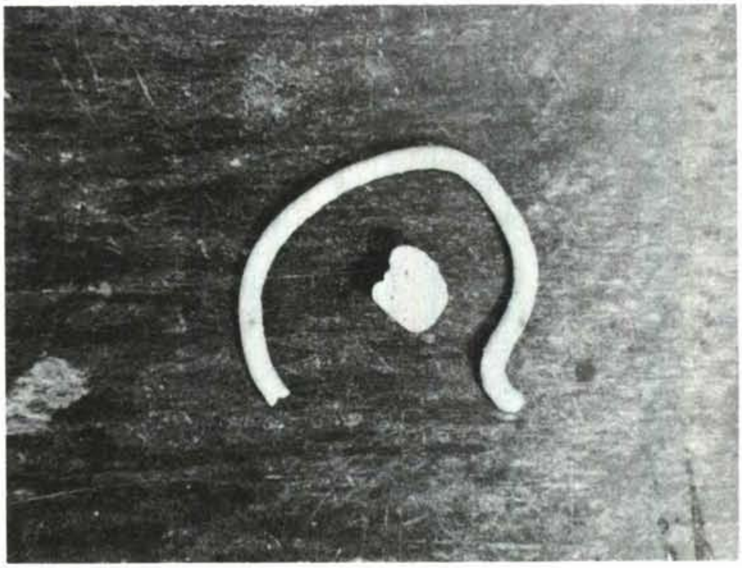


Figure 18 Closed Cell Sponge of Fluorosilicone Sealant, Formulation #5

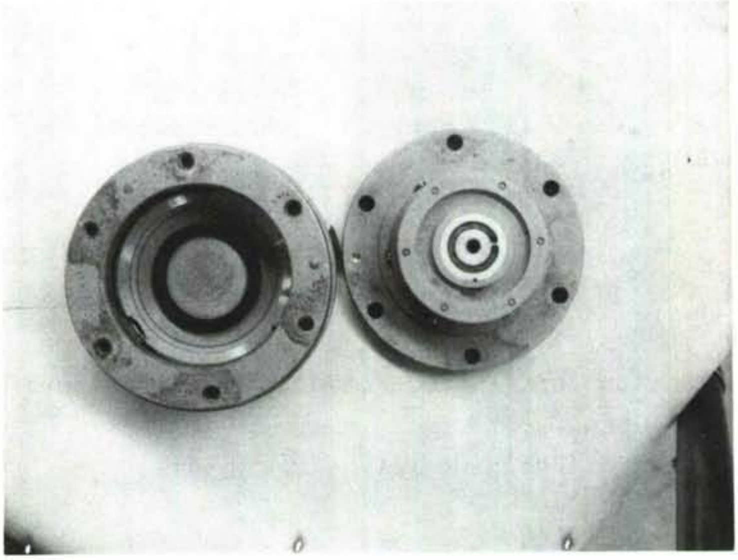


Figure 19 FCS 210 Copolymer Gel After 5 Cycles (RT to 160°C), Lower Channel Visible, Formulation #8

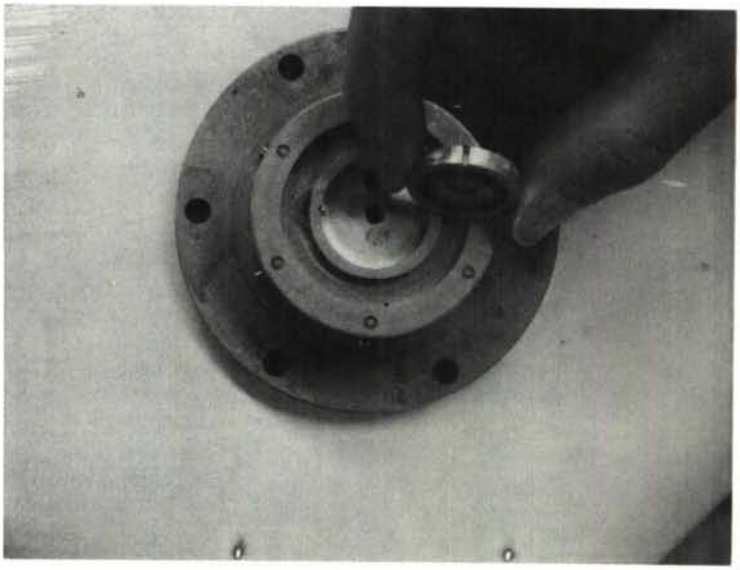


Figure 20 FCS 210 Copolymer Gel After 5 Cycles (RT to 160°C), Upper Channel Visible, Formulation #8

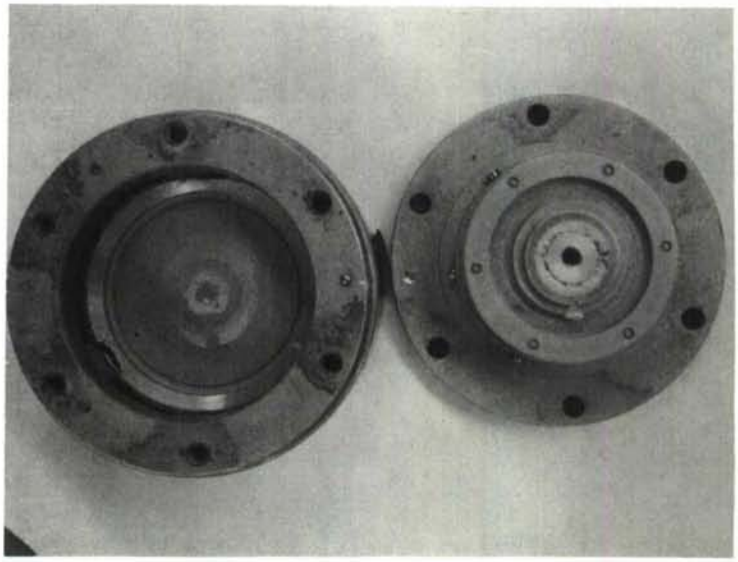


Figure 21 LS 209301 Experimental Lightly Crosslinkable Fluorosilicone Sealant After 11 Cycles (RT to 160°C), Formulation #11, (Lower Channel)

TABLE IV (Cont'd)

NO.	SEALANT FORMULATION	TEST PROCEDURE	CYCLES TO FAILURE	MECHANISM OF FAILURE
9	DC 94031 (DC 94011 plus beads)	Mod A Except pressure relieved for weekend.	Failed during pressurization after three cycles plus weekend.	Sealant extruded into fuel area and leak area. Thermal expansion/contraction plus viscosity reduction caused sealant relaxation and void formation.
10	DC 94031	Mod B (160°C-RT) 20 psi	Leaked during heat up of sixth cycle (passed five cycles).	Thermal extrusion into fuel area. Loss of adhesion, good cohesion, thermal expansion/contraction pushed out sealant; could not draw back.
11	LS 209301 Experimental crosslinkable fluorosilicone (Figures 22 & 23)	Mod B (160°C-RT) 20 psi	Leaked at exit port 12th cycle pressurization (passed 11 cycles).	Loss of adhesion. Loss of cohesion. Relaxation of internal pressure by thermal extrusion allowed fuel to seep out exit port.
12	FASIL(6) C_2H_3CN 100 parts vulcanized particles 20 parts fumed silica 2 parts iron oxide FASIL particles (Figure 24)	Mod B Followed by Mod C with one cooling to -54°C 1-1/2 hours at start of 4th cycle.	No failure at 160°C after 20 cycles. Failure after 4th cycle at 232°C (one cool down to -57°C).	Loss of cohesion. Loss of adhesion. Extrusion into fuel area. Cohesion good when kneaded. Good adhesion on dry metal. Finally failed by thermal extrusion (expansion/contraction) until not enough sealant remained to fill cavity.

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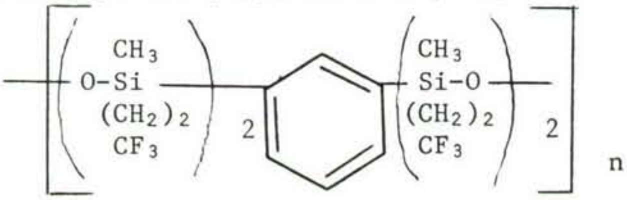
(6) AFML acronym for poly(fluoroalkylarylenesiloxanylene)



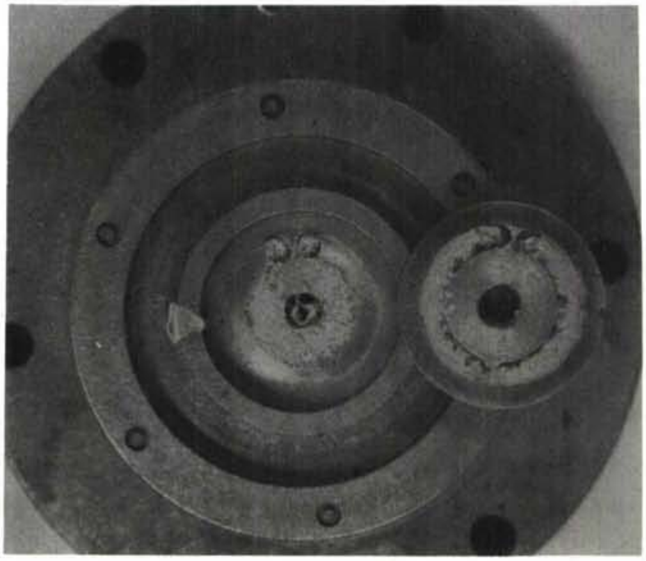


Figure 22 LS 209301 Experimental Lightly Crosslinkable Fluorosilicone Sealant After 11 Cycles (RT to 160°C), Formulation #11 (Upper Channel)

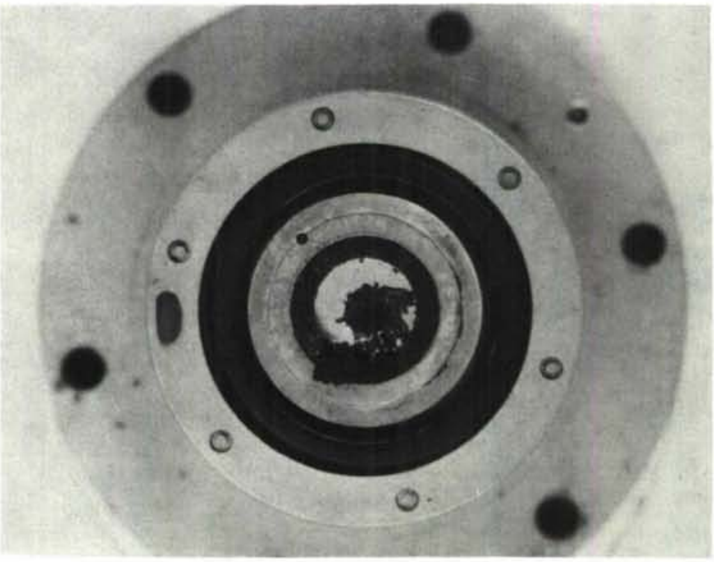


Figure 23 FASIL Sealant After 20 Cycles (RT to 160°C), 4 Cycles to 232°C With One Cooling to -57°C, Formulation #12

TABLE IV (cont'd)

NO.	SEALANT FORMULATION	TEST PROCEDURE	CYCLES TO FAILURE	MECHANISM OF FAILURE
13	DC FCS 210 (24,800,000 cps) 16 parts ware conductive carbon black 29 parts Hy-Flo Super Cel 10 parts plastic bead distribution (Figures 25 & 26)	Mod B (160°C-RT)	Failed during second cycle.	Polymer wash out. Swelled excessively and was solubilized enough to flow out the leak tube.
14	DC FCS 210 Same as above except grafted with C_2H_3CN 100 parts FCS 210 crosslinked gum particles	Mod B Followed by Mod C.	20 cycles; no leaks (160°C-RT). Leak upon heat up of second 232°C cycle.	Thermal expansion/contraction of crosslinked sealant. Good adhesion. Some corrosion from residual Cl in particles. Not repairable by reinjection.
15	DC FCS 210/LS 1:2 Copolymer 25 pts FCS 210 Cl_2 treated Cab-o-sil 5 pts Ware conductive carbon black 1.7 pts Williams 1011 conductive black (Figure 27)	Basic	1 cycle	Adhesion loss.
16	DC FCS 210/LS 1:2 Copolymer 25 pts FCS 210 Cl_2 treated Cab-o-sil 5 pts Ware conductive carbon black 1.7 pts Williams 1011 conductive black 10 pts std bead distribution (styrene/divinyl benzene). (Figures 28 & 29)	Basic	1 cycle	Adhesion loss.

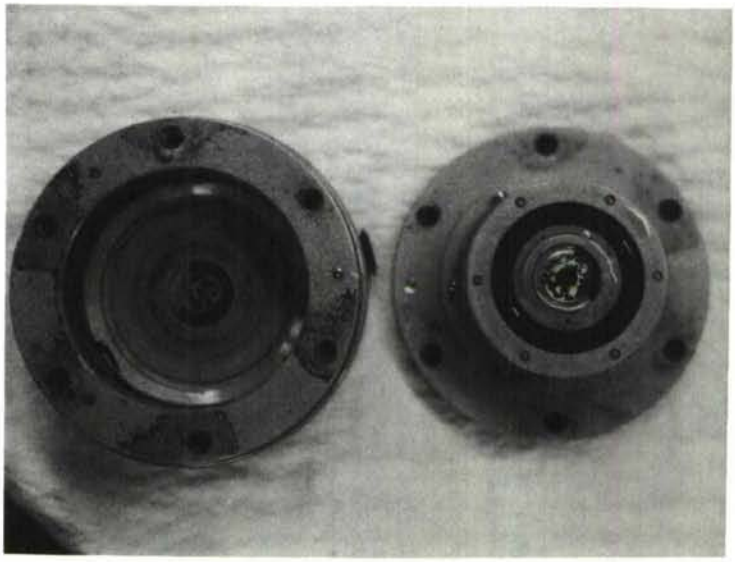


Figure 24 DC FCS 210 After 2 Cycles (RT to 160°C), Lower Channel, Formulation #13

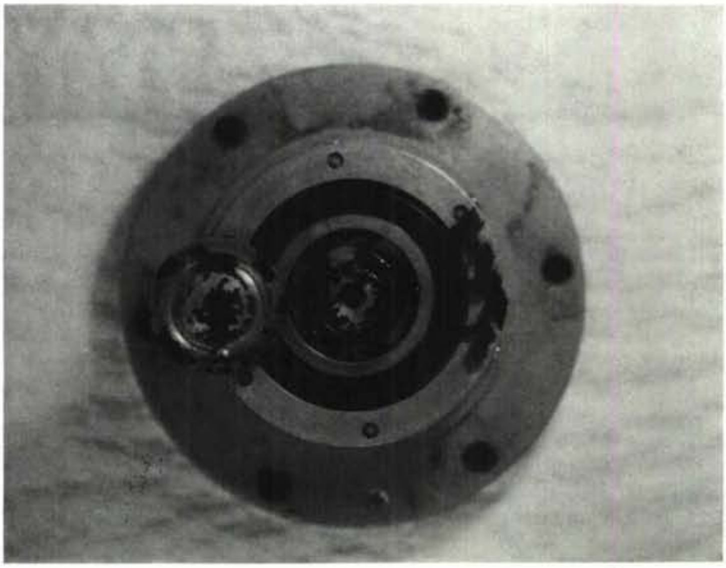


Figure 25 DC FCS 210 After 2 Cycles (RT to 160°C), Upper Channel, Formulation #13

Figure 26 DC FCS 210/LS, 1:2 Copolymer Sealant After One Cycle (177 to -54°C), Formulation #15

Figure 27 DC FCS 210/LS, 1:2 Copolymer Sealant With Beads After 1 Cycle (177 to -54°C), Lower Channel, Formulation #16

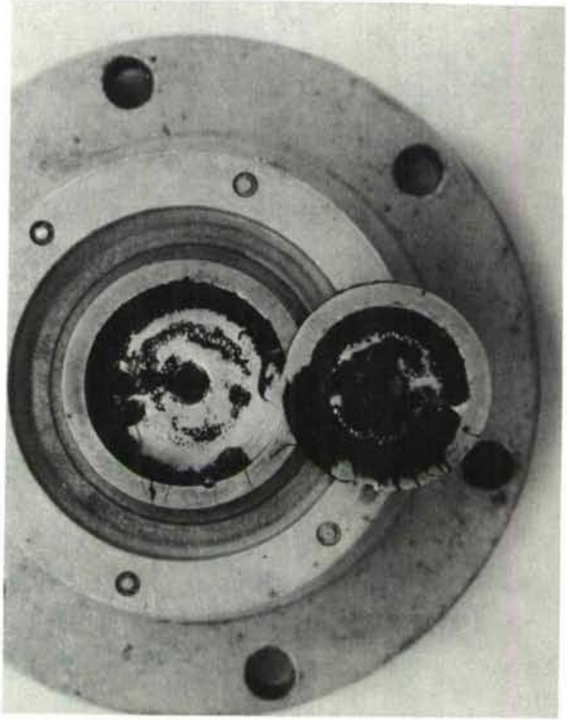


Figure 28 DC FCS 210/LS, 1:2 Copolymer Sealant With Beads After 1 Cycle (177 to -54°C), Upper Channel, Formulation #16

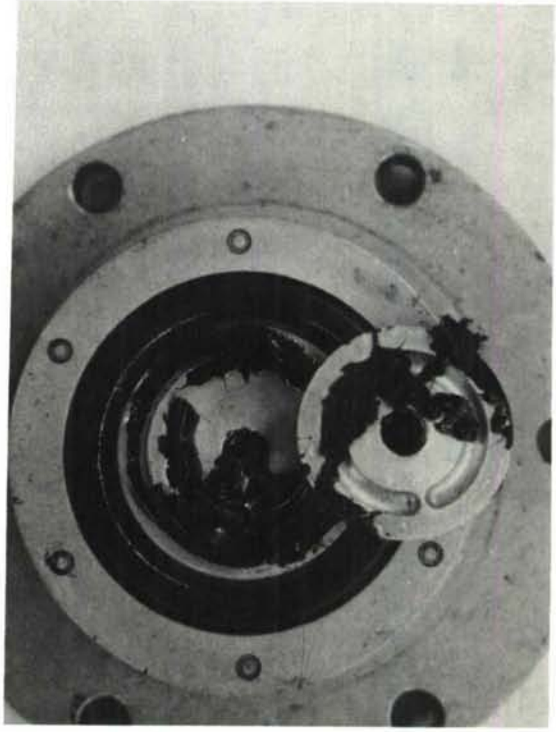


Figure 29 DC FCS 210/LS, 1:2 Copolymer Sealant With Fluorosilicone Vulcanized Particles After 3 Cycles (177 to -54°C), Formulation #17

TABLE IV (Cont'd)

NO.	SEALANT FORMULATION	TEST PROCEDURE	CYCLES TO FAILURE	MECHANISM OF FAILURE
17	DC FCS 210/LS 1:2 Copolymer 25 pts FCS 210 Cl_2 treated Cab-o-sil 5 pts Ware conductive carbon black 1.7 pts Williams 1011 conductive black 20 pts(7) LS 422 vulcanized particles(8) (Figure 30)	Basic	3 cycles	Adhesion loss.
18	DC FCS 210 (Me_3Si term) High molecular weight 100.5 pts quartz 6.7 pts treated silica 1.3 pts Teflon powder 1.3 pts Tio_2 9 pts Ware conductive carbon black 20 pts(7) LS 422 vulcanized particles (Figures 31, 32, & 33)	Basic	8 cycles	50% adhesion loss, capillary action of fuel.
19	GE-651 (Cyanosilicone with plastic beads) (Figures 34 & 35)	Mod B (160°C-RT)	15 cycles; no leaks.	Gum rubber in leak area and fuel area. Loss of cohesion (mud cracking). Thermally degraded. Not repairable by reinjection.

(7) 20 pts of LS 422 vulcanized particles added to completed formulation, i.e. 20 pts on total of other ingredients not on the basis of 100 pts polymer.

(8) Formulation for LS 422 vulcanized particles:
LS 422 fluorosilicone base (16 pts Cab-o-sil)
20 pts Cab-o-sil MS-7
.8 pts iron oxide
1.6 pts dichlorobenzoylperoxide — T=1130 psi — H=88 Shore A
Press cure 5 min. at 116°C (240°F) — E=140% — Size = .012" to .040" cubes
Post cure 24 hours at 150°C (302°F)

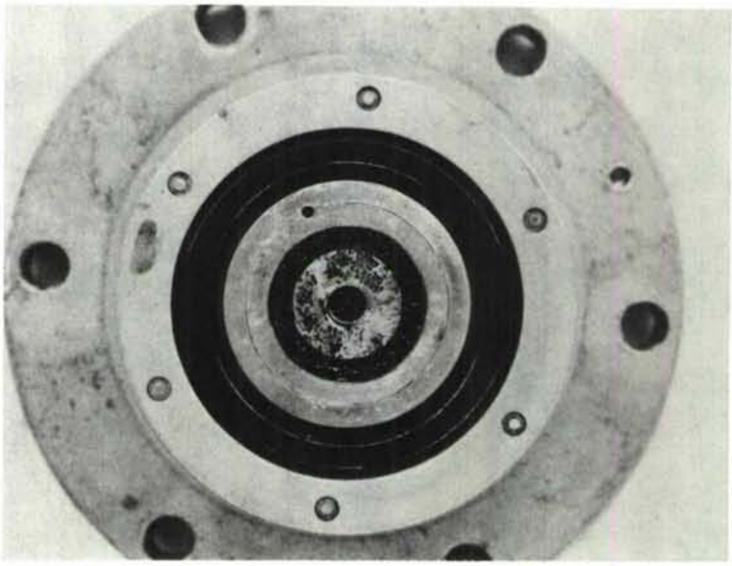


Figure 30 DC FCS 210 (Me_3Si term) Sealant After 8 Cycles (177 to -54°C), Lower Channel, Formulation #18

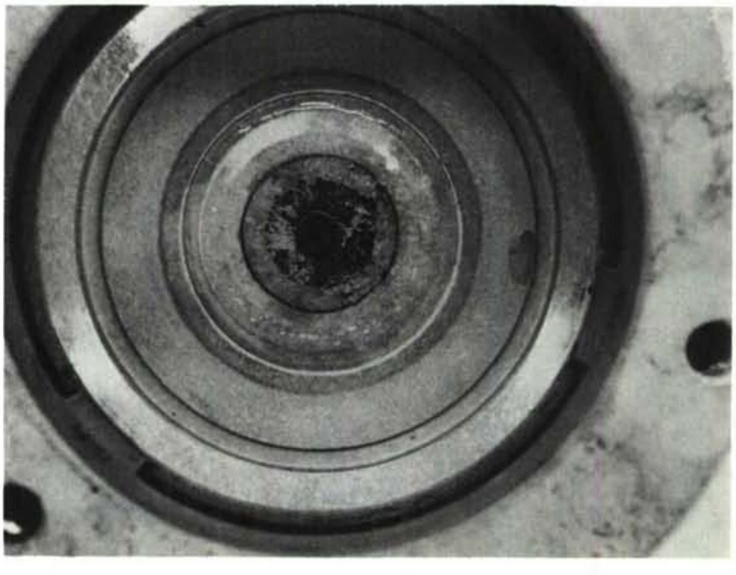


Figure 31 DC FCS 210 (Me_3Si term) Sealant After 8 Cycles (177 to -54°C), Lower Plate, Formulation #18

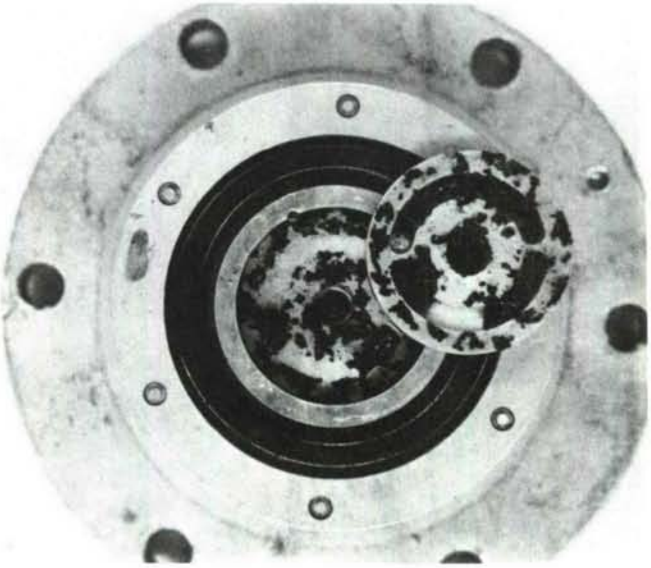


Figure 32 DC FCS 210 (Me_3Si term) Sealant After 8 Cycles (177 to -54°C), Upper Channel, Formulation #18

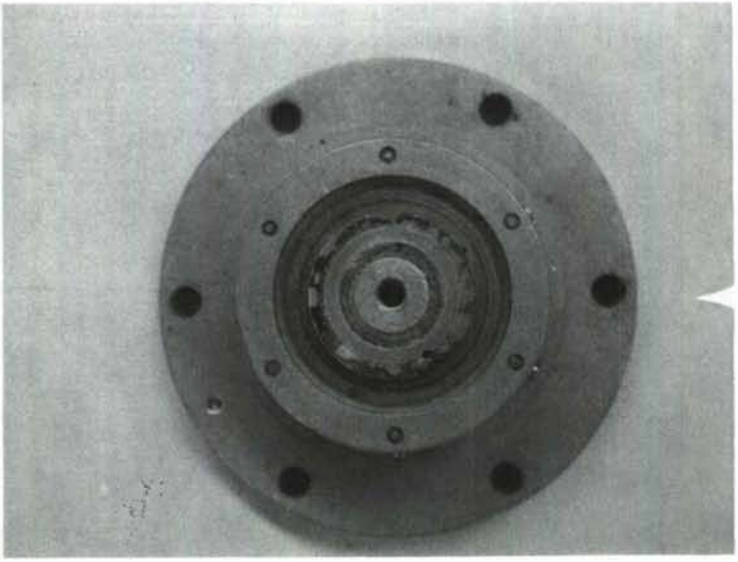


Figure 33 GE-651 Cyanosilicone Sealant With Beads After 15 Cycles (RT to 160°C), Lower Channel, Formulation #19

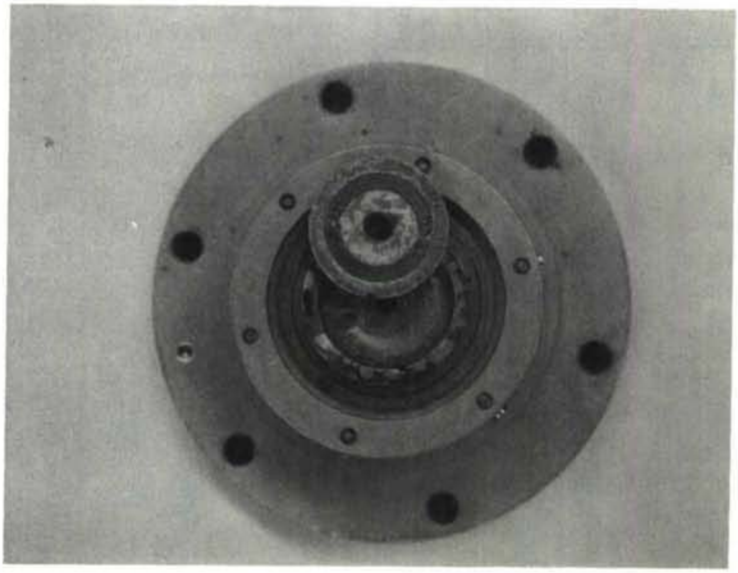


Figure 34 GE-651 Cyanosilicone Sealant With Beads After 15 Cycles (RT to 160°C), Upper Channel, Formulation #19

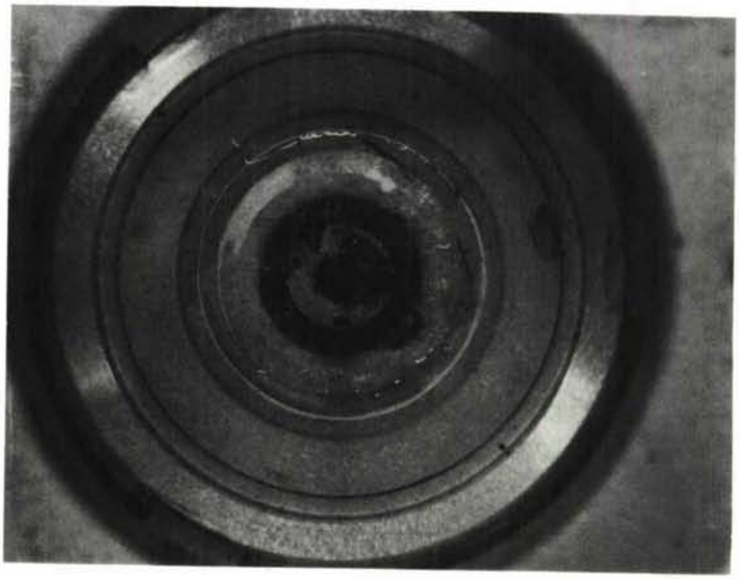


Figure 35 DC FCS 210 (OH term) Sealant After 16 Cycles (177 to -54°C) Lower Plate, Formulation #22

TABLE IV (Cont'd)

NO.	SEALANT FORMULATION	TEST PROCEDURE	CYCLES TO FAILURE	MECHANISM OF FAILURE
20	DC 94011 20 parts LS 422 vulcanized particles	Basic	20 cycles; no failure	Ready to fail from thermal expansion/contraction pumping of reverting sealant.
21	DC FCS 210 (OH term) Medium Molecular Wt. 24 parts Hy-Flo Super Cel 14.4 parts MS-75 Cab-o-sil (+177 to -54°C) 12 parts B8064 Ware conductive black 20 parts(7) LS 422 vulcanized particles	Basic	Not injectable	Crepe hardening.
22	DC FCS 210 (OH term) Medium Molecular Wt. 7.2 pts treated silica 40 pts Hy-Flo Super Cel 20 pts Ware conductive carbon black 20 pts(7) LS 422 vulcanized particles (Figures 36, 37, & 38)	Basic	16 cycles	Excessive fuel swell, viscosity reduction, extrusion to leak side.
23	DC FCS 210 (OH term) Medium Molecular Wt. 37.5 pts quartz 2.5 pts treated silica .5 pts Teflon powder .5 pts TiO_2 20 pts(7) LS 422 vulcanized particles (Figures 39, 40, & 41)	Basic	1 + heat portion of next cycle.	Excessive fuel swell, viscosity reduction, extrusion to leak side.
24	DC FCS 210 (Me_3Si term) 15 units 20 pts Cab-o-sil MS-75 20 pts Shawnigan carbon black 20 pts(7) LS 422 vulcanized particles	Basic	2 + heat portion of	Excessive fuel swell, viscosity reduction.

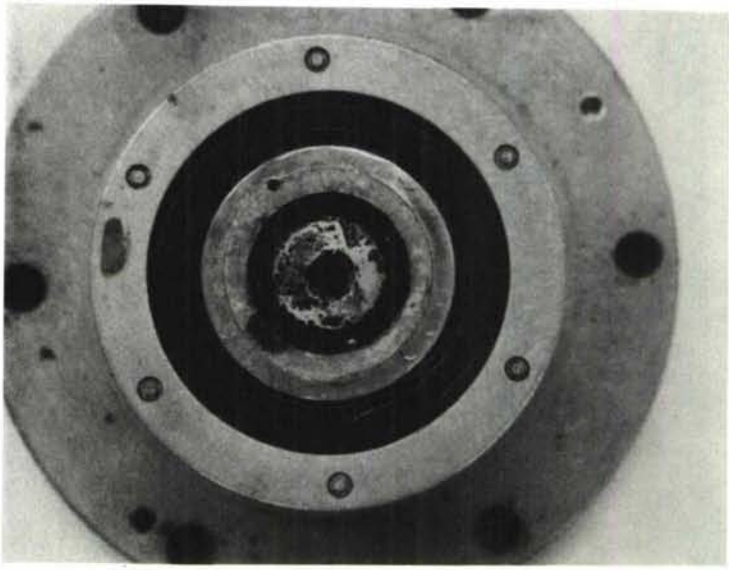


Figure 36 DC FCS 210 (OH term) Sealant After 16 Cycles (177 to -54°C), Lower Channel, Formulation #22

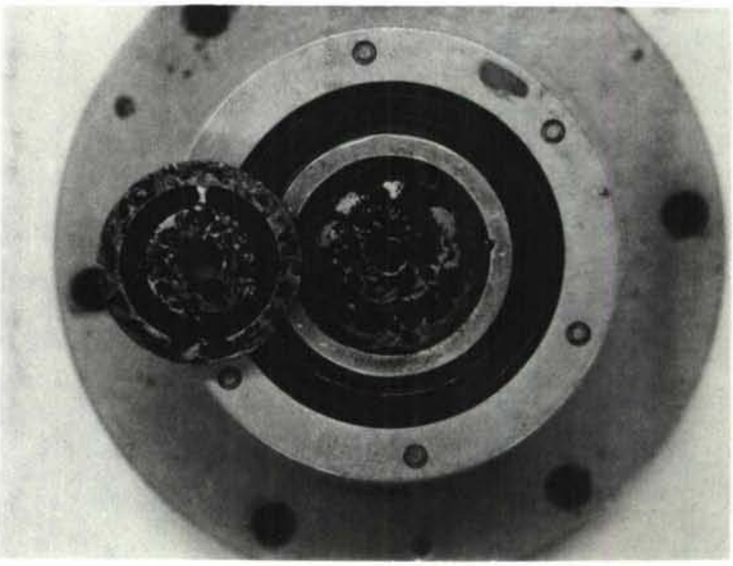


Figure 37 DC FCS 210 (OH term) Sealant After 16 Cycles (177 to -54°C), Upper Channel, Formulation #22

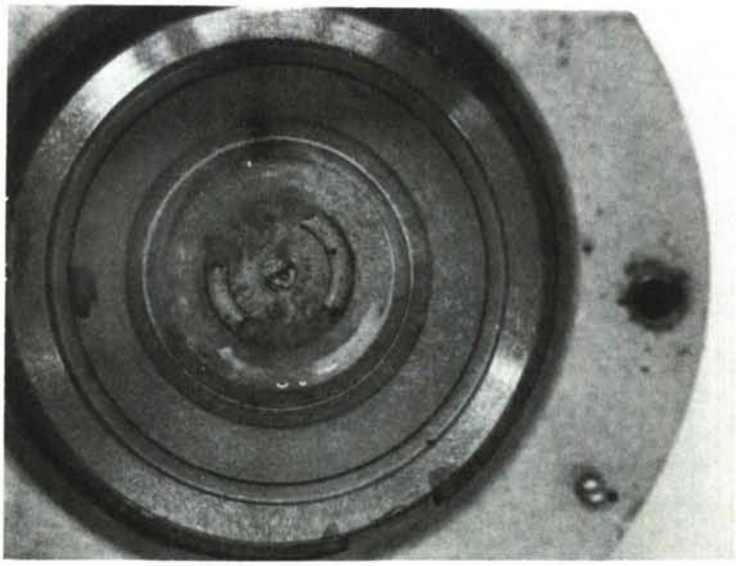


Figure 38 DC FCS 210 (OH term) Sealant After 1 Cycle (177 to -54°C) Plus Heat Portion of 2nd Cycle Lower Plate, Formulation #23

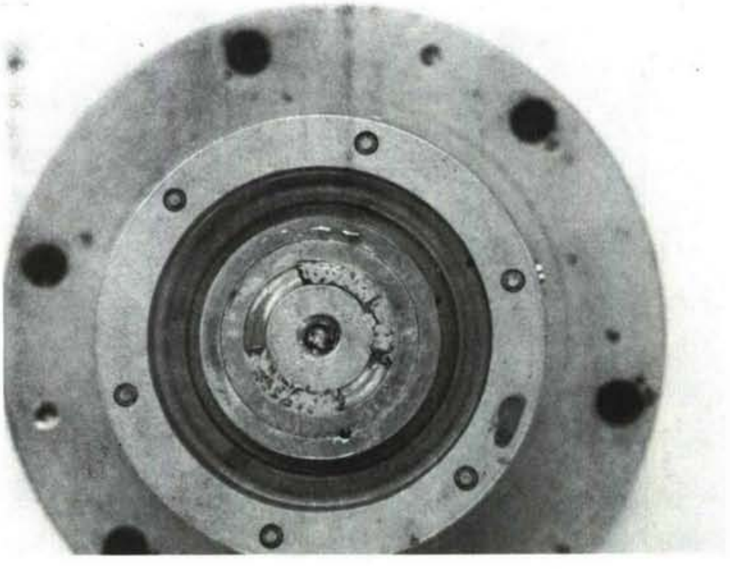


Figure 39 DC FCS 210 (OH term) Sealant After 1 Cycle (177 to -54°C) Plus Heat Portion of 2nd Cycle Lower Channel, Formulation #23

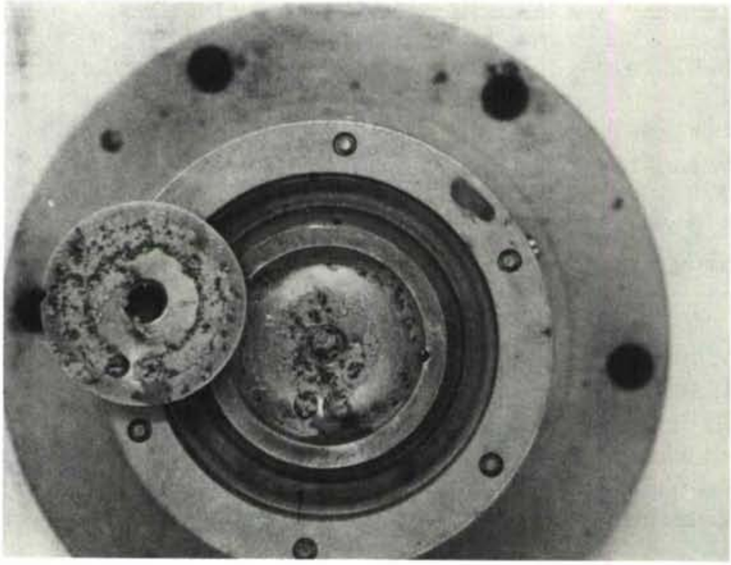


Figure 40 DC FCS 210 (OH term) Sealant After 1 Cycle (177 to -54°C) Plus Heat Portion of 2nd Cycle Upper Channel, Formulation #23

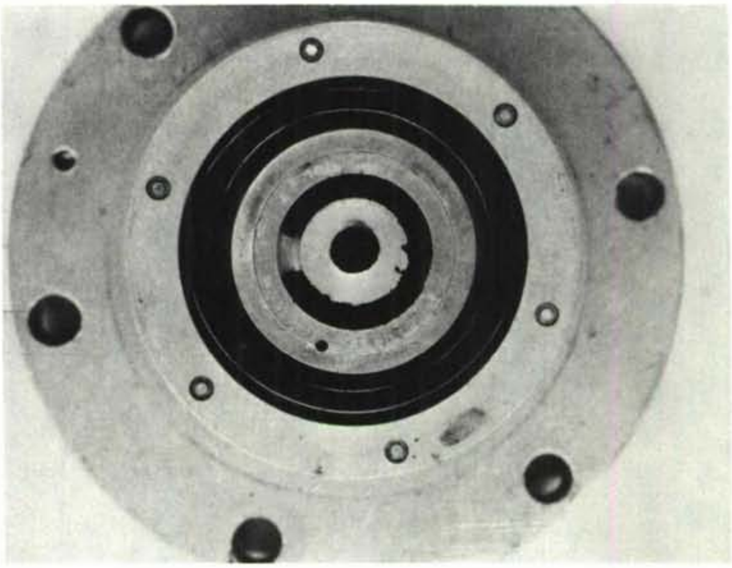


Figure 41 DC FCS 210 (Me_3Si term) Sealant - Not Injectable Into Lower Channel, Formulation #25

TABLE IV (Cont'd)

NO.	SEALANT FORMULATION	TEST PROCEDURE	CYCLES TO FAILURE	MECHANISM OF FAILURE
25	DC FCS 210 (Me_3Si term) 332 units 22 pts Cab-o-sil MS-75 12 pts Ware conductive black 20 pts(7) LS 422 vulcanized particles (Figure 42)	Basic	Not injectable	Too stiff to flow.
26	PNF-200 (Firestone) (Reverted to liquid 4 hrs at 400°F) 100 pts Lithium Aluminum Silicate (325 mesh) (Lithafrax-the Carborundum Co.) 20 pts(7) LS 422 vulcanized particles	Basic	20 cycles; no failure.	Thermal expansion/contraction evident; not close to failure. Softer than when injected. Very little fuel swell.

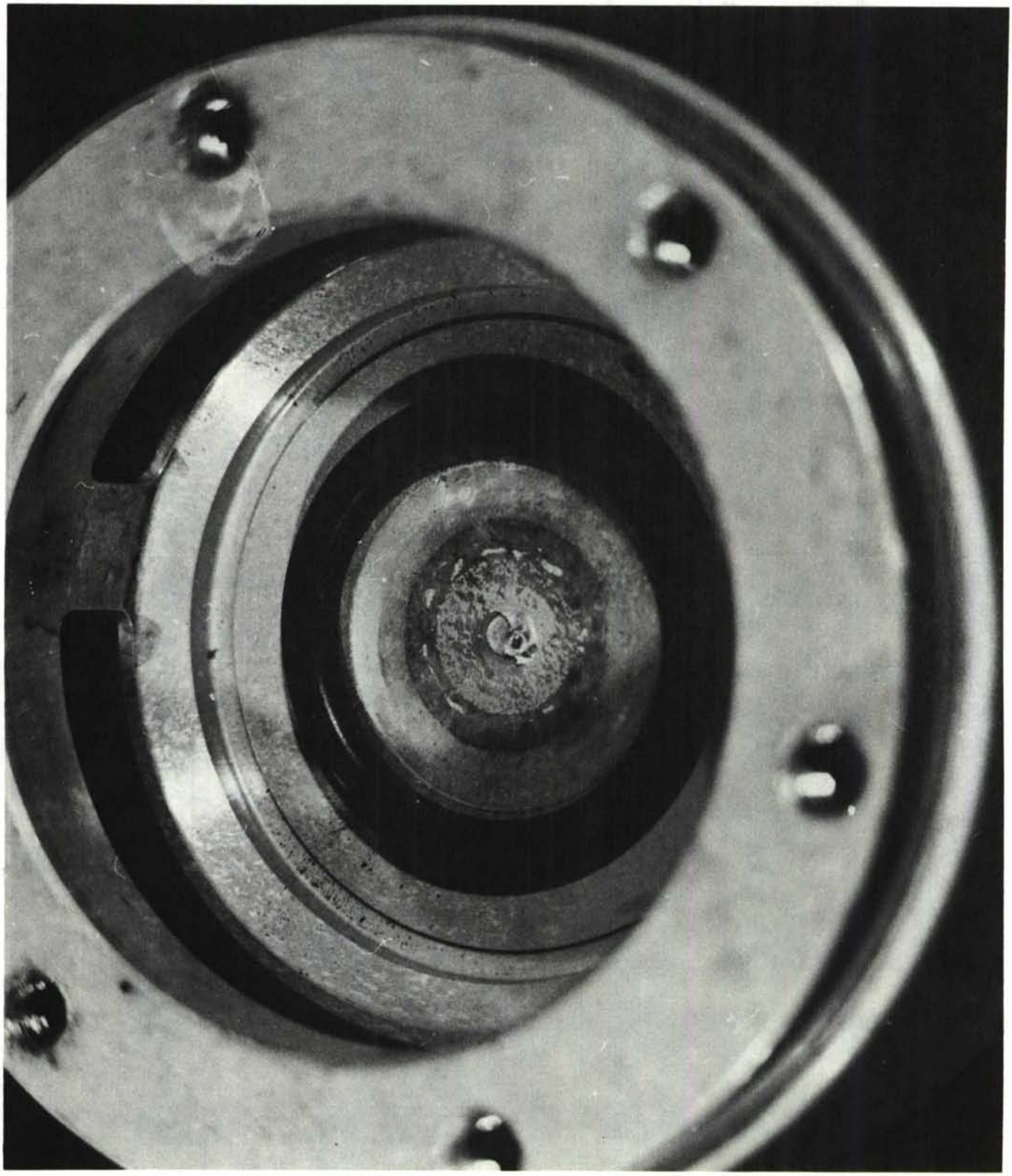


Figure 42 PNF 200 Sealant After 20 Cycles (177 to -54°C)
Lower Plate, Formulation #26

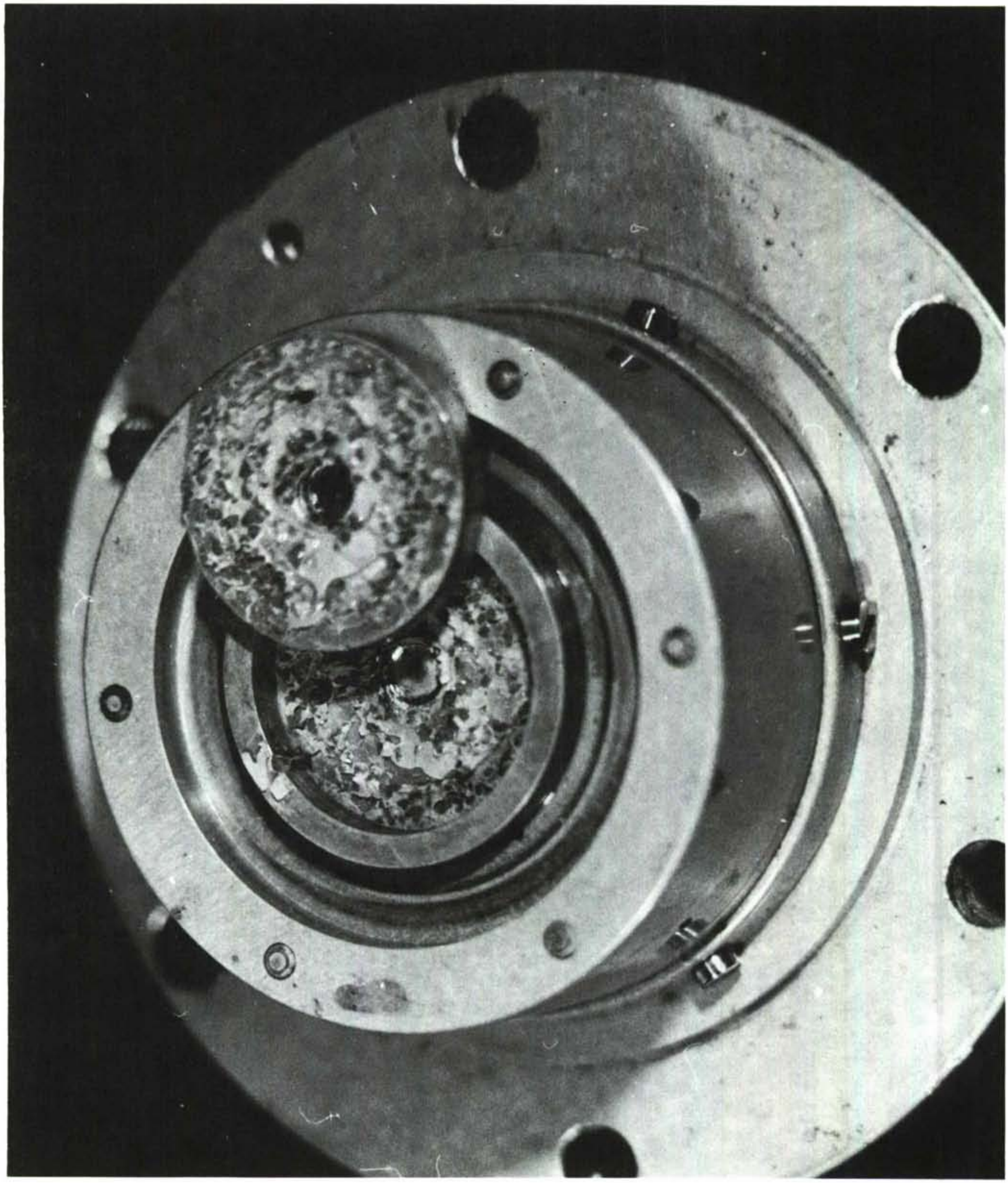


Figure 43 PNF 200 Sealant After 20 Cycles (177 to -54°C)
Upper Channel, Formulation #26

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