Synergistic Effects in Fluorocarbon Elastomer Seals Produced by a Combined Temperature and Radiation Environment

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SYNOPSIS

Fluorocarbon elastomer seals[1] were subjected to single stress radiation and temperature tests and combined stress tests with the seals immersed in silicone oil, to obtain a service life estimate. Their sealing capability was mechanically tested during the tests. In single environment tests the seals were resistant to temperature-induced stresses and very hard to radiation, showing no failures up to 10^8 rads. The combined tests, using three matched pairs of temperature and radiation dose rate, indicated a reduction in service life from 40 years at 145°C with no radiation to 21 years at 50°C with radiation, pointing to a significant synergism between radiation and temperature.

INTRODUCTION

The objective of this study was to develop an acceptable service life estimate for fluorocarbon elastomer rubber seals in a reactor environment. Until relatively recently, service life estimates were based on the results of single stress tests. Possible synergistic effects were, therefore, not considered. In addition, radiation tests were conducted using high dose rates, thereby minimizing the oxidative effects produced by oxygen diffusion at normal low-dose-rate environments.

Because of the complexity of a combined stress environment and the present paucity of experimental information, no standard accelerated aging procedure exists at present. The procedure we adopted for the rubber seal tests incorporated a mix of single stress tests and combined stress tests. The particulars of the procedure were based on experience gained in previous in-house testing which, in turn, is an extension of theoretical and experimental work conducted at the Sandia National Labs.[1-3]

In normal operation the rubber seals are immersed in a silicone oil and are subject to thermal, radiation, and mechanical stresses. The mechanical stress is provided by hydrostatic pressure. In formulating a combined stress aging test procedure, one exercises engineering judgment in selecting the more significant environmental components. In our assessment, the hydrostatic pressure would not be expected to significantly affect the seals by itself or in combination with the other stresses and was eliminated from the test procedure. The procedure focused, therefore, on thermal and radiation stresses, exclusively.

EXPERIMENTAL

In order to conduct combined stress aging using simultaneous radiation and thermal aging, it is important to verify that the dose rate effects of radiation exposure on material aging are negligible and that the activation energy of thermal degradation is independent of radiation effects. Based upon this information, radiation dose rates can then be matched to accelerated thermal aging, so that an appropriate combined stress aging test matrix can be developed. This combined stress aging test matrix takes into account the expected service life at the accelerated aging temperature, to which a radiation dose rate is matched, so that the expected dose over the life of the test is equivalent to the total dose expected at the in-service dose rate. In this case, 1.2

[1] The elastomer seals were prepared from Viton B, a fluorocarbon elastomer supplied by the E. I. DuPont Company.

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rads/h is the expected in-service dose rate. The initial assumption to be made here is that no thermal-radiation synergism exists. This, of course, will be proved or disproved by the actual test data.

The procedure adopted for this study was based on the anticipated operating environment the rubber seals would experience. Because they would be constantly bathed in silicone oil all tests were performed in the identical oil. First, it would eliminate, or at least reduce, oxygen which in conjunction with radiation and temperature has a deleterious effect on organic materials. Second, any synergism between radiation, temperature, and the oil would be incorporated into our results.

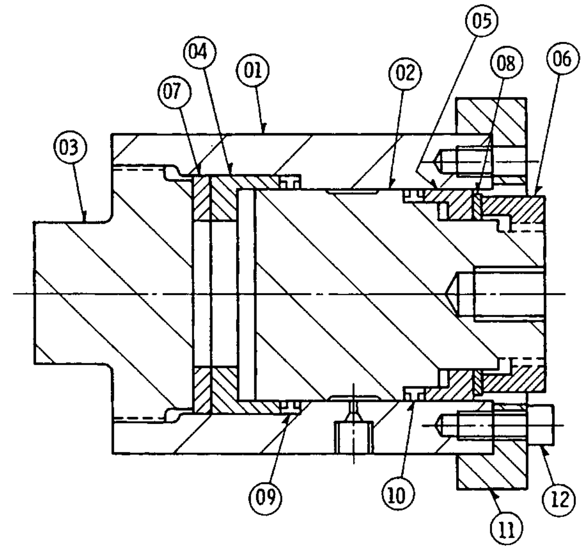
The only significant nonmechanical stresses to which these seals are subjected are temperature and radiation. The anticipated operating temperature and dose rate over the 40-year operating life is 50°C and 1.2 rads/h, respectively, for 40 years. Thus, temperatures and dose rates employed in the combined stress aging tests must be elevated for short test periods to accelerate aging and produce equivalent operating lifetime effects. In the case of temperature, care has been taken to select temperatures that do not introduce mechanisms other than those expected at the operating temperature.

The general procedure for combined stress aging is to first run single stress tests to determine what effects the individual stresses have on the material properties before combined stress testing is conducted. Synergistic effects can then be more readily identified by comparing the results of the combined stress tests with those of the single stress tests. In the following sections we will discuss in sequence rubber seal and test fixture design, proof testing, single stress testing (thermal and radiation), combined stress testing, and analytical procedures.

Rubber Seals and Test Fixture Design

In order to develop significant test data and avoid the problems associated with modeling seal performance based on basic material properties such as modulus and tensile strength, it was decided to proof test rubber seals after accelerated aging. For such testing, a fixture was required that allowed for rapid assembly and disassembly to replace seals for testing. Additionally, the fixture would have to allow for pressures in excess of 9500 psi. Another requirement imposed was that rubber seals used in this test program be an off-the-shelf size. Based upon these requirements, the test fixture shown in Figure 1 was designed and fabricated.

The fluorocarbon elastomer (Viton B) seals were purchased in pairs of 1 rod seal and 1 piston seal,



Item	Part Name	Item	Part Name
01	Housing	07	Washer
02	Piston	08	Thrust Race
03	Plug	09	Rod Seal
04	Ring	10	Piston Seal
05	Ring	11	Support Plate
06	Nut	12	Bolt

Figure 1 Seal test fixture.

AS 568-A uniform O-ring dash number 334. The rod seals had an O.D. of 2.995 in. and I.D. of 2.623 in. and the piston seal had an O.D. of 3 in. and an I.D. of 2.628 in.

Proof Testing

Seals were loaded hydrostatically from 0–9500 psi at 0.2 in./min, held at 9500 psi for 5 min, then unloaded to 0 psi at the same rate. The total piston travel during a test cycle was 0.1 in. This procedure was repeated four times per test sample pair. If a pressure drop was noted during the hold cycle at 9500 psi then the test seal pair was considered to have failed. Sample pairs that did not fail during the initial four-cycle loading were then grouped together. From this group, seal pairs were selected at random. The paired seals were reversed in the test fixture and the entire test sequence repeated.

Single Stress Testing

Thermal Aging

Thermal aging of the seals was conducted by submersing several pairs of seals in glass containers filled with SF 1145 silicone fluid, hereafter, silicone fluid. A total of four glass containers, each containing one group of seals was used. Each container was then placed in circulating hot air ovens set at 232°C, 177°C, 121°C, and 74°C. Periodically, at least two sample pairs were withdrawn from the ovens at each test temperature, hardness measurements were made and proof testing conducted as previously described. The time at elevated temperature required to achieve a failure (leaking of seals during the pressure cycle) was intended to be used to construct an Arrhenius plot of expected service life vs. service temperature for thermal aging only. This data would then be used to develop the combined stress aging test matrix. However, due to the exclusion of oxygen from the test environment by submersion of seals in silicone fluid, the time to failure was exceptionally long even for the highest temperature aging conditions. This was unanticipated and resulted in only one data point being collected, that at the highest test temperature, 232°C. A decision was made to construct a one-point Arrhenius curve by passing a line with the slope of Ea/k through the test point obtained at 232°C, where Ea is the activation energy of fluorocarbon elastomer and k is the Boltzmann constant. The fluorocarbon elastomer activation energy used had previously been obtained at Westinghouse R&D in an internal study on the retained sealing capability of O-rings. The data from that study is shown in Figure 2. The one-point Arrhenius curve is shown in Figure 3 and the results of the hardness measurements made on aged seals are given in Table I.

As can be seen by examining Figure 3 and comparing it with Figure 2, only a small shift was required to translate the slope of the Arrhenius curve based on retained sealing capability for O-rings, to an Arrhenius curve based on retained sealing capability of the test seals. Figure 3 was then used in conjunction with dose rate aging tests described in the next section to devise a test matrix for combined stress aging.

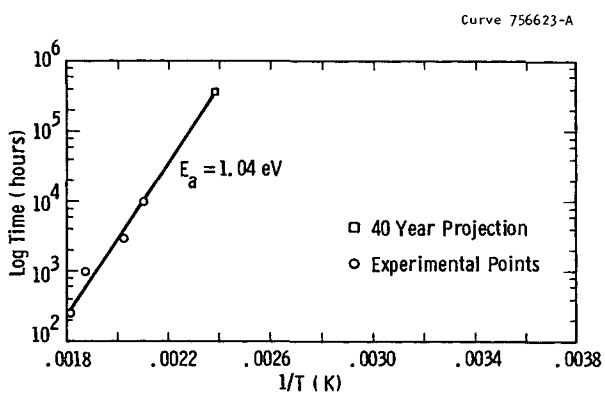


Figure 2 Retained sealing capability of viton O-rings.

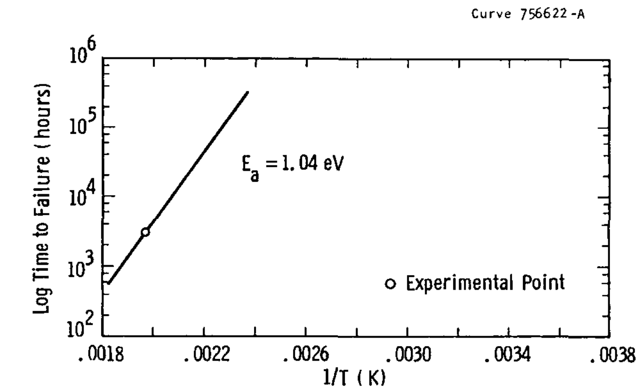


Figure 3 Arrhenius plot for viton seals based on thermal aging.

Radiation Aging

Radiation tests were first conducted at the Westinghouse R&D Center ^{60}Co hot cell. Samples of rubber seals were immersed in silicone oil and subjected to doses between 10^6 rads and 10^7 rads. The rubber seals were proof tested following irradiation and essentially no change was observed. Seal samples, also immersed in silicone oil, were then sent to the Cornell University gamma ray facility for exposure to doses of 1×10^7 rads, 3×10^7 rads and 1×10^8 rads at various dose rates. No changes were observed following these irradiations either. All irradiations were performed at room temperature. It was thus obvious that the seals were quite radiation hard in this environment and the only question was whether the combination of thermal stress and radiation stress would prove deleterious.

Table I Hardness as a Function of Thermal Aging

Time (Days)	Temperature			
	232°C	177°C	121°C	74°C
1	85, 80	84, 78		
2	87, 80	86, 79		
4	85, 82	84, 80	81, 75	80, 75
8	88, 84	82, 78		
32	97, 93	86, 85	82, 79	84, 80
128	60, 60 (D)	85, 82	85, 81	77, 77

Notes: (1) All hardness measurements made using a Shore A scale except where noted by D, indicating Shore D scale. (2) The two numbers are the hardness values for the pairs of seals tested at the time indicated for each temperature.

Combined Stress Testing

Development of Combined Stress Aging Test Matrix

The accepted practice for combined stress aging tests is to run at least three tests using pairs of temperatures and dose rates that are as widely different within the limits of practicality and the temperature constraints mentioned previously. Synergistic effects will either cause earlier failure (positive synergism) or later failure (negative synergism) than that expected from a simple combination of the effects due to single stress aging.

In order to develop a combined stress aging test matrix, the data collected for single environment stress aging were required. Additionally, it was required that the effect of dose rate on total sustainable dose to failure be negligible, as was the case for this material. Based on the data of Figure 3, an expected life in excess of 40 years at 145°C was determined. Given that the expected seal operating temperature is only 50°C, a large margin of excess temperature capability existed. However, in this data any synergism or added degradation due to radiation damage was not considered. Therefore, an assumed life of 40 years at 50°C was used to construct the combined stress aging test matrix.

Based upon the data given in Figure 3 and our previous experience with thermal aging of rubber seals and the lack of observed failures, three elevated temperatures in excess of the previous test temperatures were chosen and appropriate aging times determined. That is, assuming no synergism that would result in a change in Ea, but only an acceleration of the reaction rate, elevated temperatures were chosen and expected service lives at these elevated temperatures were determined from the curve given in Figure 3. The temperatures chosen and the corresponding service lives were 232°C, 3072 h; 250°C, 1344 h; and 270°C, 576 h. Now, assuming a 40-year life and a service dose rate of 1.2 rads/h, a total dose of 421,000 rads would be expected. By dividing this 40-year dose by the expected service life for each temperature a matching dose rate for each temperature was obtained. Table II shows the results of these calculations.

Table II Temperature, Radiation Dose Rate, and Time Correlation

Temperature (°C)	Time to Failure (h)	Radiation Dose Rate
232	3072	137 rads/h
250	1344	313 rads/h
270	576	731 rads/h

Notes: (1) Total dose of 421,000 rads computed, based on an *a priori* service life estimate of 40 years at 50°C and 1.2 rads/h dose rate. (2) Time to failure taken from Arrhenius plot shown in Figure 3 for the test temperature of column 1 of Table II.

Combined Stress Aging

The temperature–dose rate combinations adopted for this study were 232°C, 145 rads/h; 250°C, 319 rads/h; and 270°C, 711 rads/h. We have designated the aging tests associated with each of these conditions as tests 1, 2, and 3, respectively. Combined stress aging test 1 took 128 days, test 2 took 56 days, and test 3 took 24 days.

Proof testing is a pass–fail test of the sealing ability of the rubber seal. In order to evaluate items using pass–fail criterion, a large number of items and tests are required to provide an adequate statistical sample. We began with 26 samples for test 1, 22 for test 2, and 18 for test 3. Test 1 ended after testing 24 seal sample pairs, test 2 ended after testing 18 seal sample pairs, and test 3 ended after testing 17 seal sample pairs. The remaining samples were not needed after failure had been observed for two successive proof tests. Proof testing was concentrated toward the end of each calculated aging test duration, since the seals were more likely to be closer to failure. In test 1 two seal pairs were removed from the aging environment for proof testing every 8 days beginning with the 32nd day of aging. For test 2, two seal pairs were removed every 4 days beginning with the 16th day of aging and for test 3, two seal sample pairs were removed every 2 days beginning with the eighth day of aging.

The combined stress aging tests were performed in the Westinghouse R&D Center ^{60}Co Hot Cell and a schematic representation of the test layout used in the hot cell is shown Figure 4. The four ^{60}Co pencils were situated in a styrofoam block at the left. Ovens 1, 2, and 3 for tests 1, 2, and 3, respectively, were situated as shown in positions where the centers would receive the dose rates 145 rads/h, 319 rads/h, and 711 rads/h, respectively. The temperature of each oven was monitored by a digital thermocouple readout via wires marked T.C. The temperatures were also plotted as a function of time on a 24-point plotter. The ovens selected were Standard Ceramic Supply Company, Model T-8, which have no internal control and are more radiation resistant than more sophisticated ovens. These ovens were powered externally via dc power supplies and variacs.

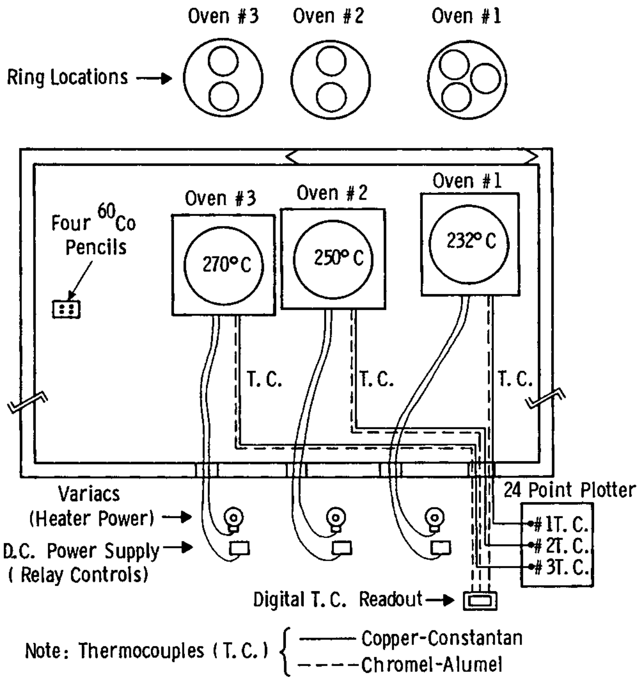


Figure 4 Layout of multistress test apparatus within the hot cell (top view).

Pyrex dishes (100 mm deep and 190 mm in diameter) were filled with silicone oil and seals. The seals were placed in the dishes as sketched in the upper part of in Figure 4. In this way, the dose variation between groups of seals was minimized. The dose variation across the seals was less than 10% for test 3, less than 5% for test 2, and less than 1% for test 1.

Following proof testing, the time at elevated temperature and radiation exposure required to achieve a failure (leaking of seals during the pressure cycle) was then used to construct an Arrhenius plot of expected service life vs. service temperature for combined stress aging of thermal/radiation exposure as shown in Figure 5.

Figure 5 has three curves, the middle line is the actual data collected and is extrapolated to a service life at 50°C. The upper and lower lines are the ± sigma, respectively, for the data collected, based on a normal distribution for both the sample set tested and the total population of all rubber seals. The data from which these curves were constructed is given in Table III. The time-to-failure was calculated as the time of the first occurrence of two consecutive seal pair failures after a successful test of seal pairs at the temperature of interest. In the case where only one seal pair failed, the test was considered successful. The extrapolated value for the mean expected service life is 183,960 h, or 21 years for continuous use at 50°C. The mean service life

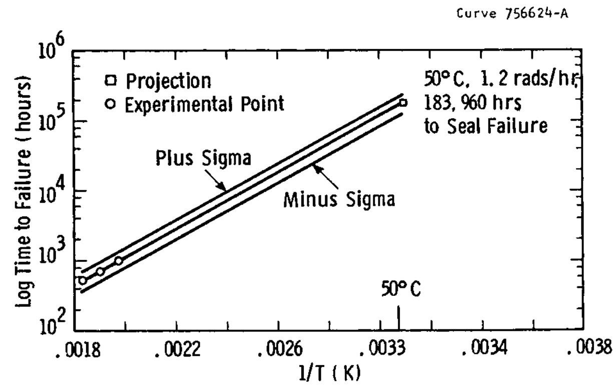


Figure 5 Service life estimate for Viton seals.

plus sigma at 50°C is 255,695 h or 29 years and the mean service life minus sigma is 132,349 h or 15 years as shown in Figure 5.

DISCUSSION

As can be readily seen by comparing the results from Figure 5 with those of Figure 3, there is quite a drastic difference in expected service life when radiation aging is added to thermal aging in a combined fashion. Not only is the reaction accelerated, but the activation energy is reduced as indicated by the change in slope of the curve from thermal aging only. That is, the service life expected when both thermal aging and radiation aging is conducted in simultaneous fashion is less than that for thermal aging alone by a factor greater than 2. This is especially important to note since the 40-year service temperature obtained from Figure 3 is 145°C, where as the 21-year expected service temperature obtained from combined stress aging is only 50°C. As noted previously, the threshold value for radiation damage to

Table III Hardness as a Function of Combined Stress Aging

Time (h)	Temperature 270°C	250°C	232°C
190	87, 90		
340	90, 96	89, 90	
500	86, 98	89, 92	
760	55, 43 (D)	45 (D)	90, 95
1000		53, 68 (D)	
1500		52 (D)	50, 51 (D)
2300			55, 55 (D)

Notes: (1) All hardness measurements made using a Shore A scale except where noted by D, which indicates Shore D scale.

rubber seals submersed in silicone fluid was in excess of 1×10^8 rads, independent of thermal considerations and the 40-year service temperature was 145°C, independent of radiation considerations. This leads to the conclusion that there is definite additive, and synergistic effects occurring with combined stress aging that would not be expected from independent radiation and thermal aging tests.

The single stress radiation tests produced no failures up to a dose of 10^8 rads. Since the expected lifetime dose on the rubber seals is only $\sim 4.2 \times 10^5$ rads, one would conclude that radiation would not play a significant synergistic role and, therefore, exclude it from the service life tests. This would be in line with virtually all proposed accelerated aging procedures. The fact that radiation and temperature, in the absence of oxygen, were able to significantly affect these seals, which demonstrated excellent thermal properties, indicates that caution should be exercised on the selection of stresses to be included in aging tests. Because of this, our decision to neglect hydrostatic pressure during tests may be questionable.

Another interesting facet in this work was the fact that an Arrhenius extrapolation could be employed on radiation–temperature synergy. To the best of the authors' knowledge this has not been reported in the literature. It is surprising because the time-to-failure in radiation tests (neglecting oxidative effects) is a linear function of dose rate, whereas, in thermal tests, the usual nonlinear Arrhenius relationship is applicable. Zhurkov[4] demonstrated that an Arrhenius relationship exists for combined temperature–tensile stress tests where the activation energy is modified by the tensile stress. It appears that in our study the radiation contribution is basically a perturbation on the thermal behavior.

By examining the hardness data of Tables I and III, it can be seen that the apparent physical mechanism of degradation is embrittlement due to additional crosslinking reactions occurring. The most likely cause of this phenomenon is the generation of free radical sites which are highly reactive and thus crosslink with each other and terminate or abstract atoms to form new reactive sites while terminating themselves. This, in turn, leads to shorter molecular chain lengths between crosslinks and increased modulus and stiffness, but lower elongation. This is also the mechanism responsible for permanent set and is typical of most elastomers.

It is important to recognize the difference between a mean failure time and the time-to-failure of an individual seal. The total sample set of all seals has a mean time-to-failure of 21 years at the in-service conditions. About this mean is a normal distribution constructed of individual seal failure times, some with longer service lives and other with shorter service lives than the mean. Based upon statistical analysis of the test data, 66% (± 1 sigma) of the rubber seal failures will occur between 15 and 29 years of service at 50°C, 1.2 rads/h dose rate of gamma exposure. Ideally, a confidence interval should be constructed about the mean extrapolated time-to-failure which requires typically more than three data points for most Arrhenius plots. However, with only three data points available, no meaningful confidence interval can be developed.

SUMMARY

Single stress (radiation and temperature) and combined stress tests were conducted on Viton B rubber seals to develop an estimate of service life. The results indicate that the service life was reduced from 40-year service at 145°C without radiation to 21 years at 50°C with radiation by the synergistic effects resulting from combined temperature and radiation stresses.

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