

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

**PERFORMANCE EVALUATION OF O-RING SEALS IN
MODEL 9975 PACKAGING ASSEMBLIES (U)**

T. Eric Skidmore

Savannah River Technology Center
Strategic Materials Technology Department
Materials Technology Section

December 1998

**DOES NOT CONTAIN
UNCLASSIFIED CONTROLLED
NUCLEAR INFORMATION**

ADC &
Reviewing
Official:

T.H. Capelotto

Date:

1/6/99

Patent Status

This internal management report is being transmitted without DOE patent clearance, and no further dissemination or publication shall be made of the report without prior approval of the DOE-SR patent counsel.

**Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808**

This document was prepared in connection with work done under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DOCUMENT: WSRC-TR-98-00439, Revision 0

TITLE: PERFORMANCE EVALUATION OF O-RING SEALS IN MODEL 9975
PACKAGING ASSEMBLIES (U)

APPROVALS



T. Eric Skidmore
T. Eric Skidmore, Author
Materials Consultation Group
MATERIALS TECHNOLOGY SECTION

Date: 12-28-98

R. J. Gromada
R. J. Gromada, Customer
Packaging and Transportation Group
ENGINEERED EQUIPMENT AND SYSTEMS DEPARTMENT

Date: 1-19-99

C. F. Jenkins
C. F. Jenkins, Technical Reviewer
Materials Consultation Group
MATERIALS TECHNOLOGY SECTION

Date: 12-28-98

R. Linnea Bickford
R. Linnea Bickford, Manager
Materials Consultation Group
MATERIALS TECHNOLOGY SECTION

Date: 1/6/99

T. L. Capeletti
Tami L. Capeletti, Manager
MATERIALS TECHNOLOGY SECTION

Date: 1/6/99

(Blank Page)

TABLE OF CONTENTS

	Page
1.0 SUMMARY	1
2.0 BACKGROUND AND ASSUMPTIONS	1
3.0 LITERATURE REVIEW	5
3.1 Viton [®] Chemistry, Formulation, and Properties	5
3.2 General Radiation/Temperature Resistance	8
3.3 Accelerated Aging of Viton [®] Elastomers	11
3.4 Limitations of Accelerated Aging Tests	27
3.5 Summary of Literature Review	28
4.0 PERFORMANCE EVALUATION	30
4.1 Seal Design	30
4.2 Critical Seal Properties	32
4.3 Failure Criteria	34
4.4 Post-Storage Transportation	35
4.5 Surveillance Program	36
5.0 CONCLUSIONS AND RECOMMENDATIONS	37
6.0 REFERENCES	40

LIST OF TABLES

Table 1.	List of Assumptions, Service Conditions, and Applicable Sources.....	2
Table 2.	General Formulation and Properties of Viton [®] GLT Fluoroelastomer.....	7
Table 3.	Properties of Parker Seals Compound V835-75	9

LIST OF FIGURES

Figure 1.	Overall Schematic of the Model 9975 Packaging Assembly.....	3
Figure 2.	Schematic of the Containment Vessel Design.....	4
Figure 3.	General Chemical Formula for Viton [®] GLT Fluoroelastomer.....	6
Figure 4.	General Structure of Principal Fluoroelastomer Monomers.....	6
Figure 5.	Time-Temperature Shifted Stress Relaxation for Parker Compound V747-70.....	12
Figure 6.	Stress-Relaxation Modulus vs Temperature for Parker Compound V747-70.....	13
Figure 7.	Time Required to Reach Relaxation Modulus Ratio at Temperature.....	13
Figure 8.	Synergistic Effects of Temperature and Radiation on Polyethylene (PE).....	14
Figure 9.	Corrected Compression Set and Sealing Force vs Time for Viton [®] O-Rings.....	17
Figure 10.	Master Curves for Compression Set vs Time/Dose Rate.....	17
Figure 11.	Dose to 80% Compression Set vs Dose Rate at 150°C.....	19
Figure 12.	Compression Set vs Time at 80°C and 13 Gy (1300 R)/hr.....	19
Figure 13.	Service Life Estimate for Viton [®] B Seals Immersed in Silicone Oil.....	21
Figure 14.	Compression Set Curves for Parker Compound V835 (20% Squeeze).....	23
Figure 15.	Helium Permeation Through Silicone Elastomer at 75°F and 450°F.....	24
Figure 16.	Cross-Sectional View of Containment Vessel Cone Plug.....	31
Figure 17.	Cross-Sectional Dimensions of O-Ring Groove Design.....	31

LIST OF ACRONYMS, TRADENAMES, AND ABBREVIATIONS

Aflas [®]	Tradename of 3M CO.; for TFE-P (tetrafluoroethylene-propylene) elastomer
APSF	Actinide Packaging and Storage Facility
ASTM	American Society for Testing and Materials
CTFE	chlorotrifluoroethylene; monomer for fluoropolymer processing
DBA	design basis accident
DED	dose to equivalent damage
EESD	Engineered Equipment and Systems Department of SRTC
EPR/EPDM	Ethylene-propylene rubber/ethylene-propylene diene monomer
ETFE	ethylene-tetrafluoroethylene copolymer
FFKM	ASTM D1418 designation for perfluoroelastomer
FKM	ASTM D1418 designation for fluorocarbon rubber
GFLT	DuPont designation for peroxide-curable, low-temperature Viton [®] type F
GLT	DuPont designation for peroxide-curable, low-temperature Viton [®]
HFP	hexafluoropropylene; monomer for fluoroelastomer processing
Hypalon [®]	DuPont tradename for chlorosulfonated polyethylene (CSM) elastomer
IEEE	Institution for Electrical and Electronic Engineers
Kalrez [®]	DuPont tradename for high-temperature perfluoroelastomer (FFKM)
KAMS	K-Area Materials Storage
LDPE	low-density polyethylene
LOCA	loss of coolant accident; also associated with DBA (design basis accident)
NBR	nitrile-butadiene rubber; also known as Buna-N or nitrile rubber
Neoprene	common name (DuPont) for polychloroprene or chloroprene rubber
phr	parts per hundred rubber; compounding units
PMVE	perfluoro(methyl vinyl ether); monomer for fluoroelastomer processing
PVC	polyvinyl chloride
RFETS	Rocky Flats Environmental Technology Site
SARP	Safety Analysis Report for a Package
SNL	Sandia National Laboratory
SRTC	Savannah River Technology Center
SS&C	sand, slag, and crucible residues from plutonium processing
TFE	tetrafluoroethylene; monomer for fluoropolymer processing
VF ₂	vinylidene fluoride; monomer for fluoropolymer processing
Viton [®]	DuPont-Dow Elastomers tradename fluoroelastomer or fluorocarbon rubber
WSMS	Westinghouse Safety Management Solutions

1.0 SUMMARY

The Materials Consultation Group of SRTC has completed a review of existing literature and data regarding the useable service life of Viton[®] GLT fluoroelastomer O-rings currently used in the Model 9975 packaging assemblies. Although the shipping and transportation period is normally limited to 2 years, it is anticipated that these packages will be used for longer-term storage of Pu-bearing materials in KAMS (K-Area Materials Storage) prior to processing or disposition in the APSF (Actinide Packaging and Storage Facility). Based on the service conditions and review of available literature, Materials Consultation concludes that there is sufficient existing data to establish the technical basis for storage of Pu-bearing materials using Parker Seals O-ring compound V835-75 (or equivalent) for up to 10 years following the 2-year shipping period.

Although significant physical deterioration of the O-rings and release of product is not expected, definite changes in physical properties will occur. However, due to the complex relationship between elastomer formulation, seal properties, and competing degradation mechanisms, the actual degree of property variation and impact upon seal performance is difficult to predict. Therefore, accelerated aging and/or surveillance programs are recommended to validate the assumptions outlined in this report and to assess the long-term performance of O-ring seals under actual service conditions. Such programs could provide a unique opportunity to develop non-existent long-term performance data, as well as address storage extension issues if necessary.

2.0 BACKGROUND AND ASSUMPTIONS

Pu-bearing materials (metal, oxides, and impurities) currently stored at RFETS (Rocky Flats Environmental Technology Site) are anticipated to be shipped to SRS in Model 9975 packaging assemblies for interim storage at KAMS prior to processing or stabilization in the APSF. The Model 9975 packaging assembly (Figure 1) generally consists of two containment vessels, primary (PCV) and secondary (SCV), each with a dual O-ring seal design as shown in Figure 2. The primary and secondary O-ring seals of the Model 9975 assembly are specified in the SARP to be Parker Seals compound V835-75, based on Viton[®] GLT fluoroelastomer, or equivalent [1].

During recent SARP revision activities to facilitate shipment of SS&C residues from RFETS, Materials Consultation reviewed the radiation and temperature resistance of the O-rings for the 2-year shipping period. Due to longer-term exposure to elevated temperatures and ionizing radiation during storage, however, Materials Consultation recommended that a literature review be performed [2, 3]. The radiation dose rates for the primary and secondary O-ring seals are conservatively bounded at 2.0 and 0.04 R/hour respectively, based on calculations for the SS&C residues [4, 5, 6]. Radiation dose rates for expected package contents (metal/oxides) are considerably lower [1, 5, 6]. O-ring seal temperatures are currently assumed to be limited to 300°F for continuous exposure, depending upon actual package contents. A summary of service conditions, assumptions, and applicable sources is provided in Table 1 for reference.

Specifically, the long-term synergistic effects of temperature, radiation, and/or oxidation on the sealing performance of Parker O-ring compound V835-75 and other Viton® GLT-based compounds were of interest. Aside from catastrophic degradation, the primary concern for any O-ring seal is the effect of environmental conditions on critical seal properties such as compression set, stress-relaxation, permeability, etc. Therefore, the focus of this report has been to summarize relevant literature on both short-term, accelerated aging data and long-term service history of Viton® fluoroelastomer, where available.

For reference, the international unit for ionizing radiation energy absorption is the Gray (Gy), which is equal to 100 Rads. A mixture of units is found in the literature depending upon the date of publication and author preference.

Table 1. List of Assumptions, Service Conditions, and Applicable Sources

<u>Service Condition/Assumption</u>	<u>Reference/Source</u> (where applicable)
• O-ring compound = Parker Seals V835-75 or equivalent	SARP, Rev. 6 [1]
• Storage Term = 10 years following 2-year shipping period	EESD/KAMS
• Maximum Internal Pressure (PCV) = 500 psi	[1], Table 2.13
• Maximum Normal O-ring Temperature = 300° F	[1], Table 2.14
• Radiation Dose Rate (PCV) = 2.0 R/hr (photon + neutron),	N-CLC-F-00141 [4]
• Internal Environment = air induced during closure (0.0596 ft ³); hydrogen concentration expected to increase due to radiolysis	[1] PCV volume
• % O-ring compression at closure = 28% (no gap)	[1], 2.1.2-37
• % O-ring compression at closure = 21% (0.01" gap)	[1], 2.1.2-38
• Installation torque = 50 ft-lbs (PCV), 100 ft-lbs.(SCV)	[1], 2.1.2-5
• Alpha radiolysis effects considered negligible; lack of intimate exposure to O-rings (multiple barriers)	
• O-ring permeability at elevated temperature not critical; outgassing possibly higher at elevated temperature, with no actual product release.	
• Silicone lubricant applied to O-ring during installation; provides oxygen diffusion barrier, minimizes leakage.	
• Silicone lubricant is thermally/radiolytically stable; no significant release of halogens expected under service conditions.	
• Multiple barrier concept, dual O-rings per vessel; each O-ring provides diffusion/permeability barrier to container environment.	
• Leak testing required for transportation and storage (<10 ⁻⁶ std cc/sec).	

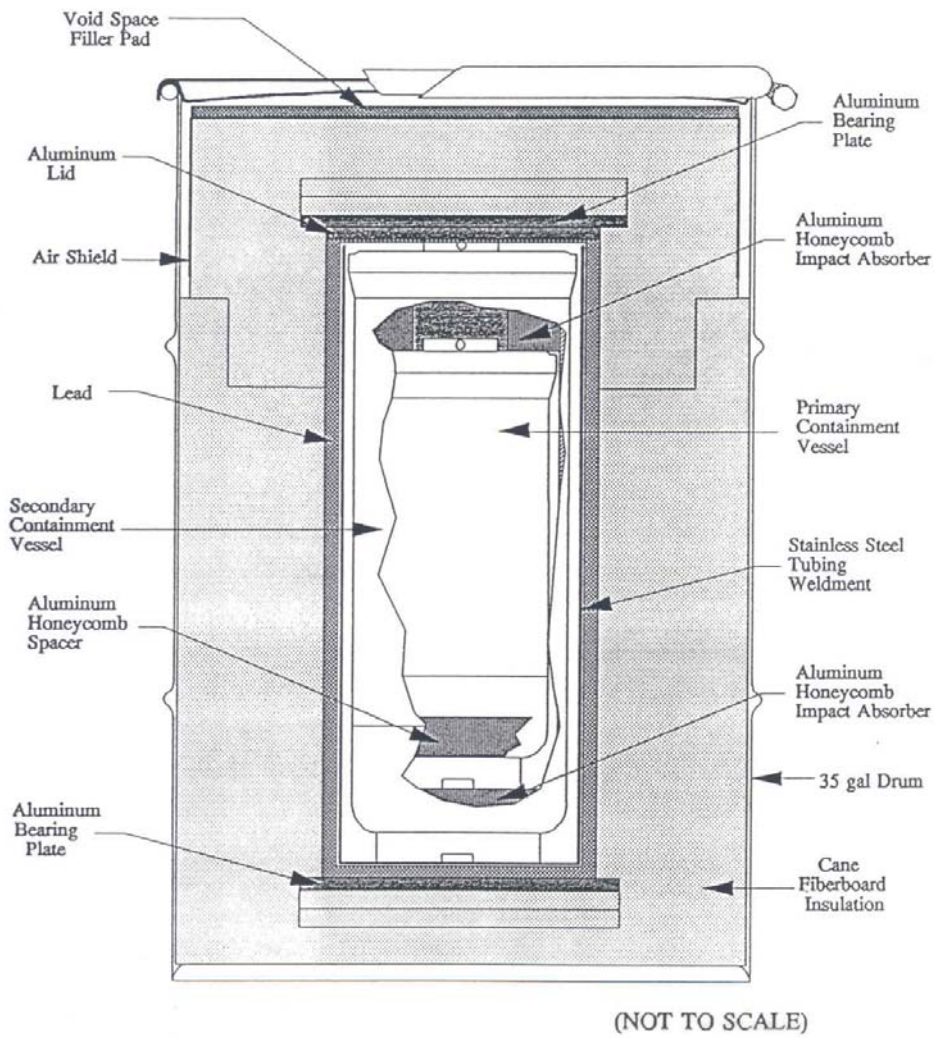
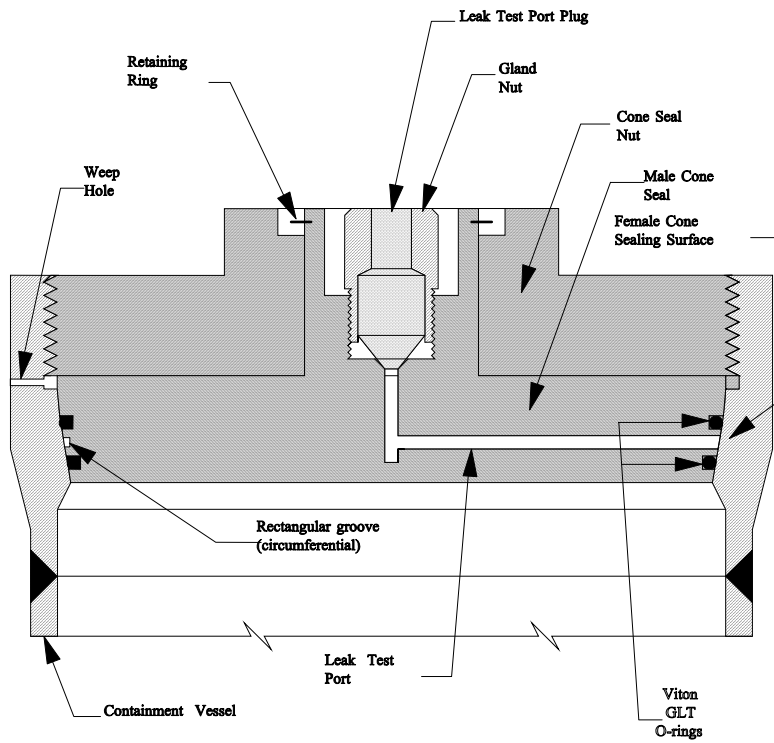


Figure 1. Overall Schematic of the Model 9975 Packaging Assembly [1].



(NOT TO SCALE)

4-42.WPG

Figure 2. Schematic of the Containment Vessel Design [2].

3.0 LITERATURE REVIEW

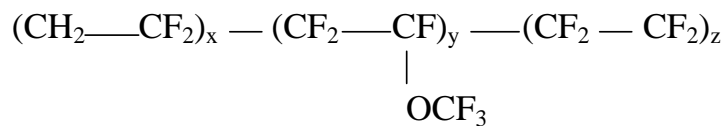
3.1 Viton[®] Chemistry, Formulation, and General Properties

The literature review was conducted under the assumption that the O-ring compound used in the 9975 packaging assembly is predominantly Parker Seals V835-75, which is based on Viton[®] GLT fluoroelastomer. Equivalent compounds from other suppliers and compounders may also be used, but evaluation of composition and properties should be performed prior to acceptance.

Fluorocarbon rubbers or fluoroelastomers are designated as FKM per ASTM D1418 [7]. In 1956, it became possible to produce an amorphous polymer with a low glass transition temperature (T_g) and high fluorine content from vinylidene fluoride (VF₂) and chlorotrifluoroethylene (CTFE) monomers. Viton[®] fluoroelastomer was then introduced by DuPont in 1957 to meet needs of the aerospace industry for both low and high-temperature resistance as well as superior resistance to various chemicals and solvents. Due to the excellent range of properties initially produced, Viton[®] has been successfully used for years in other industries, particularly automotive, chemical, and nuclear [8]. At SRS, Viton[®] fluoroelastomer is used primarily as a sealing material, particularly in the Separations areas due to superior resistance to concentrated nitric acid in combination with temperature and/or radiation as compared to other elastomers.

For most applications, specifying generic “Viton[®]” usually results in Viton[®] type A being used which is generally adequate. There are, however, three major families or types of Viton[®] fluoroelastomer: A, B, and F, with nearly 90 individual grades available. The Viton[®] A family is comprised of copolymers of vinylidene fluoride (VF₂) and hexafluoropropylene (HFP). B and F types are terpolymers of VF₂, HFP and tetrafluoroethylene (TFE), varying primarily in the specific balance between the three monomers. In general, the chemical resistance increases with fluorine content, with Viton[®] B and F types exhibiting higher resistance than Viton[®] A to certain chemicals such as concentrated nitric acid. Low-temperature flexibility, however, decreases with increases in fluorine content. Therefore, for applications requiring seals to exhibit resistance to heat and chemicals, as well as maintain low-temperature flexibility, a number of specialty types or grades of Viton[®] fluoroelastomer have been developed [8, 9].

For improved low-temperature flexibility, a perfluoro(methyl vinyl ether) or PMVE monomer is included in the polymer backbone. Viton[®] GLT, introduced in 1976, was the first commercial fluoroelastomer to use this monomer. This polymer provides the same resistance to heat, chemicals, and ionizing radiation as Viton[®] A [8, 9]. Viton[®] GFLT also includes the vinyl ether monomer to provide low-temperature flexibility but has other properties typical of Viton[®] F. A number of additional grades of Viton[®] GLT are available, depending upon specific formulation and processing additives. The general chemical formulae for Viton[®] GLT fluoroelastomer and individual monomers are shown in Figures 3 and 4 [10, 11], with general formulation and mechanical properties summarized in Table 2 [9].



where: x = 4 , y = 1 z = trace

Figure 3. General Chemical Formula for Viton® GLT Fluoroelastomer [10].

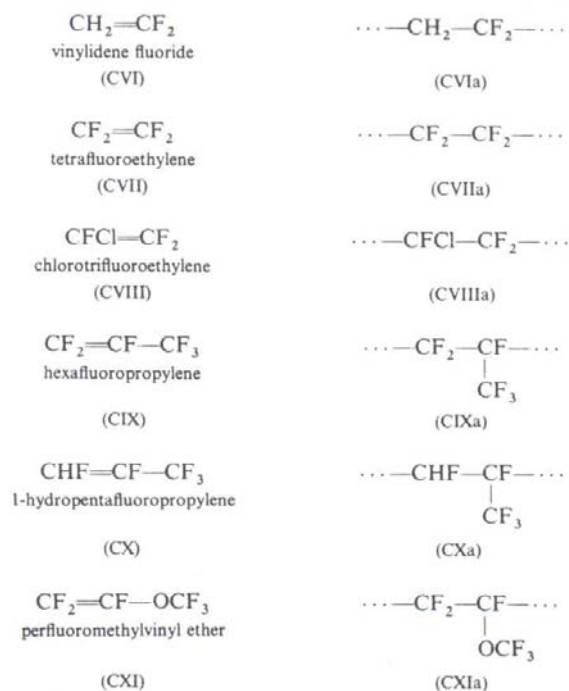


Figure 4. General Structure of Principal Fluoroelastomer Monomers [11].

Table 2. General Formulation and Properties of Viton® GLT Fluoroelastomer [9].

General Formulation (phr = parts per hundred rubber)

Viton® GLT base polymer, 30 phr MT carbon black, 4 phr calcium hydroxide, 4 phr Diak No.7 curing agent (organic triazine), 4 phr Luperc® 101XL (organic peroxide, Atochem North America), press cure for 10 min. at 177°C (350°F) or oven cure for 24 hr at 232°C (450°F).

Physical Properties

Color:	silver gray to pale amber (base polymer is translucent)
Mooney viscosity:	(ML-10 at 121°C (250°F)) ≈ 90
Specific Gravity:	1.78
Glass Transition Temperature (T _g):	-42°C
Thermal Expansion Coefficient:	1.6 x 10 ⁻⁴ mm/mm/°C (9.0 x 10 ⁻⁵ in./in.°F)
Brittle Point, °C (°F)	-51 (-59)
Clash-Berg Torsional Stiffness, 69 MPa (10,000 psi), °C (°F)	-31 (-23)
Temperature Retraction (TR-10)	-31 (-23)

Mechanical Properties

Room Temperature (24°C/75°F) 70 hr at 275°C (528°F)

100% Modulus, MPa (psi)	7.2 (1050)	4.8 (700)
Tensile Strength, MPa (psi)	18.8 (2725)	10.4 (1500)
Elongation at Break, %	185	170
Hardness, Durometer A	67	63

Low Temperature Properties

Temperature, °C (°F)	-40 (-40)	-30 (-22)
100% Modulus, MPa (psi)	-----	31.2 (4520)
Tensile Strength, MPa (psi)	39.9 (5780)	34.7 (5030)
Elongation at Break, %	60	160

Compression Set (%)
(after 70 hrs at temp)

Viton® GLT (standard)

Viton® GLT (low set formulation)

232°C (450°F)	53	36
200°C (392°F)	30	21
0°C (32°F)	47	48
-20°C (-4°F)	77	77
-30°C (-22°F)	73	73

Of the formulation or compounding variables involved, the most critical is the crosslinking or curing agent used to produce final physical properties of a specific compound. For Viton[®] fluoroelastomers, the majority of compounds are now crosslinked using bisphenol AF, first introduced in 1970. Since 1957, diamine curatives have been used for Viton[®] A types, with bisphenol now preferred over diamines to increase cure rate and to improve compression set, generally considered one of the most critical seal properties. In 1976, efficient peroxide curing of fluoroelastomers was made possible in the Viton[®] GLT formulation, with "G" indicating peroxide curability and "LT" for low-temperature flexibility. The peroxide system provides fast cure rates and superior physical properties in GLT and GFLT compounds which are not readily cured with diamine or bisphenol cross-linking systems [8, 9, 11, 12].

For specific products such as O-rings, the compounder (e.g. Parker Seals) procures the base resin and incorporates additives such as carbon black, antioxidants, UV stabilizers, acid acceptors, and processing aids to produce the final product. In most cases, such as Parker Seals compound V835-75, the specific formulation is considered proprietary. However, based on conversations with Parker Seals' technical representatives, only small additions such as carbon black are made to the Viton[®] GLT base polymer for the V835-75 compound and general properties such as chemical, radiation, and temperature resistance are essentially unchanged [13]. Parker's compound number, V835-75, simply indicates the base polymer (V=fluoroelastomer) and hardness (75 +/- 5 Shore A). The compound #835 is solely for identification and tracking purposes [14]. Properties of Parker Seals compound V835-75 are shown in Table 3 [15], with compounding effects evident when compared to properties of the base polymer (Table 2).

3.2 General Effects of Radiation/Temperature

No specific radiation resistance data for Viton[®] GLT base polymer or Parker Seals compound V835-75 was readily available from DuPont-Dow Elastomers, Parker Seals, or primary end-users. According to DuPont-Dow Elastomers, the radiation and elevated temperature resistance of Viton[®] GLT is essentially equivalent to that of Viton[®] A, although no test data was provided. This is assumed to be true based on similarity in polymer chemistry, structure, and thermal stability with specific effects of compounding and the PMVE monomer unknown under the exact service conditions expected.

In general, Viton[®] fluoroelastomers exhibit moderate resistance to ionizing radiation as compared to other elastomers, with compression set and other mechanical properties generally comparable to neoprene and nitrile rubber (NBR) at room to moderate temperatures (up to 200°F). As with other elastomers, such properties are just as dependent upon compounding as upon base polymer composition. At higher temperatures, however, Viton[®] and other fluoroelastomers such as Fluorel[®] (FKM), Kalrez[®] (FFKM), and Aflas[®] (TFE-P) exhibit a far superior balance of mechanical properties in conjunction with radiation exposure, depending upon other environmental conditions. Viton[®] and other FKM fluoroelastomers are not generally recommended for steam, hot water service, or for strong alkaline or amine solutions [8]. Where exposure to both dilute acids and strong alkaline solutions is expected, other elastomers such as ethylene-propylene rubber (EPR) or EPDM are often recommended [8, 14].

Table 3. Properties of Parker Seals Compound V835-75 [15].

<u>ORIGINAL</u>	<u>MIL-R-83485 TYPE 1, O-RINGS & COMPRESSION SEALS</u>	<u>V0835-75 ACTUAL VALUES</u>
Specific Gravity	As determined	1.75
Hardness points	75 ± 5	78
Tensile Strength, psi. min.	1600	1708
Elongation, % min.	120	180
Temperature Retraction, 10% (TR-10), °F, max.	-20	-22
<u>AFTER AIR AGING, 70 HRS. @ 75° ± 5°F. COMPRESSION SET</u>		
% of original deflection, max.	25	-- (14)
<u>AFTER AGING, 70 HRS. @ 75°F IN TT-S-735, TYPE III</u>		
Hardness Change, pts.	+5	77 (-1)
Tensile Strength decrease, % max.	30	1662 (-3)
Elongation decrease, % max.	20	165 (-8)
Volume change, % max.	1 to 10	-- (+2)
<u>AFTER AIR AGING, 70 HRS. @ 528° ± 5°F</u>		
Hardness change, pts.	+5	78 (0)
Tensile Strength decrease, % max.	35	1136 (-33)
Elongation decrease, % max.	10	235 (+31)
Weight loss, % max.	12	-- (-7)
<u>AFTER AIR AGING, 166 HRS @ 347° ± 5°F. COMPRESSION SET</u>		
% of original deflection, max.	25	-- (15)
18 hrs. cooling		-- (24)
<u>AFTER AIR AGING, 22 HRS @ 392° ± 5°F. COMPRESSION SET</u>		
% of original deflection, max.	20	-- (11)

With the exception of silicones and specialty elastomers such as FFKM perfluoroelastomers (DuPont's Kalrez[®]), the temperature resistance of Viton[®] is nearly unsurpassed. Viton[®] (all types) is rated to 400°F for "continuous" service, with the definition of continuous being somewhat vague. In most cases, the upper service temperature is based upon a specified period of time (e.g. 1000 hours) until a critical parameter such as compression set exceeds a pre-established value or acceptance criteria (e.g., 90%), in the absence of radiation or chemicals [14]. Although this is generally acceptable for conventional applications in which the O-ring may be periodically replaced, data for true long-term use is more limited. Such data is particularly limited for applications involving simultaneous exposure to ionizing radiation or chemicals as well as temperature. For such applications, material manufacturers and compounders always recommend testing in specific service environments.

The effects of radiation and temperature upon bulk material properties are very similar due to the nature of chemical and/or structural changes induced. Due to increased molecular activity, thermodynamic considerations, and/or kinetically-controlled mechanisms, damage to the molecular structure is generally manifested as one of two modes. Imparted energy can result in breaking of primary polymer bonds (chain scission) along the polymer chain or induce cross-links (bonds between adjacent polymer chains) to form. In most polymeric materials, including Viton[®] fluoroelastomer, one or both modes of damage may occur but one is usually dominant. In addition, the dominant mode may change depending upon the dose rate, presence of oxygen, and/or temperatures involved. Free radicals (OH[·], etc.) are formed during radiation energy absorption that can also further degrade the material [16-20].

Interestingly, some materials such as Teflon PTFE (polytetrafluoroethylene) are highly susceptible to chain scission, and therefore exhibit limited resistance to ionizing radiation although temperature resistance is superior to many other thermoplastics. Other polymers such as polyethylene tend to form cross-links, which is generally a more gradual damage mechanism that allows the material to remain useful to higher radiation doses, although temperature resistance of polyethylene is much lower than that of most other thermoplastics [16-20]. Therefore, the relationship between polymeric structure, crystallinity (long-range order), molecular weight, polymer composition, etc. and resistance to radiation, thermal degradation, stress-cracking, impact, etc. is highly complex and specific to each polymer type.

Many polymers, including most elastomers, also exhibit a significant difference in radiation and temperature resistance between oxidizing and non-oxidizing or vacuum environments, particularly at high dose rates, thus pointing to a strong synergistic relationship between radiation, temperature, and oxygen [16-20]. While this relationship varies in significance among polymer types, the general observation is that materials exposed to radiation and/or temperature in limited oxygen environments or vacuum exhibit significantly higher resistance, as defined by measurement of certain mechanical properties such as tensile strength and elongation. Such properties are usually measured for convenience and relative comparison, but are not necessarily the most relevant for all applications such as O-rings or gaskets. In addition, the relative change in some properties may be higher or lower than others, making complete evaluation of environmental resistance more complex. Therefore, critical properties should always be evaluated based on the nature of the application when possible.

3.3 Accelerated Aging of Viton[®] Elastomers

Although many references are available on the radiation resistance of plastics and elastomers, most provide only generic rankings or ratings of performance and radiation effects, based primarily upon tensile strength or elongation properties as a function of cumulative radiation dose. Of these, the majority of materials listed or tested are evaluated at room temperature following irradiation at high dose rates, and are not necessarily evaluated after extended exposure to elevated temperatures. In addition, such references rarely account for variation in formulation and processing, or the effect of long-term oxidation which can occur at lower dose rates. Actual long-term data for most polymers is also very limited, due in part because in most applications, polymeric components are periodically replaced as needed.

DuPont-Dow Elastomers (Viton[®] GLT producer), Parker Seals, International Seal Company (alternative Viton[®] GLT-based O-ring supplier), and subsequent O-ring customers (NASA, etc.) were contacted to obtain long-term performance history or data relevant to elevated temperature and/or radiation exposure, particularly for sealed systems. As Viton[®] GLT was developed for low temperature flexibility, long-term data at elevated temperature (with or without radiation) is practically non-existent. No relevant case histories were obtained and manufacturers were understandably reluctant to discuss seal performance due to product liability concerns.

DuPont product literature indicates that Viton[®] vulcanizates (raw polymers), irrespective of filler or type, can withstand 10^5 - 10^6 rads with little or no measureable effect on physical properties and up to 10^7 rads with moderate effect such as 50% loss of elongation and 50% increase in modulus. A cumulative dose of 10^8 rads severely reduces elongation to less than 20%. This data is for materials cured and aged at 400°F for 24 hours prior to radiation exposure, but does not indicate property changes at elevated temperature [21].

An early reference indicates that Viton[®] A disintegrated when irradiated to 10^6 rads in air at 200°C, but remained “usable” at higher doses in inert environments such as argon or diester oil [22]. Viton[®] B was indicated as being at least twice as resistant as Viton[®] A, but the difference is considered to be insignificant. This study was one of the first references to address the synergistic effects of time/temperature/radiation and proposed a method to calculate rates of stress relaxation from measured decay curves. Viton[®] A and B were evaluated using dose rates applied ranging from 2.9×10^4 to 7.8×10^5 rads/hr, with limited conclusions.

R. L. Clough and K. T. Gillen at the Sandia National Laboratory (SNL) are two of the leading and most prolific investigators in the area of environmental aging of polymers. They and others have investigated the synergistic effects of time, temperature, and radiation for many materials over the last 15-20 years. One of the earliest and more applicable references addressed the physical and chemical stress relaxation of Parker Seal compound V747-70, which is based on Viton[®] E-60C, a common low compression set formulation [23]. The material was evaluated by measuring stress relaxation at elevated temperatures and extrapolating to longer times at lower temperatures using superposition principles. Temperature tests were performed up to 319°C, using samples pulled to approximately 10% strain.

Chemical relaxation was assumed to be negligible below 110°C, with physical relaxation components subtracted from the total stress relaxation curve to isolate chemical effects. Time-temperature shifted stress-relaxation curves for Viton® V747-70 are shown in Figure 5 below. By calculating the slope (activation energy) for each curve and using a least-squares fit, a stress-relaxation vs log time plot for Viton® V747-70 at various temperatures was obtained (Figure 6). By crossplotting elevated temperature data and using shift factors determined from superposition, the time required to reach a given relaxation modulus was obtained (Figure 7).

Materials Consultation contacted Dr. Gillen to discuss the results of this investigation and to obtain insights as to the significance of such data upon the 9975 packaging application [24]. Using the curves in Figure 7, and assuming a temperature of 149-150°C (300° F), and a service life of 10 years (87,600 hours), a stress relaxation modulus ratio of approximately 0.6 is extrapolated. This represents a 60% reduction in stress retained in a sample extended to 10% strain at 300°F and held for 10 years. Although this value indicates excellent stability of mechanical properties at this temperature for such a long period, comparison of this data to an O-ring of the same material in compression is difficult, however, due to variation in molecular response to compression vs tension. Such tests were also performed in air environments in the absence of radiation and therefore do not necessarily represent the actual conditions within the 9975 shipping container. 10 years is also at the extreme end of the extrapolation curve which may lead to higher error in lifetime prediction.

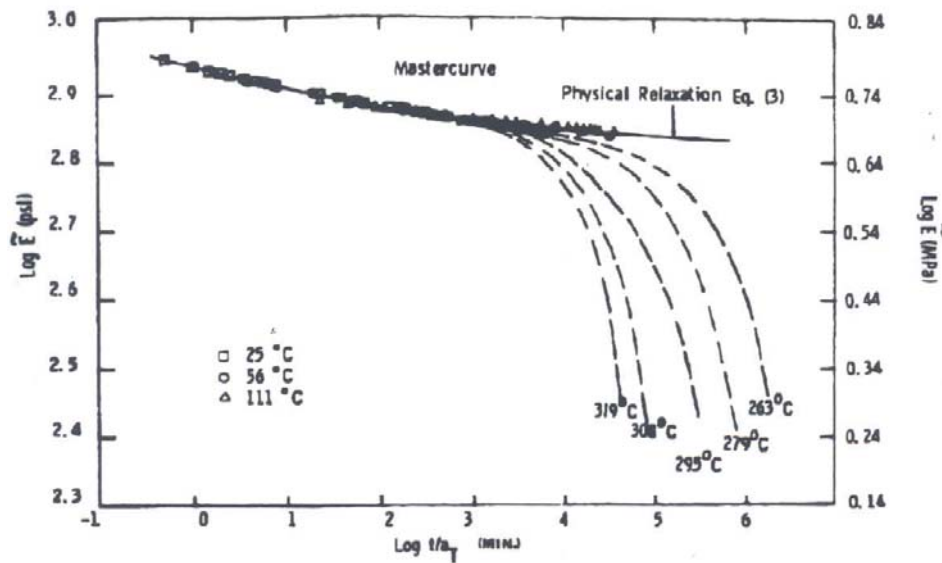


Figure 5. Time-Temperature Shifted Stress Relaxation for Parker Compound V747-70 [23].

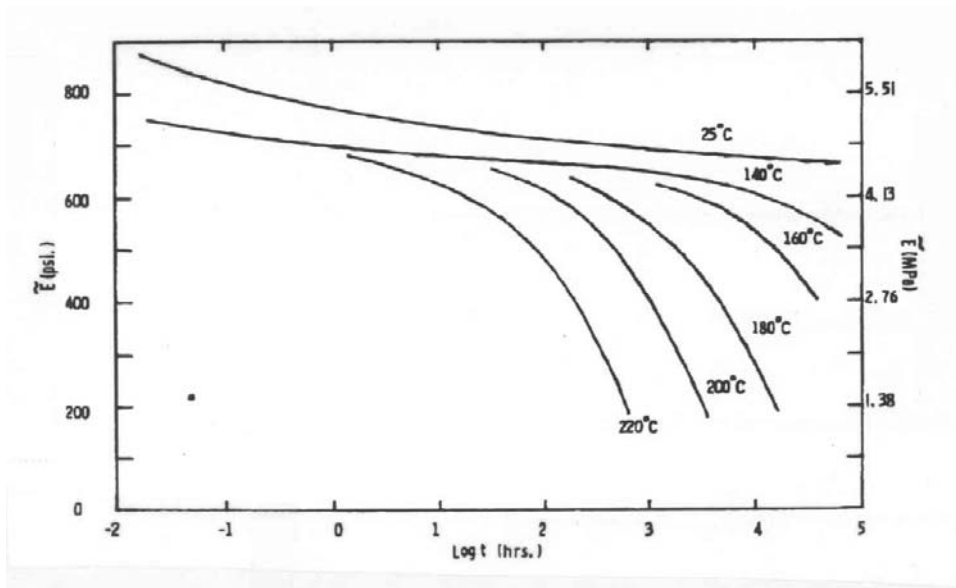


Figure 6. Stress-Relaxation Modulus vs Temperature for Parker Compound V747-70 [23].

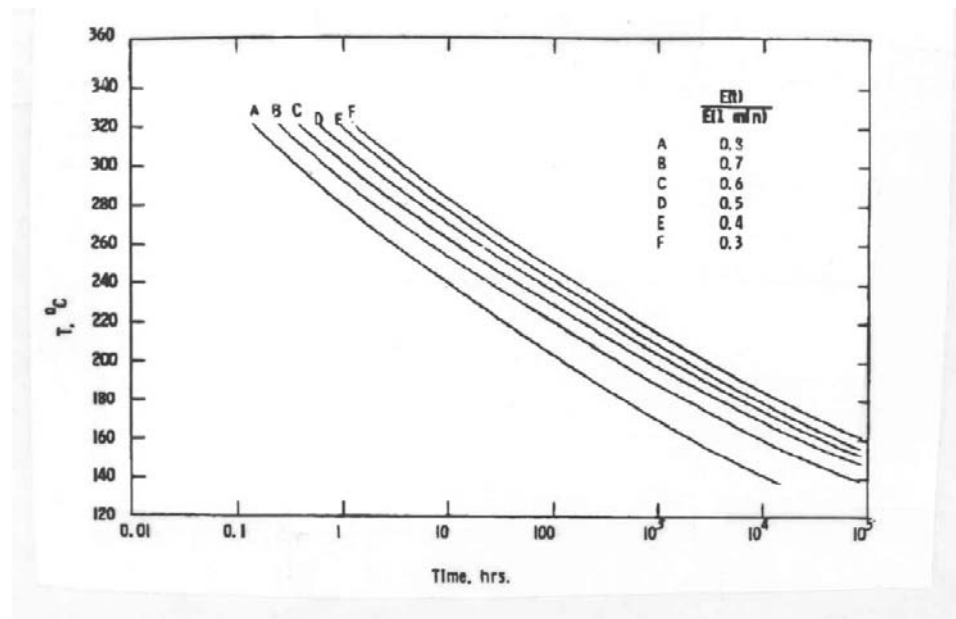


Figure 7. Time Required to Reach Relaxation Modulus Ratio at Temperature [23].

A subsequent Clough and Gillen investigation of the effects of radiation-thermal degradation of polyvinylchloride (PVC) and polyethylene (PE) cable insulation was among the first studies to show the significant effects of high vs. low dose-rate testing as well as the strong synergism between temperature and radiation [25]. Cable insulation materials were found to be severely damaged after only 2.5 Mrad actual exposure (25 R/hr for 12 years), well below that predicted by high dose-rate testing for the same degree of damage. Samples of both materials were separately exposed to elevated temperature (80°C), and to gamma radiation (5kR/hr), and to the same cumulative radiation dose at 80°C, with significant synergistic effects as shown in Figure 8 [25].

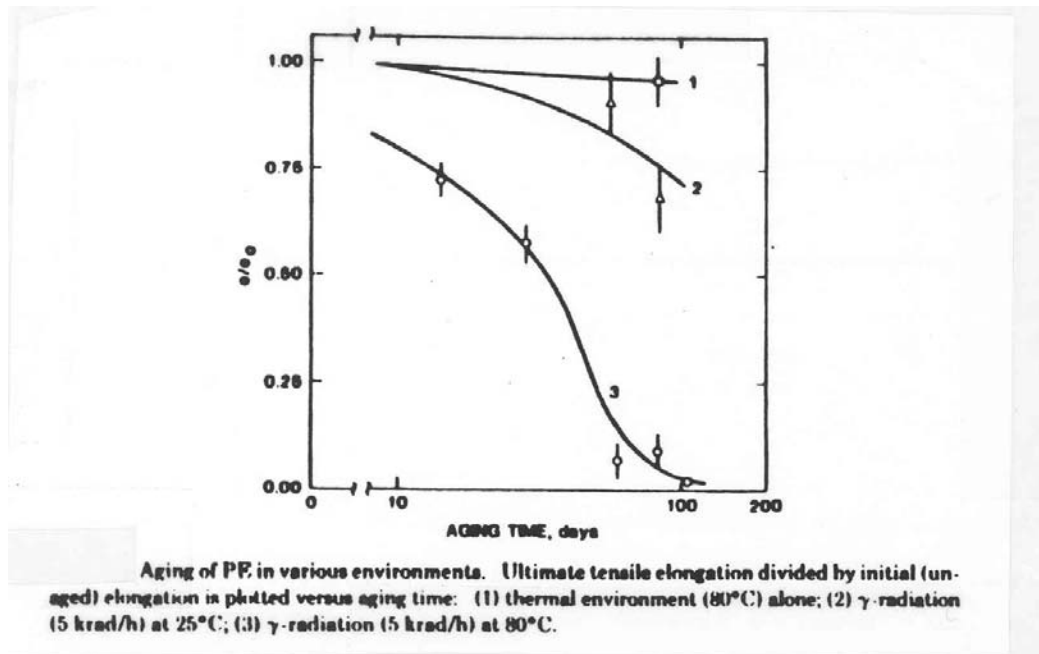


Figure 8. Synergistic Effects of Temperature and Radiation on PE [25].

This Clough/Gillen study was one of the first to identify that the order of sequential exposure plays a significant role in determining actual performance. For material irradiated at room temperature followed by thermal exposure, the elongation of PE was reduced to 17% of the initial value, approaching the degradation level induced by simultaneous exposure. When the order is reversed, elongation was only reduced to 72% of initial value. Another important observation by Clough/Gillen in this study was that strong dose-rate dependent effects occur at temperatures below levels at which thermal degradation alone occurs. This is attributed to progressive oxidation, as evidenced by the presence of carbonyl groups which were not observed in material exposed to the same radiation/temperature conditions in a nitrogen atmosphere. Degradation in both materials (PVC and PE) was attributed to peroxide formation from free radicals combining with oxygen, leading to a chain branching mechanism.

Clough and Gillen again evaluated the use of accelerated-aging tests for predicting long-term radiation degradation of organic materials, with particular interest in materials for nuclear containment facilities in commercial power plants and the use of LOCA (loss of coolant accident) scenarios to qualify safety-related equipment [26]. The issues of dose rate effects and synergism between temperature and radiation were addressed in a comprehensive review. Of primary concern was the extensive use of polymeric or elastomeric cable insulation. Organic protective coatings were also addressed but were considered less of an issue due to the higher radiation tolerance.

Of particular interest is the concept that during high-dose rate irradiation, relatively thick samples are oxidized only on the surface because the oxygen is used before it can diffuse into the material. For materials irradiated at a lower dose rate (such as in actual service exposure), oxygen is allowed to completely permeate the material, inducing progressively greater oxidation for an equivalent dose. For many years, the oxygen-diffusion limitation mechanism was widely believed to be the primary if not the only important mechanism leading to dose-rate effects. More recent evidence, however, indicates that other dose-rate mechanisms exist. Decker et.al. [27] eliminated diffusion effects by using thin samples and found chemical evidence of dose rate effects in different materials.

Many studies have also shown that most elastomers exhibit dose-rate effects with the magnitude or significance varying between materials. This is also observed to some degree for thermoset materials that are tolerant of higher cumulative doses than most elastomers and thermoplastics [16, 25]. Empirical formulas have been developed to account for the oxygen-diffusion mechanism by using an overdose effect. Such formulas can be misleading, overestimating damage in some materials and underestimating damage in others. For this reason, the use of such formulae has been dropped from IEEE standards for accelerated aging of electrical insulation [28]. Another effect that is ignored by the use of such formulas is the fact that certain properties in some materials may decrease at first but then level out with the value dependent upon dose rate [16-20, 25].

In the mid-to-late 1980's, R. L. Clough, K. T. Gillen, and other authors also investigated the phenomenon of heterogeneous oxidative degradation in irradiated polymers, with Viton[®] fluoroelastomer often evaluated due to common use in nuclear applications [29-34]. Most of the testing and analysis performed prior to such investigations involved the measurement or evaluation of bulk mechanical properties without regard to localized or heterogeneous degradation due to oxygen-diffusion limitations.

Viton[®] fluoroelastomer (type generally unspecified) was observed to primarily cross-link at high dose rates ($>10^5$ R/hr), whereas at lower dose rates, the material predominantly exhibits chain scission to yield a soft, stretchable material. Such behavior is completely ignored by accelerated aging tests at high dose rates only. These reports definitively establish that the use of accelerated, high dose-rate tests or "margin" to accurately predict long-term behavior at lower dose rates is inadequate and practically futile for Viton[®] and other elastomers which may exhibit the same behavior.

Additional investigations into physical techniques using a modulus profiling apparatus to detect heterogeneous degradation were also performed in this period, with Viton[®] fluoroelastomer consistently exhibiting dose-rate sensitivity and heterogeneous oxidation effects. Regardless of the degradation mode, critical seal properties such as compression set are affected due to either stiffening or stress-relaxation. Although the results obtained in such studies are meaningful, even the lowest dose rates evaluated were orders of magnitude higher than that assumed for the 9975 packaging assembly (<10R/hr). At such low dose levels, thermal effects are therefore assumed to dominate overall degradation of the material, with possible offset of cross-linking effects by softening due to slow chain scission depending upon oxygen availability.

Burnay and Hitchon performed measurements of leakage rates, sealing force, and compression set on polyurethane and fluoroelastomer (Viton[®] E-60C) seals over a limited range of temperature and irradiation conditions to compare these techniques for their effectiveness in determining seal lifetimes [35]. Time-temperature superposition principles were then used over a range of dose rates and temperatures. Compression set measurements were also performed in addition to sealing force measurements to correlate property changes with sealability. O-rings made of Viton[®] E-60C (low compression set compound) were tested at temperatures of 200 and 250°C under gamma irradiation at a dose rate of 10kGy/hr (10^6 R/hr).

Sealing force was effectively zero after 0.45 MGy (4.5×10^7 R) at 250°C and after 0.6 MGy (6×10^7) at 200°C. Measurements revealed that at 10kGy/hr and 200°C, compression set is approximately 100% (no recovery) after approximately 80 hours, when corrected for thermal expansion at the higher temperature. Krypton leak rates were difficult to interpret due to high permeability (i.e., gas detection was due to in part to permeation as well as actual leakage). Corrected compression set and sealing force curves are shown in Figure 9.

These results indicate that compression set tests accurately reflect the degree of sealing force retained, particularly when thermal expansion differential is accounted for in elevated temperature experiments. The value of 80 or 90% compression set often used for failure criterion of elastomeric seals is also considered to be valid based on sealing force measurements, with slight error on the side of safety. Krypton leak rate measurements also indicate that for an undisturbed seal, the lifetime is considerably longer than that predicted by compression set only, but that thermal or pressure cycling or mechanical vibration can result in failure if compression set is not minimized.

For superposition of performance, Burnay and Hitchon then performed a series of radiation exposure tests at temperatures from 150 to 300°C over a range of dose rates (0.11 to 11 Mrad/hr), followed by compression set tests. Linear plots for data were observed below 250°C, above which deviation from linearity occurs and is attributed to another dominant degradation mechanism at the higher temperatures. This data shows that at temperatures below 250°C, oxidative degradation is not the dominant process. The low activation energies observed suggest that chain scission and crosslinking from irradiation is the dominant process, particularly at the higher dose rates. Master curves for lifetime prediction are shown in Figure 10, with lifetime defined in this case as time to reach a known value of compression set (e.g. 90%).

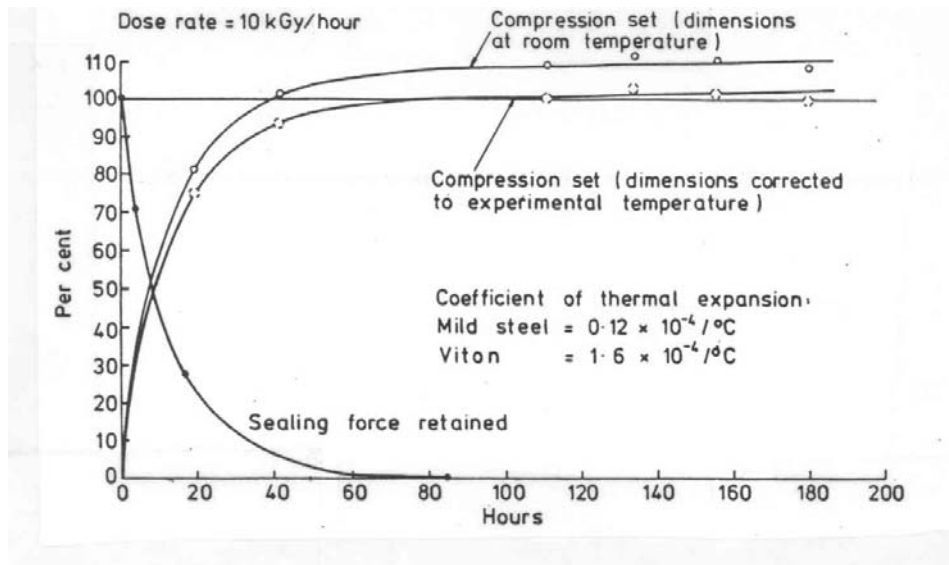


Figure 9. Corrected Compression Set and Sealing Force vs Time for Viton® O-Rings [35].

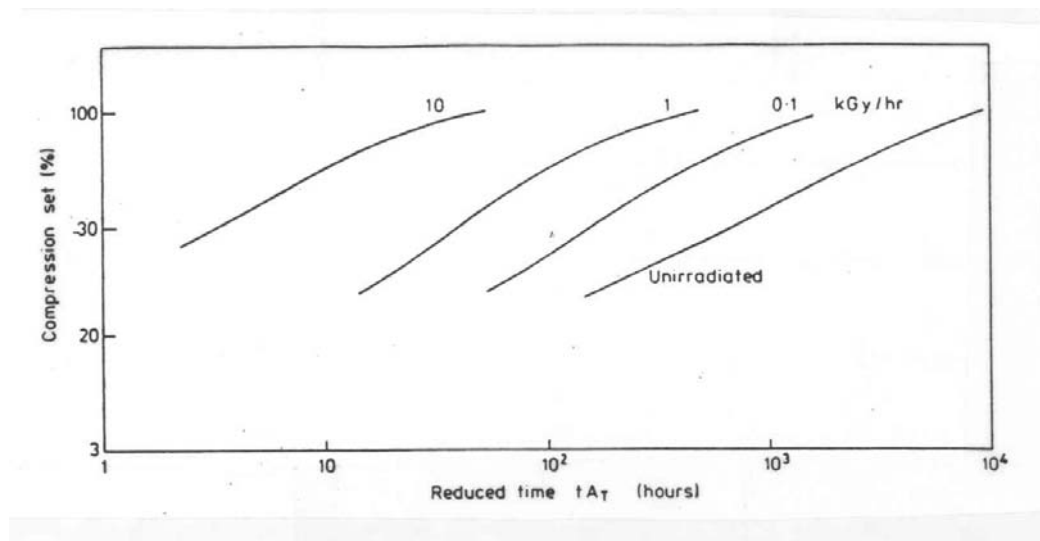


Figure 10. Master Curves for Compression Set vs Time/Dose Rate [35].

Using the thermal and dose rate shift factors determined from individual exposure tests, the formula shown below was used to predict time to failure as defined by the property of interest. Essentially, time to failure (t_f) is equal to the time to reach a known property value or failure criterion at the reference temperature (t_m) divided by the product of the thermal shift factor (a_T) and the dose rate shift factor (a_R).

Assuming a 100-year exposure at room temperature to reach 90% compression set (5 times 20-year shelf-life (unaffected properties during ambient storage)), and using shift factors ($a_T = 1.0$, $a_R = 6.5$ for 0.11 Mrad/hr) determined for 150°C in the Burnay/Hitchon study, the following estimate for O-ring lifetime is calculated:

$$t_f = t_m / (a_T \times a_R) = 100 \text{ years} / (1.0 \times 6.5) = 15.4 \text{ years to reach 90\% compression set at 150°C and 0.11 Mrad/hr}$$

Although the temperature (150°C) is comparable to that of the 9975 packaging assembly, the dose rate is still much higher than that anticipated (2 R/hr). Therefore, while this lifetime approximation indicates excellent stability, several factors are unaccounted for. Long-term permeation of oxygen, which may be limited by silicone lubricant and seal design, is not completely accounted for using such shift factors and high dose rates. Also, 90% compression set is high and could be reached in less than 100 years at room temperature, but is also tolerable in many static seals in stable environments.

Burnay and other investigators continued to refine the superposition approach in order to develop a predictive model of radiation degradation in elastomeric materials [36, 37]. Based on the previous model, thermal and dose shift factors for individual effects were combined into a single shift factor $a(T, D)$ to be used to superpose data at different dose levels and temperatures. Dose rate effects were superposed with a shift factor $b(T)$ as a function of temperature only. Dose to equivalent damage (DED) was determined based on 80% compression set at different temperatures for different compounds. A high temperature elastomer, unspecified but assumed to be fluoroelastomer-based, was modelled over a temperature range of 80-250°C (Figure 11). Based on the low radiation dose levels expected within the 9975 packaging assembly (2 R/hr = 5.6×10^{-6} Gy/sec), 80% compression set cannot be induced in the material at any temperature between 80-250°C assuming a total dose of 10^5 R (10^3 Gy) or approximately 12 years exposure.

In reference 37, Phillips and Burnay summarize superposition principles as applied to the most common seal materials used in the nuclear industry, namely fluoroelastomers, silicones, nitriles, and ethylene-propylene rubbers. Again, using 80% compression set as a "bounding" property for seal performance, the dose to equivalent damage (DED) and superposition principles used in previous studies were applied to a fluoroelastomer (type/compound unspecified). As shown in Figure 12, compression set measurements at 80°C over time are compared to that predicted by the superposition model using higher temperature data at a dose rate of 13 Gy/hr. From comparison of the predicted curves and actual measurements, the model is considered to be quite accurate for this particular material. Limitations of the model are that a single degradation mechanism is dominant, and that heterogeneous oxidation effects are ignored, particularly for higher dose rate exposures.

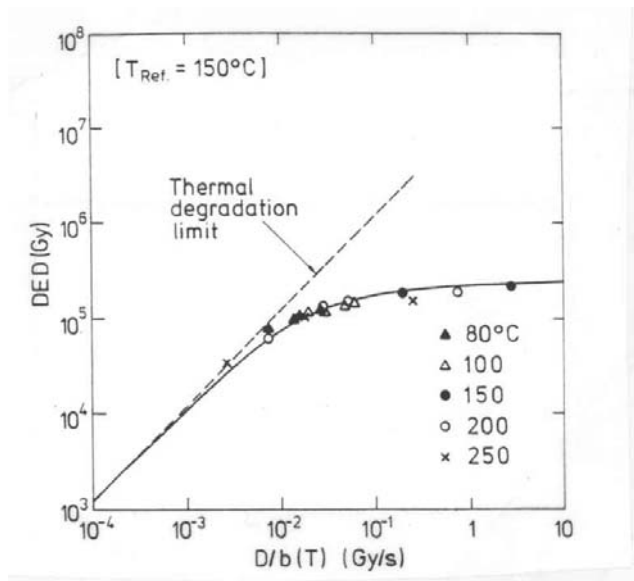


Figure 11. Dose to 80% Compression Set vs Dose Rate at 150°C [36].

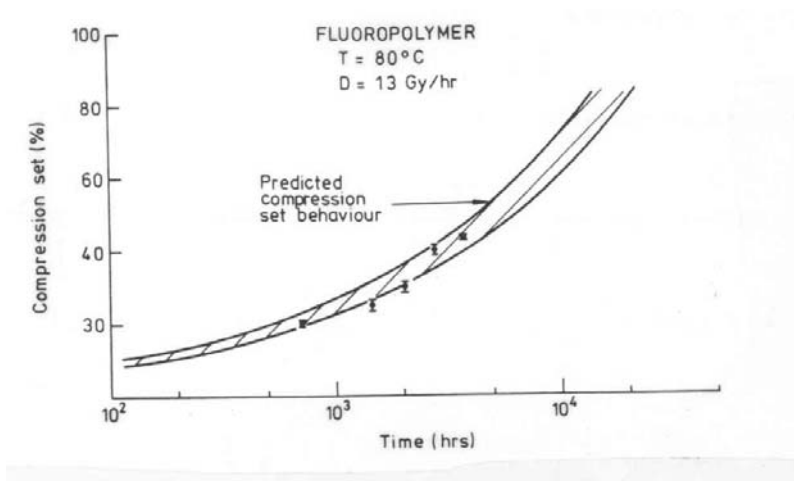


Figure 12. Compression Set vs Time at 80°C and 13 Gy (1300 R)/hr [37].

A Parker Seals report indicates that Viton[®] fluoroelastomer is not suitable for dose levels above 10^7 rads, without regard to formulation, temperature, or dose rate effects [38]. Tests performed on Parker Seals compound V747-75 (based on Viton[®] E-60C) indicate a 66.7% compression set after 10^7 rads as compared to 14.7% unirradiated, with tensile strength increased by 5%, elongation reduced by 32%, and hardness increased by only 1 durometer point [14]. Although test data was limited to high dose-rate exposure, the relative difference in effect of exposure on various properties is significant. Therefore, based on tensile strength or hardness data only, O-ring performance may be over-estimated. Such data reemphasizes the need to evaluate the effect of environmental conditions upon critical seal properties based on the nature of the application.

Gillen and Clough [39] again investigated the use of time-temperature-dose rate superposition as a methodology for extrapolating accelerated radiation aging data to low dose rate conditions. The study resulted in a procedure for deriving an isothermal curve for a given amount of damage versus dose rate at a selected reference temperature, thus allowing prediction of performance at much lower dose rates, such as those encountered in actual service. Four materials were evaluated, with data for two of these being in excellent agreement with 12 years actual exposure. Although none of the four materials (PVC, neoprene, Hypalon[®], LDPE) are fluoroelastomer-based, the methodology was shown to be applicable to various materials.

Materials stripped from actual unaged low-voltage electrical cables similar to those in service for 12 years were exposed to gamma radiation at dose rates ranging from 10Gy/h (1000 R/hr) to 10^4 Gy/hr (10^6 R/hr) and temperatures ranging from ambient to 150°C. Steady flow of air was supplied to facilitate continuous oxidation during irradiation. At a dose rate of 1 Gy/hr (100 R/hr) the time to reduce the elongation of neoprene by 25% is approximately 20 years at 25°C vs approximately only 1 year at 75°C, in the absence of other environmental conditions. Based on these results, extensive degradation of neoprene was predicted for exposure times exceeding 8 years at 45°C, the assumed normal temperature for the application.

Bartko and Siemon [40] evaluated service life of fluorocarbon elastomer seals (Viton[®] B) subjected to radiation and temperatures up to 270°C while immersed in silicone oil to minimize oxidation. In these tests, seal lifetime (as defined by pressure drop during hold cycle at 9500 psi) was reduced from 40 years at 145°C in the absence of radiation to approximately 21 years at 50°C with radiation, suggesting a significant synergism between radiation and temperature in an oxygen-reduced environment.

Service life tests were based on both simple and combined stress tests (radiation and/or temperature) to simulate the performance of such seals in nuclear reactor service. As hydrostatic pressure was not expected to deteriorate seal properties by itself or in combination with other conditions, it was eliminated from the test procedure as a variable. The effects of silicone oil were also considered negligible due to the established chemical resistance of Viton[®] to such fluids. In order to conduct combined stress aging tests, Bartko/Siemon assumed that the dose rate effects of radiation exposure on aging are negligible and that the activation energy of thermal degradation is independent of radiation effects. This is contradictory to the assumptions and results of Gillen and Clough in previous studies.

The service dose rate assumed in the Bartko/Siemon study was 1.2 R/hr, which is quite comparable to the 2 R/hr for the 9975 primary O-ring dose rate. The immersion in silicone oil limits the amount of oxygen available for oxidation, which is also comparable to the limited supply of oxygen within the shipping container. Service life in this study was based on leakage during pressure sealing tests rather than a direct measurement of critical mechanical properties such as compression set, making comparison with other data difficult. Seals were irradiated to cumulative dose levels of 1×10^6 , 1×10^7 , 3×10^7 and 1×10^8 rads at various (unspecified) dose rates, with the dose rates assumed to be significantly higher than the service dose rate of 1.2 R/hr. Seals exposed to radiation while immersed in silicone oil exhibited no significant change in properties at room temperature, presumably due to limited oxygen.

For combined testing, a 40-year service life at 1.2 R/hr was used to calculate a total dose of 4.21×10^5 rads. By dividing the total dose by the expected service life at each temperature tested, a matching dose rate for each temperature was obtained. The temperature/dose rates adopted were: 232°C at 145 R/hr; 250°C at 319 R/hr; and 270°C at 711 R/hr. Seals were placed into Pyrex® dishes filled with silicone oil, which were then placed into different ovens in a cobalt-60 hot-cell at varying locations to provide the proper dose rate/temperature combinations. Following exposure to the cumulative total dose, seals were then subjected to proof/leak testing as before.

Using superposition principles as in other studies, a service life estimate curve was generated for the specific compound with log time to failure determined as a function of the inverse of temperature at 1.2 R/hr (Figure 13). At 50° C, the time to failure (as defined in the 9500 psi leak test) is estimated as 184,000 hours or approximately 21 years as compared to 40 years at 145°C in the absence of radiation. At 300°F (422 K) and a dose rate of 1.2 R/hr, the lifetime of Viton® B seals in this study was estimated to be approximately 8,000 hours or 333 days.

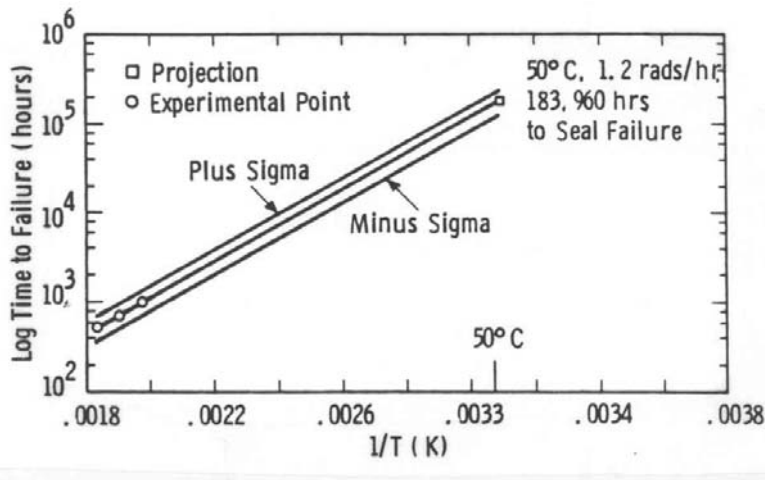


Figure 13. Service Life Estimate for Viton® B Seals Immersed in Silicone Oil [40].

Although experimental data was taken for temperatures (232, 250, and 270°C) higher than expected for the 9975 shipping container, the effect of temperature-radiation synergy is quite apparent as evidenced by the limited service life at the higher temperatures. A primary limitation of this study, however, is the use of leakage at 9500 psi as failure criterion. Such high pressures require only slight changes in physical properties such as compression set to produce leakage, whereas the same O-ring may seal perfectly well at much lower pressures. Therefore, although these results are insightful, they do not accurately represent conditions within the actual shipping container.

Therefore, the service life estimate for Viton[®] B at 300°F and 1.2 R/hr obtained from the Bartko/Siemon study (333 days) cannot be used for direct comparison with the shipping container application due to such high pressures. Assuming a linear relationship between leakage and pressure differential, reducing the pressure by an order of magnitude (950 vs 9500 psi) increases service life to approximately 10 years. Using 500 psi as a maximum value, pressure is reduced by a factor of 19, thus increasing service life to approximately 17.3 years. Such values are comparable to the 12-year storage plus shipping/transportation period.

This study is used as an example to show the difficulty in comparison of data between studies due to variation in failure criteria and test technique, rather than actual lifetime prediction for the 9975 packaging assembly O-rings. Such data is also compound-specific and should therefore be considered an approximation only. In addition, the relationship between leakage and pressure differential is generally considered to much stronger than linear and is generally proportional to the square of the pressure differential, thus possibly further increasing service life.

More recently, a few investigators have included Parker Compound V835-75 in their studies due to increased use in aerospace applications, presumably due to the superior overall balance of elevated temperature stability, ionizing radiation resistance, and low-temperature flexibility. Zee performed accelerated aging tests on four materials, designated only as silicone S383, silicone S650, Viton[®] V835, and Viton[®] V747 [41], which are assumed to all be Parker compound numbers [14]. Materials were exposed to a variety of thermal, oxygen, inert gas, vacuum, and gamma radiation conditions, with compression set and stress-relaxation evaluated as well as dynamic mechanical thermal analysis (DMTA). The temperature range examined was from ambient to 130°C, with low temperature behavior surprisingly not evaluated.

Compression set vs temperature (up to 200°F) as a function of percent squeeze or compression was first determined, with master curves for compound V835 shown in Figure 14. The vertical axis is the log of compression set and the horizontal axis is the log of the product of time and $a(T)$, where $a(T)$ is the shift parameter related to the activation energy of the thermal degradation process given as:

$$a(T) = A \exp(-E_a/RT)$$

where E_a is the activation energy, A is a pre-exponential constant, R is the gas constant, and T is the absolute temperature. The master curves show that for each material, compression set values for different squeeze levels overlap, indicating that temperature is the only influential parameter.

Compression set values are higher, however, for 10% and 40% squeeze values as compared to those at 20% squeeze, particularly at 200° F. Such behavior is consistent with known variation in elastomer recovery with different squeeze or deflection values, which occurs due to a number of reasons that are not completely understood [12, 14].

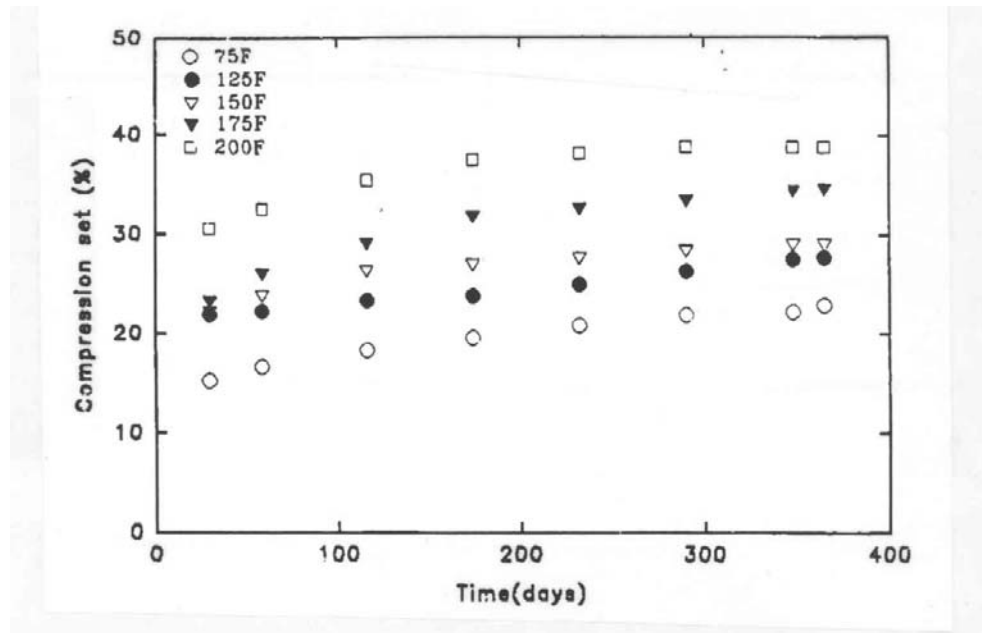


Figure 14. Compression Set Curves for Parker Compound V835 (20% Squeeze) [41].

Results of stress-relaxation tests on samples strained to 50% indicate that Viton® V835 exhibits a higher relaxation rate than either of the two silicone compounds when tested in either air, vacuum, or inert gas. Results for vacuum vs inert gas exposures reveal that compound V835 is more susceptible to outgassing under vacuum, as indicated by higher relaxation rates in vacuum at 100°C than in an inert gas atmosphere at 130°C. For samples exposed to gamma radiation (1 MeV) under strain, Viton® V747 was also included for comparison of fluoroelastomer compounds. Relaxation rates were observed to increase an average of two orders of magnitude over those due to thermal effects alone. Unstressed samples exhibited a much lower effect of radiation exposure upon stress-relaxation as compared to samples stressed during irradiation.

Although specific data for compound V835 was obtained in this study, conclusions drawn from Zee's report are considerably limited with regard to O-ring performance and sealability. Higher relaxation rates compared to silicone compounds at the temperatures tested are not unexpected due to the higher thermal stability of the silicone polymer structure (polysiloxane) and limited outgassing effects under vacuum are not considered significant for most applications. In addition, the compression set values observed (<50%) are highly tolerable for most static seals.

Bronowski and other investigators have recently evaluated leak testing techniques and the performance of elastomeric seal materials specifically used in radioactive material packages [42-44]. As failure of seals is considered to be more likely at high temperatures rather than low, the focus of these reports was to investigate seal testing and leak behavior at elevated temperatures.

Bronowski and Sorenson [42] evaluated the use of residual gas analyzers (RGAs) as an alternative to helium mass spectrometer leak detector (MSLD) technology typically used for sensitive leak detection. As temperatures increase, permeability of elastomeric seals increases and helium tracer gas more easily permeates through the material thus masking real leakage around the seal (Figure 15). Although this behavior can be accounted for to some degree by limiting helium exposure time thus minimizing gas diffusion, most leak tests are performed at room temperature at which such behavior requires longer periods of time to occur. As operational packages are expected to be at elevated temperature (and increased pressure), leakage behavior at elevated temperature is of significant interest but becomes more complex.

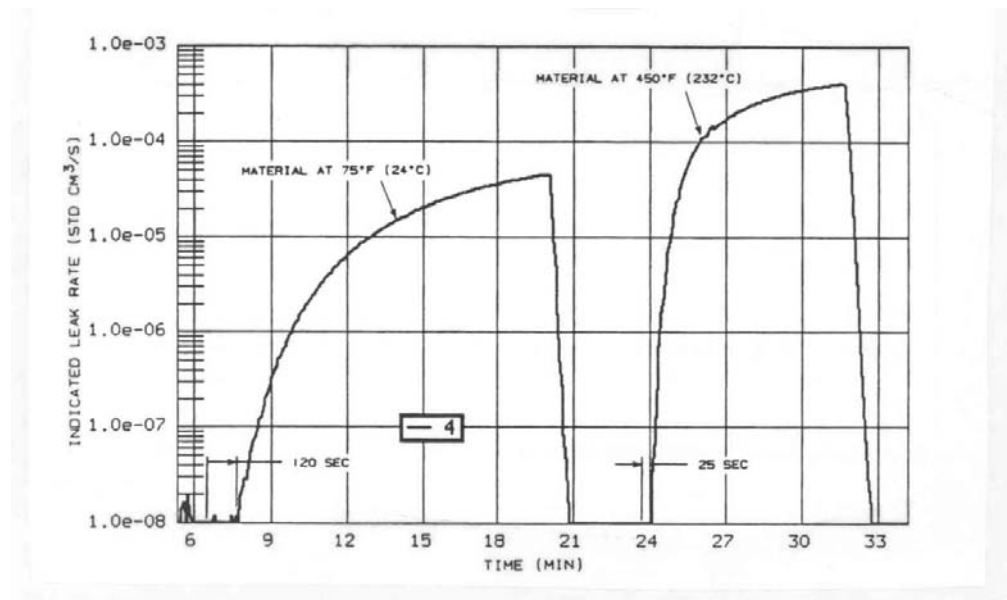


Figure 15. Helium Permeation Through Silicone Elastomer at 75°F and 450°F [42].

Unlike a common MSLD tuned to a single gas, an RGA allows the introduction of multiple tracer gases of varying molecular weight to reduce permeability while maintaining required sensitivity. One of the difficulties in tracer gas selection is to use a gas that is not hidden by normal background presence or influenced by the elastomer, particularly at elevated temperature. In order to isolate the RGA from background gases and those evolved from the elastomer during testing, a liquid nitrogen trap was added. Although overall background was reduced, most candidate gases, particularly halogens, were also condensed by the trap thus limiting detection.

After several trials, a 50/50 mixture of helium and neon was selected, with helium providing the primary leak rate measurement and the mass 22 isotope of neon providing a secondary measurement of bypass leakage only. A simultaneous rise in both signals indicated a true leak, while a delayed response between the two signals denoted permeation. Overall sensitivity to 5×10^{-9} cc/sec was demonstrated due to the use of helium as the primary indicator. Such a system is not recommended for routine leak detection, but was shown to be useful in leak detection of elastomeric seals at elevated temperature.

Bronowski and McConnell evaluated the response of several Parker seal compounds, including V835-75, to both low and high temperature extremes [43]. Performance characteristics examined included leakage rate vs temperature, physical property inspections, and tracer gas permeation. For leak testing, nominal compression of 25% was used as specified by most O-ring manufacturers for vacuum/gas service. A leak rate of 10^{-7} cc/sec was used as leaktight criterion, with leak rates higher than 10^{-4} cc/sec considered as failure. Low temperature tests were first performed, with O-rings and fixtures cooled to an initial temperature of 20°F (-7°C), then cooled in 10°F (5.5°C) steps with a leak test performed at each step. Fixtures were tested to failure or -90°F (-68°C), the lower limit of the chamber. Response at temperatures lower than the -40°F/°C regulatory requirement was evaluated for comparison with manufacturer's usage ratings.

With few exceptions, most compounds did not maintain a leaktight seal (10^{-7} cc/sec) at the manufacturer's low temperature ratings. This is assumed to be due to the fact that manufacturer ratings are generally based on liquid leakage ($>10^{-4}$ cc/sec) as encountered in most automotive or hydraulic applications, which is much less stringent. Many compounds did remain leaktight to the regulatory -40°F/°C temperature, with several others exhibiting average failure temperatures at or below the -40°F/°C target. Of interest, fluoroelastomer compounds V747-75 and V835-75 did not perform well, with only a few individual tests passing at -40°F/°C and average failure temperatures significantly higher. This was as expected as these compounds are only rated to the -40°F/°C temperature, presumably at higher leakage rates.

High temperature leak tests were performed using the residual gas analyzer technique as described in reference 42. Although compound V835-75 did not perform well in the low temperature tests, it was included in high temperature tests due to wide usage in radioactive material packaging designs. Target temperatures were selected based on manufacturer's upper temperature limit, as typically defined by 1000 hours and specific property changes, and temperature ratings for 10-hour use. Such values typically exceeded the standard ratings by 50-90°F (28-50°C), depending upon compound family. The higher temperatures were selected to evaluate response during and after fire accident scenarios. At high temperatures, thermal expansion of the seals allowed more complete filling of test fixture grooves, requiring fixtures to be redesigned.

Compound V835-75 was leak tested at 470°F (243°C) for 10 hours, and at 500°F (260°C) for 3 hours, with no leakage detected above the 10^{-7} cc/sec criterion. Although data obtained is useful to show short-term stability during elevated temperature scenarios, such data is not useful for evaluating long-term performance at lower temperatures. Compression set was not measured for test materials, and is not expected to significantly change during the short duration of the test and

at the temperatures involved. In addition, thermal expansion of seal materials may offset short-term changes in physical properties by expanding to fill seal grooves. Finally, such tests do not address pressure differential across the seal which develops in a sealed container, particularly when internal pressure is increased over time due to radiolysis, gas generation, etc. Therefore, although the material may pass a short-term leakage test under low pressure differential, it is likely that longer-term exposure will result in higher compression set and stress relaxation which can dominate thermal expansion effects. Such behavior may or may not result in actual leakage, however, depending upon pressure differential, leak rate/failure criteria, and environmental stability.

McMurtry and Hohnstreiter [44] investigated the dynamic response of O-rings to short-term closure movements, such as might occur during rapid pressure increase or pressure surge due to gas generation. A series of tests were performed on several materials including silicone, nitrile (NBR), and Viton[®], with no compound numbers identified. O-rings were placed between flanges and compressed using a 50 Kip MTS tensile machine, with the load required to completely compress the O-rings recorded for a variety of Durometer (hardness) values in both lubricated and dry conditions. Load was released quickly (78 inches/sec) so that the only load remaining was the weight of the top flange. Using flanges of two different weights, the dynamic response of the O-ring was measured.

As the hardness of O-rings increased, the force required for compression increased but dynamic behavior remained similar. Silicone compounds were the most responsive and Viton[®] compounds were the least, with the overall difference relatively insignificant. Most compounds exhibited significant damping behavior, with initial recovery to a position between initial and fully compressed positions, followed by complete recovery within seconds to minutes depending upon the material. Such results indicate that although initial response to such an event may result in a gap increase between the O-ring and mating surfaces, the O-ring will eventually recover enough to stop leakage.

The limitations of such testing, however, are that materials tested were unaged (assumed) and therefore exhibit near-ideal dynamic recovery. As thermal, radiation, and oxidation effects produce changes in molecular structure, dynamic recovery can be significantly reduced if not eliminated. Also, such testing does not account for thermal expansion of the O-ring material at elevated temperatures which may offset some reduction in dynamic recovery.

Ito more recently investigated the effect of temperature on radiation-induced degradation of fluorine containing elastomers, specifically Aflas[®] and Viton[®] [45]. Although not specifically mentioned, the Viton[®] formulation was stated as being a copolymer of hexafluoropropylene and vinylidene fluoride, which is consistent with the Viton[®] A base polymer. Materials were irradiated at high dose rates (2.5 kGy/hr) at temperatures ranging from 90-200°C. Tensile properties were measured at room temperature. Although critical properties such as compression set were not evaluated, the effects upon modulus, elongation, and tensile strength were significant for Viton[®] (A) at doses above 1 MGy, as would be expected.

3.4 Limitations of Accelerated Aging Tests

The simplest and yet most difficult approach is to use aging conditions as close as possible to the actual service environment. In the case of radiation aging, dose rates of 10^3 - 10^4 rads/hr in air are suggested, a dose rate incorporated into the International Electrotechnical Commission's Guide for Determining the effects of Ionizing Radiation on Insulating Materials [28]. The obvious drawback to this approach is the length of time required for test results when the required cumulative dose is high. In addition, the possibility exists that some dose-rate mechanisms are active below this level, thereby still underestimating the actual amount of degradation that occurs in service.

Another approach is to use oxygen overpressurization to eliminate the oxygen diffusion-rate limiting step in the degradation process. This is similar in concept to the development of ASTM D3911, the standard used to evaluate the performance of protective coatings under DBA conditions for nuclear power plants. Coatings are heated under pressure to increase internal oxygen/moisture absorption, then the temperature and pressure is suddenly decreased to simulate thermal shock and osmotic pressure effects that occur during rapid cooling.

The approach that appears to be most promising is the use of extrapolation or superposition principles applied to a series of accelerated-aging tests at varying dose rates and temperatures. Extrapolation is not always linear due to the different mechanisms that are present. The primary limitation of this technique is that numerous experiments must be performed to establish a bounding matrix of conditions. Care must also be taken to ensure that significant physical transitions are not encompassed by exposure conditions to minimize variation in the degradation mechanism. Also, the possibility always exists that other mechanisms are dominant at extremely lower dose rates such as encountered in actual applications. Finally, the criterion against which properties are to be evaluated must be carefully considered and should be best representative of actual service conditions.

J. C. Vivic et.al provided a brief summary on the use of accelerated aging techniques to estimate service life of elastomers, with several examples applied to failure life estimation for actual components [46]. Using the general Arrhenius-type relationship for reaction rate as a function of temperature, lifetime to failure (of varying definition) can be extrapolated for varying temperatures. Among the limitations of these techniques are that the use of a constant activation energy over the temperature range anticipated may not be valid, and that extreme extrapolation of higher temperature results to lower temperatures does not always provide an accurate result due to competing degradation mechanisms. In addition, specific failure criterion must be directly applicable to the service conditions and seal design.

Due to the synergy of all competing mechanisms, variation in compound formulation, and specific service conditions, accelerated aging can therefore never completely duplicate the accuracy of true long-term aging data in actual service.

3.5 Summary of Literature Review

Due to the wide range of variables and testing conditions such as temperature, radiation dose and dose rate, oxygen availability, and compound formulation, no direct relationships between studies can be made for a specific type of Viton[®]. Only a few of the more recent studies relevant to shipping containers have evaluated the performance of Viton[®] GLT and/or Parker compound V835-75, with only specific properties under specific conditions evaluated. Although such variability exists, a number of common characteristics and conclusions observed in the literature are summarized as follows:

- 3.5.1 Prediction of seal lifetime is complex and difficult due to competing mechanisms, dose rate effects, compound formulation, and variation in failure criterion and properties evaluated. Specific data for Parker Seals compound V835-75 is very limited, with only recent studies addressing specific short-term properties.
- 3.5.2 Although Viton[®] has been used for 40+ years, with Viton[®] GLT in use for over 20 years, no practical long-term aging data or case histories relevant to the 9975 shipping container were found. Practical applications of Viton[®] fluoroelastomer in service for 10-15 years are known to exist (flue gas chimney linings, expansion joints, etc.), but variation in formulation and service conditions precludes direct comparison. Additional investigation would be necessary to obtain relevant case histories of Viton[®] GLT-based O-rings in similar service. Manufacturers are also highly reluctant to discuss or predict seal performance for specific applications, particularly when radioactive material and/or personnel safety is involved.
- 3.5.3 Viton[®] fluoroelastomers in general are susceptible to dose rate effects; high dose rates tend to result in rapid increase in tensile strength and compression set, with rapid decrease in elongation, as expected. Low dose rates (<1E+05 R/hr) result in softening which could possibly offset such changes. Dose rates expected in the 9975 packages are much lower than those tested in most studies due to equipment/time limitations. Such low dose rates are expected to increase overall degradation only slightly above that induced by temperature/oxidation alone.
- 3.5.4 Compression set is one of the primary properties relevant to seal performance, but the significance of changes in compression set is highly dependent upon service conditions and stability thereof during service life. A seal that begins to leak at 9500 psi is not likely to leak at 150, 500, or even 1000 psi for a given amount of compression set. The use of compression set vs leakage testing is highly practical and the results are well correlated for the prediction of seal performance.
- 3.5.5 The resistance of Viton[®] GLT and other types of Viton[®] to elevated temperature is generally rated to 400°F for “long-term” service. This rating, however, is only “official” for use in dry environments in the absence of ionizing radiation. Upon simultaneous exposure to chemicals, moisture, and/or radiation, this rating becomes less-well defined. Therefore, manufacturers and suppliers traditionally

recommend that the material be tested by the customer or end-user in simulated or actual conditions.

- 3.5.6 Time-temperature-dose rate superposition principles applied to specific properties such as compression set are the best way to currently predict long-term performance of an elastomeric material from accelerated short-term tests, provided that degradation mechanisms are constant and chemical transition points are not traversed. Although this approach is meaningful, insightful, and generally accepted as sound engineering practice, there is absolutely no substitute for practical long-term aging data under known and well-documented conditions.
- 3.5.7 In the absence of high dose rates, the primary factor is oxygen in combination with elevated temperature. In the presence of ionizing radiation, both cross-linking and chain scission occurs, forming free radicals which destroy the polymer chain by breaking primary bonds. Based upon the limited oxygen environment within the containment vessel, however, the effects of oxidation in combination with radiation and/or temperature are expected to be significantly reduced. The use of silicone lubricant during O-ring installation is also believed to further minimize oxidation by providing a diffusion barrier, with the degree of benefit currently indeterminate.
- 3.5.8 Based on review of existing data for various Viton[®] compounds under varying conditions, prediction of absolute property changes and impact upon sealing performance is not possible without additional accelerated aging tests on specific compound(s) of interest. Assuming that degradation is dominated by temperature-induced cross-linking and possible chain scission contributions from low dose rate irradiation, compression set is estimated to be increased to a maximum of 70%. Values observed in most studies indicate such values are only reached at high dose rates, with 40-50% compression set more likely due to temperature alone. Chain scission contributions may lower this value, while being offset by limited oxidation. Such values of compression set are highly tolerable in static seals under stable environmental conditions.
- 3.5.9 Stress-relaxation as determined by tensile stress tests is not necessarily directly applicable to compression set due to variation in response to tensile vs compressive stresses, but such data can be useful for comparison. Stress-relaxation values of 40% observed in the literature under conditions similar to those in the 9975 shipping container are comparable but not equivalent to compression set values of approximately 60%.
- 3.5.10 Property changes are expected to occur more rapidly during initial exposure periods due to thermal effects, with damage rate decreasing but continuing over time due to diffusion-limited oxidation and slow chain scission. Seal performance is expected to be maintained based on environmental stability, but only a surveillance program can validate such a conclusion and determine actual effects.

4.0 PERFORMANCE EVALUATION

4.1 Seal Design

Pu-bearing materials are contained within a carbon steel food-service type can, which is bagged within either a nylon "6+6" copolymer or low-density polyethylene (LDPE) bag (100 g limit) [1]. The bagged inner can is then placed into a secondary carbon steel container prior to emplacement into the 9975 primary containment vessel (PCV). Although no credit is generally taken for such internal barriers, Pu-bearing material must first breach the inner can, polymer bag, and outer can before even reaching the primary containment vessel. Product must then migrate to the inner O-ring seal before direct contact is made, assuming ideal handling conditions. Therefore, alpha radiolysis effects of Pu-bearing materials upon the O-ring seals are currently considered negligible.

Cross-sectional views of the cone plug and the O-ring seal location are shown in Figures 16 and 17, respectively [47]. All dimensions with the exception of overall diameter(s) designated as "A" and "B" in the drawing are the same for both primary and secondary containment vessels. Based on a nominal O-ring outer diameter of 0.25", the percent compression or "% squeeze" is calculated to be between 21-28%, depending upon the gap at closure [1]. This value is typical for seal designs involving near metal-to-metal contact to balance properties such as %compression, compression set, pressure retention, and thermal expansion, as well as to minimize internal stress in the O-ring, which has been shown to affect leak rates and permeability [12, 14, 48]. As shown in the schematic (Figure 16), a leak test port is incorporated into the design to allow leak detection to be performed between the inner and outer O-rings on the containment vessel.

This % compression also corresponds closely to 25%, which is the value used to determine the % compression set in elastomers per ASTM test standards D395 [49] and D1414 [50]. Values of compression set can be misleading if not tested to identical %compression or %squeeze, as recovery ability of some elastomers has been shown to vary with the amount of original deflection [12, 14].

Cone plug threads and O-rings are lubricated with Krytox[®] (Dow), a fluorinated silicone grease for high vacuum service, prior to installation. The cone plug is then screwed into the threaded female section of the containment vessel until hand-tight. The cone plug nut is then threaded and tightened to a torque of 50 (primary) or 100 (secondary) ft.-lbs. The effects of radiation, temperature, and oxidation upon lubricant stability and subsequent release of halogens are expected to be insignificant at the dose levels and temperatures assumed for the O-rings, based on review of general temperature and radiation resistance data for lubricants of similar composition [51, 52]. Data for this particular lubricant under actual service conditions is limited, but can be investigated further if deemed necessary to confirm such behavior.

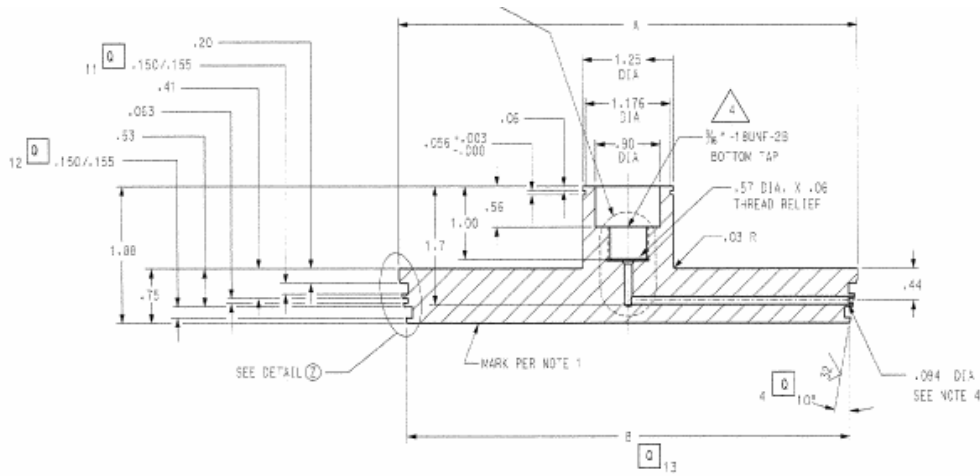


Figure 16. Cross-Sectional View of Containment Vessel Cone Plug [47].

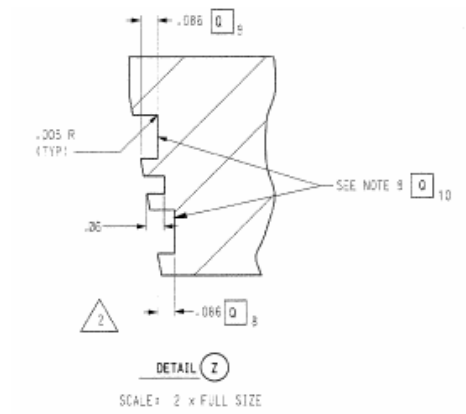


Figure 17. Cross-Sectional View of O-Ring Groove Design [47].

4.2 Critical Seal Properties

Throughout this report, the primary focus has been the effect(s) of environmental conditions upon critical seal properties over the anticipated storage period (currently assumed to be 10 years following initial 2-year transportation period). In this section, a more detailed review of such seal properties and their relative importance in maintaining a seal is provided. As physical integrity is not expected to be deteriorated to the point where sealing cannot be maintained, the limiting factors in O-ring performance are as follows:

- a) The amount of compression set and/or stress relaxation sustained during storage due to competing mechanisms such as temperature, oxidation, radiation, etc., and,
- b) The maximum internal pressure that can be retained at temperature to specified leak criteria, assuming that high compression set and/or stress-relaxation occurs. Such requirements are considered to be more applicable to post-storage transportation than to interim storage under stable conditions, but should be considered to bound actual performance.

4.2.1 Compression Set

Of the many properties required of an elastomeric material to maintain a seal, compression set is widely considered to be one if not the most critical, depending upon the particular service conditions and the nature of the sealing environment (liquid vs gas, etc.) [12, 14, 25, 36-42]. Compression set is generally defined as the amount of permanent deformation or recovery lost following a specified amount of deflection or applied load [14]. The difference between the initial, undeflected thickness of the material and the final thickness following load application and/or deflection to a specified degree is the amount of permanent "set" sustained. Compression set, as with many other properties of elastomers, is highly empirical in nature and is not necessarily directly related to other properties such as hardness, tensile strength, etc. Such properties of elastomers are highly dependent upon specific formulation and test technique rather than being strictly inherent to the material.

For test and evaluation purposes, ASTM test standards D395 [49] and D1414 [50] are used to determine compression set in elastomers by using either a known applied load or a percent compression, generally 25%. Percent deflection or compression is used more often as such parameters are more easily controlled and measured in actual application as compared to the applied load. The use of a constant percent deflection value therefore allows comparison of elastomers on an equal basis. An interesting phenomenon that has been observed in many elastomers is that the compression set value is not necessarily constant for a given material at varying levels of deflection [12, 14, 25]. Materials compressed much lower or higher than 25% can exhibit different compression set values, and values can also change with the time under compression. Although this is not completely understood, factors such as viscoelasticity, energy hysteresis, and molecular realignment are believed to play a role. For most applications, the amount of compression in the actual design is comparable to that normally tested.

Compression set can be affected in opposite ways in the same application, thus often nullifying the overall effects predicted for single mechanisms. This behavior is particularly true for elastomers in applications involving exposure to liquids [12, 14]. Whereas temperature, oxidation, and/or radiation may tend to increase compression set and reduce elasticity, liquid exposure can often result in absorption, volume swell, and softening which can sometimes offset the effects of compression set increase. This behavior is particularly beneficial in static seals in which service conditions such as temperature and pressure are relatively constant. Volume swell often makes re-installation of an exposed O-ring, for example, more difficult due to dimensional change and expansion upon release from the seal groove.

Therefore, although compression set is a very important factor or property for evaluating seal performance, it is often evaluated too conservatively particularly for static seals [14]. O-rings sustaining 80, 90, even 100% compression set (worst case; no force retention) can often provide an adequate seal depending upon the stability of the service environment. If conditions such as pressure, temperature, and/or mechanical vibration are increased, the probability of leakage increases at higher compression set. For the 9975 packaging assembly, environmental conditions during storage are assumed and expected to be fairly constant, with the exception of accident scenarios such as fire, flood, earthquake, impact, etc.

As discussed in the literature review, prediction of performance by using compression set is the most common practice, but there are limitations due to competing mechanisms and variability in failure criteria. The amount of compression set that can be tolerated in a given seal is highly dependent upon the pressure differential and leak rate criteria, as well as competing mechanisms of elevated temperature and low-dose rate irradiation under a limited oxygen environment.

Based on review of all obtained references and individual test techniques, temperature is the dominant damage mechanism at the temperature and radiation dose rates involved. Softening attributed to low dose-rate effects which has been observed for Viton[®] fluoroelastomers is expected to reduce or offset this to some degree, but the exact level is unknown. High dose-rate irradiation data indicates a maximum compression set of 66.7% following exposure to 10^7 rads gamma radiation, with the dose rate unspecified [14]. This data is for compound #V47-75 (based on Viton[®] E-60C) and not specifically for compound #V835-75.

Unfortunately, no definitive leak rate vs compression set vs temperature data exists for this specific O-ring compound at this percentage of squeeze for this particular seal design. Due to the number of variables involved, limited short-term testing is recommended. Such testing would focus on bounding the leak rate vs compression set for this particular compound rather than trying to extrapolate long-term performance from misleading short-term exposure tests. By inducing a known and measured amount of compression set into a particular O-ring and subjecting that O-ring to leak rate testing under pressure, the amount of pressure retained for a given amount of damage can be

determined. Corrections for thermal expansion and permeability at elevated temperature can also be applied. Such testing is currently in process, with the results to be documented in a separate report.

- 4.2.2 Permeability - The permeability of gas through an elastomer depends upon many factors, including but not limited to cross-link density, polymer type/structure, percent squeeze or compression, temperature, and gas molecular weight [12, 14, 36, 41, 48]. As cross-link density and other properties which control permeability are directly dependent upon formulation and compounding, permeability is considered to be highly compound-specific. No permeability data specific to Parker compound V835-75 was available from Parker Seals, and no specific data was available from DuPont-Dow Elastomers for the base polymer. Generic data available for certain gases at particular temperatures for generic material types is provided in the Parker O-Ring Handbook for comparison [14].

Due to the multiple barrier design concept (dual O-rings per vessel, two vessels), and established thermal stability of Viton[®] fluoroelastomer, permeability of the O-rings is expected to increase slightly with temperature up to 300°F but is not expected to affect the release of vessel contents. Hydrogen generated during radiolysis of plastic bags, water, etc. may permeate through the O-rings at a faster rate than the remaining container environment, thus reducing hydrogen build-up within the container. If permeability at elevated temperature is deemed critical to the application, additional testing/investigation is required.

4.3 Failure Criteria

The true measure of seal performance is usually whether or not a seal is maintained to a certain leakage criterion, rather than defining a specific property value. For transportation, the SARP currently specifies a 1×10^{-7} cc/sec helium leak rate with one atmosphere differential pressure across the seal boundary [1]. Helium is a very low molecular weight gas and permeates rapidly through elastomers; therefore, leak testing must be performed in a manner such that leakage is distinguished from permeation. As with permeability, gas leakage around an O-ring is dependent upon the pressure differential across the seal boundary. A leak rate of 1×10^{-7} std cc/sec at one atmosphere pressure differential will generally increase at higher pressures, as leak rate is generally proportional to the square of the pressure differential [14].

Therefore, the question of gas leakage and the rate at which it occurs is strongly dependent upon the amount of compression set sustained, temperature/thermal expansion effects, pressure differential, and environmental stability. Although vessel contents (metal, oxides, fluorides, etc.) are not expected to be released as they must first breach the product container barrier(s), outgassing of hydrogen and other gases through and/or around the O-ring(s) may occur as pressures within the container increase.

In the current SARP [1], results of testing to evaluate the structural integrity and leak-tightness of 9965 and 9968 containment vessels utilizing Viton[®] GLT O-rings at elevated temperatures and pressures are outlined but no reference is provided. Containment vessels were sealed and

pressurized to 1000 psig in a furnace. Temperature was increased gradually and held at each temperature for four hours until failure as defined by a 10^{-7} std cc/sec helium leak test. At 1000 psig (twice that currently assumed as the maximum normal operating pressure of 500 psig), the O-rings failed at approximately 783°F. Containment vessels were resealed with new O-rings, pressurized to 1000 psig and held at 600°F for 16 hours. Helium leakage from the containment vessel was not detected.

Such tests establish that the O-rings are able to maintain a leak-tight seal at 1000 psig at elevated temperatures for short durations. The effects of such short-term exposures, however, even to temperatures as high as nearly 800°F may not induce the same degree of physical property changes induced by longer-term exposure to lower temperatures and low dose-rate irradiation due to time/diffusion-limited oxidation effects. In addition, physical property changes were not reported and thus no direct correlations can be made between such short-term tests and long-term performance.

4.4 Post-Storage Transportation

For long-term storage, significant outgassing or leakage of product is not expected to occur. Degradation of the O-ring will be manifested in gradual changes in physical properties rather than bulk deterioration, cracking, crumbling, etc. The package also provides a number of multiple barriers through which the contents must travel or migrate for leakage to be of concern. In addition, the exposure conditions for secondary vessel O-rings are even less aggressive due to lower dose rates and possibly lower temperatures.

For post-storage transportation, however, increases in compression set over the duration of the storage period may limit the ability of a particular package to pass necessary leak-testing requirements prior to transportation. This is particularly true if a low leak rate criterion is required. If after extended storage, the packages must be subjected to such testing prior to transportation and do not pass, additional measures may be required such as O-ring replacement in secondary and/or primary containment vessels, overpacking, and/or establishing technical justification for reducing leak rate criteria for post-storage transportation. Therefore, in order to address such issues and to bound O-ring performance, scoping or confirmatory tests are recommended and are currently being performed in a parallel study.

In order to meet current schedule requirements, the scope of the tests is limited to the determination of leak rate as a function of pressure differential and compression set for Parker O-ring compound V835-75. Primary containment vessel O-rings are to be subjected to high dose-rate irradiation and/or elevated temperature exposures to determine the exposure conditions necessary to induce specific values of compression set. Target values of compression set to be evaluated are 40-50% (nominal), 60-70% (maximum predicted in service), and 80-90% (100% worst-case). O-rings with artificially-induced compression set values are to be installed onto cone plugs and into a primary containment vessel (with leak detection ports) per procedures outlined in the SARP. Leak rates vs. pressure differential across the seal boundary at room temperature for known compression set values are to then be determined.

4.5 Surveillance Program

As previously stated, based on all available data and consideration of service environment, significant physical deterioration of the O-rings within the seal groove is not expected. Changes in properties such as compression set, elongation, etc. are expected, however, with actual or absolute values dependent upon many competing degradation mechanisms. Due to the number of variables involved such as formulation-dependency, limited oxygen, presence of lubricant, low radiation dose rates, temperature, pressure differential, etc., a surveillance program is suggested to validate the assumptions made in this report and observations made in other short-term, accelerated aging studies.

Although long-term exposure to temperature in oxygen is expected to be the dominant degradation mechanism, secondary effects of cumulative low dose rate irradiation are currently indeterminate. The effect of limited oxygen availability and presence of lubricant may also serve to inhibit overall degradation, and the rate of degradation may also vary with time in service. Such questions can only be answered using a surveillance or monitoring approach. Based on the outcome of scoping tests currently in process, however, the need for surveillance may be reduced. If O-rings sustaining a high degree of damage (e.g. high compression set) are shown to pass applicable leak testing criteria, O-ring performance during storage may be considered less of a concern.

Evaluation of critical seal properties following years of exposure to the actual service environment also provides a truly unique opportunity to validate the technical basis for long-term storage of Pu-bearing materials utilizing elastomeric O-rings in the package design. Such a program would provide meaningful insights into degradation mechanisms, as well as identifying potential problems early in the degradation process, thus allowing the facility adequate time to address such issues. This would be especially useful if transportation of packages is anticipated within the 10-year storage period. The program could also be used to validate storage extension if necessary due to delays in development and implementation of processing and/or stabilization of the stored Pu-bearing materials.

The focus of the surveillance program would be to monitor/determine the effects of service environment upon critical seal properties such as compression set, permeability, elongation, dynamic recovery, etc., along with the effects (if any) of degradation products upon mating surfaces. The scope of the surveillance program could be limited to a small number of containers for statistical purposes, with those containers selected to represent bounding exposure conditions. Packages containing actual Pu-bearing product could be used, or surrogate source materials may be used to induce similar dose rates while minimizing contamination concerns associated with Pu-bearing materials. Such a program could be combined with evaluation of other degradation processes such as corrosion if deemed necessary. Details of such a program are to be outlined in a separate report. If a surveillance program is implemented, a separate accelerated aging study is also recommended to obtain compound-specific (V835-75) data which currently does not exist. The primary purpose of such a study would be to validate current accelerated aging methodology as applied to the packaging assembly application.

5.0 CONCLUSIONS AND RECOMMENDATIONS

Based on review of available literature and data relevant to the long-term performance of Parker compound #V835-75 and Viton[®] GLT fluoroelastomer, the following conclusions and recommendations are made:

5.1 Conclusions

5.1.1 O-rings consistent with Parker compound V835-75 based on Viton[®] GLT fluoroelastomer are expected to provide adequate sealing performance in the Model 9975 packaging assemblies for up to 10 years during storage of Pu-bearing materials subsequent to the 2-year shipping/transportation period. Significant degradation and loss of structural integrity of the O-rings is not anticipated due to the relatively low radiation dose rate, established thermal stability, limited oxygen, and static nature of the seal environment.

5.1.2 Although the O-rings are expected to remain intact and maintain sealing capacity, properties such as compression set and stress-relaxation are expected to be affected. Due to competing degradation mechanisms, however, prediction of the absolute value of property changes is not possible. Based on high dose-rate irradiation studies, a maximum compression set of approximately 70% is estimated. Based on limited extrapolation of heat-aging studies performed on similar compounds, stress-relaxation of approximately 40% is also estimated. Such values are highly tolerable in static seals with a relatively stable service environment, with the potential for leakage and leak rate being dependent upon actual pressure differential and environment stability.

5.1.3 The degree of property changes is most dependent upon actual temperatures and oxygen availability, which is expected to be further limited by the presence of silicone lubricant. The effect of limited oxygen is therefore assumed to be beneficial but the degree of benefit is currently indeterminate, due to cross-linking and/or chain-scission effects which can both occur in the absence of oxygen.

5.1.4 The performance of Viton[®] GLT-based Parker Seals compound V835-75 has been evaluated primarily on comparison of data obtained for other Viton[®] compounds under varying conditions, with some specific properties of compound V835-75 evaluated in a few studies. Although this approach is considered to be valid based on similar chemistry and resistance to elevated temperatures and/or radiation, test data for this compound is extremely limited. The majority of test data for compound V835-75 and Viton[®] GLT is focused upon applications requiring low-temperature flexibility, for which the elastomer was primarily developed. The resistance of Viton[®] GLT to ionizing radiation, elevated temperature, etc. is assumed to be comparable to that of other Viton[®] types based on similarity in chemistry and structure. The additional PMVE monomer which provides low-temperature flexibility is not expected to alter these properties significantly under the outlined service conditions.

Comment:

5.1.5 The response of aged O-rings to dynamic changes (not expected) in storage conditions due to vibration, increased temperatures, pressure surges, etc. under accident scenarios has not been evaluated in this report. Although O-ring performance is not expected to result in release of product under such conditions, behavior such as dynamic recovery, thermal expansion, permeability of aged O-rings is expected to be affected over time. Specific conditions may be reviewed in detail in a future report if deemed necessary, but existing data is expected to be very limited.

5.2 Recommendations

5.2.1 Based on review of all available data and assumed service conditions, O-rings made of Parker Seals compound V835-75 for the 9975 primary and secondary containment vessels are recommended for up to 10 years storage of Pu-bearing materials following the 2-year shipping period.

5.2.2 In order to bound long-term performance and address potential post-storage transportation issues, limited scoping tests are recommended and are currently in progress. The focus of the scoping tests is to establish leakage behavior under maximum normal operating pressures for O-rings which have sustained bounding values of compression set. Compression set will be induced by accelerated aging via radiation and/or temperature exposure.

5.2.3 Although performance of compound V835-75 based on Viton[®] GLT fluoroelastomer is expected to be comparable to that of other Viton[®] types, a short-term accelerated aging test program is recommended to develop compound-specific data. Such data would be beneficial in eliminating formulation-dependency as a variable in lifetime prediction and could be used to validate the assumptions and predicted behavior outlined in this report. The focus of the test program would be to determine critical seal properties (compression set, stress-relaxation, leak-tightness, etc.) as a function of elevated temperature and/or low dose-rate irradiation in the limited presence of oxygen.

5.2.4 In order to fully eliminate the limitations of accelerated aging tests and to completely account for the effects of competing degradation mechanisms, a surveillance program is recommended. The focus of the surveillance program would be to evaluate the effects of actual service environment upon critical O-ring properties and the effects (if any) upon mating surfaces. Details of such a proposed program will be outlined in a separate report to be issued at a later date.

5.2.5 Due to the specific need of the 9975 O-rings to meet the $-40^{\circ}\text{F}/^{\circ}\text{C}$ transportation requirement, FTIR (Fourier Transform Infra-Red) photospectroscopy analysis is recommended on a batch/lot basis if and when certification of material composition is unavailable or in question. Although storage temperatures will not be that low, O-ring material verification may be required for post-storage transportation. The Materials Consultation Group of SRTC coordinates commercial grade dedication of materials, with the Analytical Development Section currently providing FTIR analysis support.

5.2.6 In order to completely eliminate concerns over organic/polymeric material degradation, the development of metal seals may be considered. Although most time-dependent degradation mechanisms would be eliminated, modification of existing cone plug designs would be necessary to accommodate a non-elastomeric seal. In addition, higher torque values would be required to achieve a metal-to-metal seal. The effects of higher sealing stresses, material compatibility, thermal expansion, creep/stress-relaxation, etc. upon seal performance must therefore all be considered. Re-qualification of the package design may also be required, with associated impact upon schedules and costs.

6.0 REFERENCES

- 1) Safety Analysis Report – Packages, 9965, 9968, 9972-9975 Packages (U), WSRC-SA-7, Revision 6, October 1998.
- 2) T. E. Skidmore to B. R. Seward, SRT-MTS-98-4088, “Viton[®] O-Ring Lifetime Analysis for Model 9975 Packaging Assemblies”, June 17, 1998.
- 3) T. E. Skidmore to M. N. VanAlstine, SRT-MTS-98-4117, “Radiation Resistance of Viton[®] GLT O-Rings for Model 9975 Packaging Assemblies”, September 30, 1998.
- 4) N-CLC-F-00141, Rev.0, “N-CLC-F-00141, Rev 0, "Shielding Analysis for Plutonium Fluoride Payload in 9975 Shipping Container," September 1998.
- 5) C. Kelsey to D. Gromada, WSMS-CRT-98-0022, March 19, 1998.
- 6) WSMS-CRT-98-0097, S. Nathan to E. Skidmore, December 18, 1998.
- 7) ASTM D1418-94, “Standard Practice for Rubber and Rubber Latices – Nomenclature”, 1995 Annual Book of ASTM Standards.
- 8) “Viton[®] Selection Guide”, Technical Information Bulletin #301794A, 6/98.
- 9) “Viton[®] GLT Low Temperature Fluoroelastomer”, Technical Information Bulletin 300682A, DuPont-Dow Elastomers, 8/97.
- 10) R. J. Kaiser, G. A. Miller, D.A. Thomas, L.H. Sperling, “Synthesis of Transparent Fluorocarbon Elastomers: Effect of Crosslinker Type and Electron Beam Irradiation Level on Physical and Mechanical Behavior”, *Journal of Applied Polymer Science*, Vol 27, 1982.
- 11) D. C. Blackley, Synthetic Rubbers: Their Chemistry and Technology, 1983, p.285.
- 12) W. Hofmann, Rubber Technology Handbook, 1989. Hanser Publications.

- 13) Private communication, Mr. Dan Ewing, Parker Seals, 1-606-268-5013.
- 14) Parker O-Ring Handbook, ORD 5700, Parker Seals, O-Ring Division, 1990.
- 15) Parker Report #KJ0835, Test of Parker Compound V835-75 to MIL-R-83485, Type I, 10/10/89.
- 16) W. W. Parkinson and O. Sisman, "The Use of Plastics and Elastomers in Nuclear Radiation", *Nuclear Engineering and Design*, Vol. 17, 1971.
- 17) A. Charlesby, Atomic Radiation and Polymers, Pergamon Press, 1960.
- 18) F. A. Bovey, The Effects of Ionizing Radiation on Natural and Synthetic High Polymers, Interscience Publishers, 1958.
- 19) R. L. Clough, S.W. Shalaby, Radiation Effects on Polymers, ACS Symposium Series 475, 1991.
- 20) D. W. Clegg, A. A. Collyer, Eds. Irradiation Effects on Polymers, Elsevier Pubs., 1991.
- 21) "Radiation Resistance of Viton[®]", DuPont Data Bulletin V-A-4-303, 1978.
- 22) M. Ito, S. Okada, I. Kuriyama, "Radiation-Induced Chemical Stress Relaxation of Heat-Resistant Rubbers," *Reports on Progress in Polymer Physics in Japan*, Vol. 22, 1979.
- 23) E. A. Salazar, J. G. Curro, K. T. Gillen, "Physical and Chemical Stress-Relaxation of a Fluoroelastomer", *Journal of Applied Polymer Science*, Vol. 21, 1597-1605, 1977.
- 24) E-Mail communication with K. T. Gillen, December 22, 1998.
- 25) R. L. Clough, K. T. Gillen, "Combined Environmental Aging Effects: Radiation-Thermal Degradation of Polyvinylchloride and Polyethylene", *Journal of Polymer Science: Polymer Chemistry Edition*, Vol. 19, 1981.
- 26) R. L. Clough, K. T. Gillen, et.al, "Accelerated-Aging Tests for Predicting Radiation Degradation of Organic Materials", *Nuclear Safety*, Vol. 25, No. 2, 1984.
- 27) C. Decker, F. Mayo, H. Richardson, "Aging and Degradation of Polyolefins, III. Polyethylene and Ethylene-Propylene Copolymers, *Journal of Polymer Science, Polymer Chemistry Edition*, Vol. 11: 2879-2898, 1973.
- 28) IEEE Standard for Qualifying Class 1E Equipment for Nuclear Power Generating Stations, IEEE Standard 323-1983.

- 29) R. L. Clough, K. T. Gillen, C. A. Quintana, "Heterogeneous Oxidative Degradation In Irradiated Polymers", *Journal of Polymer Science, Polymer Chemistry Ed.*, Vol. 23, 359-377, 1985.
- 30) R. L. Clough, K. T. Gillen, "Inadequacy of Margin In Qualification Tests", SAND-83-2085C, presented at the International Symposium on Aging in Tests of Safety Equipment for Nuclear Power Plants, Paris, France, May 1984.
- 31) R. L. Clough, K. T. Gillen, "Physical Techniques for Profiling Heterogeneous Polymer Degradation", SAND-83-2171C, 1984.
- 32) K. T. Gillen, R. L. Clough, "A Kinetic Model for Predicting Oxidative Degradation Rates in Combined Radiation-Thermal Environments", *Journal of Polymer Science, Polymer Chemistry Edition*, Vol.23, pp. 2683-2707, 1985.
- 33) K. T. Gillen, R. L. Clough, C. A. Quintana, "Aging Studies of Elastomers Using A Modulus Profiling Apparatus", SAND-87-0326C, 1987.
- 34) K. T. Gillen, R. L. Clough, "Polymer Aging Insights Available From Modulus Profiling Data", *Polymer Engineering & Science*, January 1989, Vol. 29, No.1.
- 35) S. G. Burnay, J. W. Hitchon "Prediction of Service Lifetimes of Elastomeric Seals During Radiation Aging", *Journal of Nuclear Materials*, Vol. 131, 1985.
- 36) S. G. Burnay, "A Practical Model for Prediction of the Lifetime of Elastomeric Seals in Nuclear Environments", Chapter 33, Radiation Effects on Polymers, Eds. R. L. Clough, S. W. Shalaby, ACS Symposium Series 475, 1991.
- 37) D. C. Phillips, S. G. Burnay, "Polymers in the Nuclear Industry", Chapter 9, Irradiation Effects on Polymers, Eds. D. W. Clegg, A. A. Collyer, p.345-381.
- 38) D. Ramsdell, R. Barbarin, "Selecting Elastomer Seals for Nuclear Service", Parker Seal Group, Technical Bulletin # 23B, March 25, 1989.
- 39) K. T. Gillen, R. L. Clough, "Time-Temperature-Dose Rate Superposition: A Methodology for Extrapolating Accelerated Radiation Aging Data to Low Dose Rate Conditions", *Polymer Degradation and Stability*, Vol. 24, 1989.
- 40) J. Bartko, J. Siemon, Jr., "Synergistic Effects in Fluorocarbon Elastomer Seals Produced by a Combined Temperature and Radiation Environment", *Journal of Applied Polymer Science*, Vol. 42, 1991.
- 41) R. Zee, "Lifetime Prediction of Materials Exposed to the Natural Space Environment", NASA-39131-DO#8, 1993.

- 42) D. R. Bronowski, K. B. Sorenson, "Development of a Technique for the Leak Testing of Elastomeric Seal Materials at High Temperature", PATRAM'95 Proceedings, The 11th International Conference on the Packaging and Transportation of Radioactive Materials, December 3-8, 1995, pp.1775-1782.
- 43) D. R. Bronowski, P. E. McConnell, "Performance Characteristics of O-Ring Seals for Radioactive Material Packages When Subjected to Extreme Temperatures", PATRAM'95 Proceedings, The 11th International Conference on the Packaging and Transportation of Radioactive Materials, December 3-8, 1995, pp. 1791-1798.
- 44) W. M. McMurtry, G. F. Hohnstreiter, "Determination of Spring Modulus for Several Types of Elastomeric Materials (O-Rings) and Establishment of an Open Data Base for Seals", PATRAM'95 Proceedings, The 11th International Conference on the Packaging and Transportation of Radioactive Materials, December 3-8, 1995, pp. 1814-1820.
- 45) M. Ito, "Radiation-Induced Degradation of Fluorine-Containing Elastomers at Various Temperatures", *Radiation Physics and Chemistry*, Vol. 47, No. 4, 1996.
- 46) J. C. Vicic, D. Cain, S. Roldan, L. Su, C.C. Chen, "Life Estimation of Elastomers Using Temperature-Stress Acceleration Techniques", *Materials Performance*, June 1991.
- 47) Engineering Drawing #R-R4F-0013, Rev. 2., "9972-9975 Series Packaging Containment Vessel Details (U)".
- 48) J. Comyn, Ed. Polymer Permeability, Elsevier Pubs., 1985.
- 49) ASTM Standard D395-89, "Standard Test Methods for Rubber Property – Compression Set", 1995 Annual Book of ASTM Standards, Vol. 9.01.
- 50) ASTM Standard D1414-94, "Standard Test Method for Rubber O-Rings", 1995 Annual Book of ASTM Standards, Vol. 9.02.
- 51) R. M. Mortier, S. T. Orszulik, Eds., Chemistry and Technology of Lubricants, VCH Publishers, 1992.
- 52) R. O. Bolt, "Radiation Effects on Lubricants", CRC Handbook of Lubrication, Volume I: Application and Maintenance, E. R. Booser, Ed., CRC Press, Inc., 1983.

Acknowledgements

The author acknowledges the timely assistance from Susan Issacs and Glenda Dotson of 773-A Library Services and Jim Buchanan of EESD for the location and/or procurement of relevant references, Doug Flowers (EES/Drafting) for engineering drawings, technical representatives of Parker Seals and DuPont-Dow Elastomers for seal property data, C. F. Jenkins, Ph.D. for extensive technical review, and all others for design inputs and discussion of relevant seal properties.

The author especially acknowledges Ken T. Gillen, Ph.D. and Roger L. Clough, Ph.D. for their extensive work in the area of accelerated aging of polymeric materials, and for specific discussions regarding the useable service life of Viton[®]-based compounds in the 9975 packaging assembly application.