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**Fireset Materials
Aging Study**

By H. M. Smith
and C. Arnold and M. E. Bailey
Sandia National Laboratories Albuquerque

Published July 1982

Final Report

Prepared for the United States Department of Energy
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**Kansas City
Division**

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By H. M. Smith
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Sandia National Laboratories Albuquerque

Published July 1982

Final Report
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**Kansas City
Division**

FIRESET MATERIALS AGING STUDY

BDX-613-2791, Final Report, Published July 1982

Prepared by H. M. Smith, The Bendix Corporation, Kansas City Division, and C. Arnold and M. E. Bailey, Sandia National Laboratories Albuquerque under EP 45764

A thermally-accelerated aging study of 10 selected organic materials used in a fireset has been conducted. The study included both quantitative and qualitative gas analyses as well as the measurement of physical properties before and after accelerated aging. The test plan involved single material aging, as well as pairs and larger groups to look for synergistic interactions. The material types tested were epoxies, polyurethanes, polysulfides, silicones, phenolics, polyolefins, and diallyl phthalates. Only two of the materials tested showed evidence of degradation as a result of aging.

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SUMMARY

Bendix Kansas City and Sandia National Laboratories Albuquerque are engaged in a joint project to perform a fireset life prediction study. Because removing materials from a failed fireset in a testable configuration usually is not feasible, a materials aging program was designed to age fireset materials in parallel with the fireset aging program. To identify possible synergisms among materials, the test was designed to age materials individually as well as in pairs and in larger groups. Ten selected materials and four selected pairs were subjected to thermally accelerated aging. To achieve the desired acceleration, the materials were aged at 50, 60, and 70°C in dry air for time intervals up to 2 years. The study included both gas analysis and the measurement of physical properties as a function of time and temperature.

The 10 materials selected for study were: glass microballoon (GMB) filled epoxy; pigmented EN-7 polyurethane; phenolic microballoon-filled polysulfide; silicone RTV potting material; filled diallyl phthalate (DAP); polysulfide sealant; silicone RTV 21 sponge; mica-filled epoxy; polyolefin heat-shrink tubing; and 91 LD phenolic. The order of decreasing oxygen consumption was found to be: EN-7, polysulfide sealant, phenolic-filled polysulfide, 91 LD, DAP, mica-filled epoxy, and GMB epoxy.

The two silicones and the polyolefin heat-shrink tubing essentially were unreactive with oxygen. Several of the materials evolved significant quantities of carbon dioxide. However, in no case did the rate or amount of CO₂ evolution correlate with oxygen consumption. Three of the materials, EN-7, polysulfide sealant, and phenolic-filled polysulfide, were found to evolve relatively small amounts (up to 0.12 cm³/g) of hydrogen gas. Most of the materials evolved a surprising variety of organic compounds. Some of the off-gassed products were found to react with other materials. For example, polysulfide sealant was observed to react with CO₂ evolved from DAP.

The results from the gas analyses already have proved to be of value in understanding the gas composition of capsule atmospheres. Using data from this study, United Kingdom scientists have been able to predict within a factor of two the oxygen consumption and CO₂ and H₂ evolution found in UK capsules. Previous attempts to explain these observations were in error by almost an order of magnitude.

Significant physical property changes were few in number. Polysulfide sealant showed a linear decrease in Shore A hardness, and the process had an activation energy of approximately 22 kcal/mol. Thus, the sample aged 2 years at 70°C is the age equivalent of 76 years at 35°C, which is three times the anticipated life of the part.

Silicone RTV potting material showed qualitatively an apparent decrease in tear strength or tensile strength, but the test specimens were not configured to quantitate this change. Subsequent quantitative examination of tensile specimens at Sandia National Laboratories Albuquerque revealed that tensile strength dropped 50 percent after 1 year at 70°C in air.

No other significant physical property changes were observed. In particular, no changes that could be attributed to any material interactions were noted.

DISCUSSION

SCOPE AND PURPOSE

Sandia National Laboratories Albuquerque and Bendix Kansas City are engaged in a joint project to perform a fireset life prediction study. As an integral part of this program, a materials accelerated aging and evaluation study of selected materials used has been performed. The purpose of the materials accelerated aging study was to attempt to define the aging characteristics of the selected materials, so that aging predictions may be made over a 25-year period. A comparison of the data from the materials aging study with the fireset aging study should provide information useful for projecting the stockpile life of the fireset. The chief advantage of this approach is that, by correlating the extent of material deterioration with fireset functional failure, the service life predictions should be greatly enhanced.

The materials aging study included both gas analysis and the measurement of physical properties as a function of time and temperature. It should be noted that materials in most finished products cannot be removed from the product in a testable form. For example, most physical property tests require a sample of defined geometry. Therefore, this materials program has been run in parallel with the fireset aging study to provide testable samples of fireset materials.

PRIOR WORK

No work on this subject has been conducted previously at Bendix.

ACTIVITY

Materials Tested

Some 61 organic materials and parts are included in the fireset. If all these materials were aged individually, disregarding the pair combinations, the test matrix would be unmanageably large. Therefore, the 61 organic materials were narrowed down to 10 individual materials and four pair combinations. The selected individual materials and four pair combinations are given in Tables 1 and 2, respectively. The materials and pair combinations were selected on the basis of the following general considerations:

Table 1. Materials Selected for Individualized Aging

Designation	Material
1	GMB Epoxy
2	EN-7 and White Pigment
3	Polysulfide/Phenolic Microballoon Coating
4	Silicone RTV Potting Material and Catalyst
5	Green Diallyl Phthalate
6	Polysulfide Sealant
7	Silicone RTV 21 Sponge
8	Mica-Filled Epoxy
9	Polyolefin Heat-Shrink Tubing
10	91 LD Phenolic

Table 2. Material Pair Combinations

Designation	Material Pairs*
A	EN-7 and White Pigment (2) Green Diallyl Phthalate (5)
B	EN-7 and White Pigment (2) 91 LD Phenolic (10)
C	Silicone RTV Potting Material and Catalyst (4) Green Diallyl Phthalate (5)
D	Polysulfide Sealant (6) Green Diallyl Phthalate (5)

*Parenthetical numbers are designations of individual materials given in Table 1; applicable specifications also are given in Table 1.

- Location of materials in the fireset,
- Inherent stability of the materials,
- Quantity of materials in the fireset,
- Criticality of function, and
- Prior existence of aging data.

Test Design

The materials accelerated aging study is a system for subjecting samples of materials and material combinations to elevated temperatures for selected times, followed by gas analysis and physical testing to determine the effects of thermally-accelerated aging. Two test matrices were employed: the alpha matrix for the study of individual materials and selected pairs, and the numeric matrix for a group study of the synergistic effects of all the materials and pairs. In the alpha matrix, samples of each individual material and four selected material pairs were subjected to different temperatures. Gas samples were taken at intervals over a period of 1 year. The numeric matrix contained samples of all individual materials and material pairs in each container. These containers were subjected to different temperatures for different periods of time. One gas sample was taken from each container at the end of the thermal exposure interval.

Alpha Matrix

The objective of the alpha matrix was to determine the outgassing properties and thermal aging characteristics of the 10 individual materials and four material pairs in the absence of synergistic effects from other materials. The test matrix consisted of 70 gas sampling containers and four canister type containers exposed to the test matrix shown in Table 3. The containers in alpha matrix D were aged for 6 months, those in A, C, and E for 1 year, and those in B for 2 years. The aging temperatures were 50°C for A and B, 60°C for C, and 70°C for D and E. With the exception of matrix E, gas samples were taken at the conclusion of the aging period. For E, gas samples were taken at intervals of 2 weeks, 1 month, 3 months, 6 months, and 1 year. At the end of each aging period, the materials were subjected to physical testing.

Numeric Matrix

The objective of the numeric matrix was to examine the thermal aging characteristics of the 10 materials and four material

Table 3. Alpha Test Matrix

Material Designation	Container Numbers				
	A (50°C, 1 yr)	B (50°C, 2 yr)	C* (60°C, 1 yr)	D (70°C, 6 mo)	E (70°C, 1 yr)
1	A1	B15	C29	D43	E57
2	A2	B16	C30	D44	E58
3	A3	B17	C31	D45	E59 and X71**
4	A4	B18	C32	D46	E60
5	A5	B19	C33	D47	E61
6	A6	B20	C34	D48 and R73***	E62 and R74***
7	A7	B21	C35	D49	E63 and X72**
8	A8	B22	C36	D50	E64
9	A9	B23	C37	D51	E65
10	A10	B24	C38	D52	E66
A (2 + 5)	A11	B25	C39	D53	E67
B (2 + 10)	A12	B26	C40	D54	E68
C (4 + 5)	A13	B27	C41	D55	E69
D (6 + 5)	A14	B28	C42	D56	E70

*The "C" containers have glass sample cavity for visual observations during aging.

**Special canister-type containers for single temperature aging of compression-deflection test discs.

***Special canister-type containers for single temperature aging of volume resistivity test discs.

pairs under exposure conditions that permitted the possibility of synergistic interactions among the materials. The test sequence consisted of eight containers subjected to the time and temperature conditions shown in Table 4. Each container had samples of the 10 individual materials and four material pairs. Gas communication was allowed among all the materials in each container, with the exception of the two polysulfides (materials 3 and 6) and the polysulfide-DAP pair (combination D). Samples of these materials were encapsulated in GMB epoxy to more closely approximate the actual use environment. At the end of the indicated storage period for each container a gas sample was taken, and the materials were subjected to the physical tests selected.

Table 4. Numeric Test Matrix by Container Number

Storage Time (Months)	Aging Temperature (°C)		
	50	60	70
3			N1
6	N2	N4	N6
12	N3	N5	N7
24			N8

Material Preparation

Samples of each material required were prepared and cleaned in a manner duplicating as closely as possible the production methods used for the fireset. Details of preparation and cleaning were taken from production documents. Color photographs of the material samples were retained for reference.

Test Containers

Alpha Matrix Containers

For the alpha matrix, 70 gas sampling containers and four canister type containers were required. The gas sample container was a tube (14 glass, 56 stainless steel) closed at one end and welded at the other end to a Conflat type 2.750-in. outside diameter (OD) vacuum flange. A second flange, with a stainless steel bellows valve attached, was sealed to the tube flange by means of knife edges with copper gaskets. The sample tube portion of the container was approximately 6 in. long and 1 in. inside diameter (ID). The leak rate for this container was 4×10^{-9} atm-cm³/s or less. The four canister-type containers consisted of a 6-in. OD Conflat type double-sided vacuum flange sealed between two 6-in. OD Conflat type blank flanges by knife edges with copper gaskets. One of the two blank flanges was equipped with a stainless steel bellows valve for evacuation and backfilling.

Numeric Matrix Containers

Eight test containers were required for the numeric matrix. The containers were a 3.78-in. ID stainless steel tube, approximately 5 in. long, closed at one end and welded at the other end to

a 6-in. OD Conflat type vacuum flange. A second 6-in. OD flange with a stainless steel bellows valve attached, was sealed to the first by means of knife edges with copper gaskets. The leak rate for the container was 1×10^{-7} atm-cm³/s or less. Both container types are shown in Figure 1.

Gas Analysis

Gas sampling and analysis were both qualitative and quantitative. Qualitative analysis was accomplished by gas chromatography/mass spectrometry (GC/MS). Quantitative analysis was accomplished using the relative percentages determined by GC for each gas identified times the total quantity of gas in the container. The quantity of gas in the container was determined from a knowledge of the free volume of the container and the internal pressure of the container, as measured by a sensitive capacitance manometer (Baratron) at the time of each gas sampling. Gas samples were taken after each container had been thermally stabilized at the appropriate aging temperature.

Sample Container/Gas Chromatographic Interface

The interface consisted of a gas sample loop and a Baratron pressure indicator. The interface, together with the sample container, was housed in a temperature-controlled forced draft oven to perform gas sampling at the specified aging temperature.

Backfilling

The sample containers were equilibrated at the specified aging temperature before backfilling. The container was purged with dry air five times and evacuated. The free volume of the container was determined at the aging temperature before backfill by gas expansion of dry air from a calibrated volume, with pressure determined using the Baratron. The container was then backfilled with dry air to approximately 600 torr and the backfill pressure was measured precisely.

Gas Sampling

The gas sample loop and connecting lines were connected as closely as possible to the sample container bellows valve to obtain a reliable sample of the outgassing products and keep dead volume to a minimum. The sample container was equilibrated at the specified aging temperature before sampling. After temperature equilibration, the sample loop was evacuated to 1 torr or less, the vacuum pump sealed off, the bellows valve opened, and the pressure reading recorded for quantitative analysis. The sample container valve was then closed and the sample gases injected into the gas chromatograph.

Figure 1. Test Containers

Gas Chromatography

The gases/vapors were purged from the gas sample loop by a carrier gas onto a Tenax (porous polymer packing based on 2,6-diphenyl-p-phenylene oxide) column controlled at 25°C. This column retained organic components and allowed low molecular weight (MW) materials such as H₂, O₂, N₂, CO, CO₂, NH₃, H₂O, and CH₄ to continue onto a Poropak P molecular sieve column. These gases continued onto a mass spectrometer (MS) for positive identification and recording of their spectra on magnetic tape in a data system. The electrical signal from the thermal conductivity detector (TCD) simultaneously displayed each component eluting from the column as a peak on a strip chart recorder and stored the area under each peak in a computer.

When the last low MW component was eluted from the column, a switching valve was activated to divert the carrier gas flow to the Tenax column. This column was programmed slowly to 300°C to elute and resolve the organic components to be detected by a flame ionization detector (FID), identified by MS, and stored in the data system. After the last organic component was eluted from the column, the computer was activated and a print-out of

the peak areas was obtained. Because of a lack of calibration data, no quantitative results for organic components were obtained.

Mass Spectrometry

After quantitative analysis by gas chromatography, the samples passed through the jet separator into the source of the mass spectrometer for qualitative identification of each gas chromatographic peak. Identification of each peak was made using reference spectra and a computer-searchable library of 40,000 compounds stored on magnetic tape. The combination of the GC computer for quantitation and the mass spectrometer for identification gave the fastest turn-around time possible for each individual sample. Hard copy output was available from the GC computer and mass spectrometer CRT displays.

Data Analysis and Temperature Selection

The objective of the data analysis was to predict material performance over a stockpile life of 25 years. It was assumed that changes in material characteristics with temperature would follow the Arrhenius equation. It was further assumed, until proven otherwise, that diffusion would play an important role and that consequently activation energies would be low to moderate (10 to 20 kcal/mol). With these assumptions in mind, temperatures of 50, 60, and 70°C were chosen to provide an adequate spread of data points over an equivalent age of 25 years at 35°C. Table 5 lists the expected position of data points in 35°C aging for three different assumed activation energies.

Experimental Gas Analysis Results

The gas sampling test data are given in Appendix A. For each material, a brief discussion of the results, including the weight of the sample obtained in the test container is followed by the data taken in the test. Gas analysis data from matrix B and container N-8, which were sampled after 2 years aging, are not included because of a failure of the gas chromatographic detection system during sampling. Matrix EE, which was used for gas analysis only, was a reconstitution of matrix E for the purpose of obtaining undisturbed gas samples for 1 year at 70°C.

The selection of the appropriate numerical form for the reporting of the gas analysis results presented something of a problem. The original intent had been to report absolute quantities (that is, millimoles, $\text{cm}^3\text{-atm}$, and so on) of gases present as a function of time and temperature. Matrix E, which was sampled frequently, was to be used to obtain kinetic data for modeling changes versus time. Assuming the same model applied at 50 and 60°C, matrices C, together with E, would then be used to obtain activation

Table 5. Effective Age (Years) at 35°C for
Three Activation Energies (Ea)

Aging Temperature (°C)	Aging Time (Months)			
	3	6	12	24
Ea = 12.95 kcal/mol				
50		1.3	2.6	
60		2.4	4.9	
70	2.1	4.3	8.6	17.3
Ea = 15.0 kcal/mol				
50		1.6	3.1	
60		3.1	6.3	
70	3.0	6.1	12.2	24.4
Ea = 20.0 kcal/mol				
50		2.3	4.6	
60		5.8	11.6	
70	7.0	14.0	28.0	56.0

energies for the appearance or disappearance of various gaseous species. It soon became apparent that, despite effort to minimize sampling volume, the samples periodically withdrawn from matrix E were too large relative to the total container volume not to perturb the results. This was particularly true in cases where oxygen was being depleted by reaction with the test material. In those instances, sampling removed significant quantities of oxygen from the container that otherwise would have reacted in the future. Because of these limitations, a decision was made to report the absolute total quantity of gas in each container at the time of sampling (Q_t), and the relative percentage of each gas detected. The reader will recognize that for matrix E, the absolute total quantity of gas in the containers is a function of the rate of oxygen depletion, the rate of production of other gases, and the quantities withdrawn by sampling, and thus in general is not a simple smooth function versus time. Calculations of the cumulative quantity of each of the low molecular weight gases (N_2 , O_2 , CO_2 , CO , CH_4 , and H_2) versus time were made, despite the probability of error in the oxygen values, and are available to those interested.

Organic species and water, reported under the "percent other" column of the data tables, were determined by difference. The number of different organic components observed defied any attempt to perform quantitative calibrations for each of them because of limitations in manpower and funds available for this project. They are, however, listed in order of decreasing abundance based on the peak area obtained from the gas chromatographic data.

Matrix EE has already been mentioned as having been reconstructed at the conclusion of testing on matrix E for the purpose of obtaining unperturbed gas samples after 1 year aging at 70°C. A comparison of the results from matrix EE with those from Matrix E revealed some significant differences, particularly in the amount of CO₂ evolved from materials such as EN-7, DAP, and 91 LD phenolic. In these materials substantially less CO₂ was evolved from matrix EE samples than from matrix E samples, despite there being essentially no difference in oxygen consumption.

The principal difference between samples used in matrices A through E and those used later in matrix EE is the length of exposure to ambient atmospheric conditions before containment in dry air for accelerated aging purposes. The samples for matrices A through E were placed in the aging containers in dry air within 3 months of fabrication, whereas those for matrix EE were exposed to ambient conditions uncontained for approximately 2 years before use. These observations indicate that the evolution of CO₂ from these materials proceeds by some mechanism other than simple oxidation and that this mechanism may have proceeded to a significant extent during the 2 years of ambient storage before accelerated aging began. If so, then the matrix EE samples cannot be considered identical to those used in matrices A through E, and the aging results cannot be compared directly. Nevertheless, the matrix EE data are included in the data tables because the differences themselves may prove to be useful.

Physical Property Test Results

Physical property tests appropriate to the nature and function of each material were conducted at zero time and at the conclusion of each aging period, in both the alpha and numeric matrices. In addition, samples of "unaged" materials were tested along with thermally-aged specimens at the conclusion of every aging interval. These unaged samples served the purpose of internal standards and were used primarily to assure that no drift in instrument response, test method, or execution had occurred.

The physical tests used in this study included weight change, dynamic shear modulus, shore A hardness, thermomechanical analysis (TMA), flexural modulus, compression-deflection, volume resistivity, and density. The bulk of the specimens used were

Rectangular bars 0.5 by 0.125 by 3 in. However, disc specimens were required for the compression-deflection and volume resistivity tests. Compression-deflection samples were discs 1.129 by 0.125 in., and volume resistivity samples were discs 2.00 by 0.125 in.

The physical property test data are given in Appendix B. The tables for each material are preceded by a brief discussion of the results, including a listing of tests performed on each material. No discussion or data tables are included for material number 9, polyolefin heat-shrink tubing. The only physical test originally planned for this material was TMA analysis; however, when this material was heated during the TMA test such severe distortion occurred that the results were meaningless. Consequently, only visual observation and gas analysis remained, and these indicate that no significant changes in the material occurred.

ACCOMPLISHMENTS

The stated objective of predicting material performance, whether gas composition changes or physical property changes, has in general been only partly realized. In the case of the gas analyses, the limitations of too large sampling volumes, thus perturbing the system, and too few data points versus time prohibit the prediction of quantitative gas behavior at any high confidence level. There are, fortunately, exceptions to this observation. The evolution of hydrogen from polysulfide sealant appears to have a maximum of 0.12 to 0.14 $\text{cm}^3\text{-atm/g}$, despite the fact that whether the reaction is first or second order cannot be resolved. This observation, coupled with the apparent high activation energy (31 to 33 kcal/mol) would indicate that the upper limit of 0.12 to 0.14 $\text{cm}^3\text{-atm/g}$ would not be exceeded under stockpile conditions.

A similar argument may be made concerning the evolution of carbon monoxide and methane from DAP, although in this case for somewhat different reasons. After aging for 1 year, the quantities of these two gases appear almost independent of temperature, indicating that the upper limit has been reached.

Perhaps the most serious failures of prediction relate to oxygen depletion and carbon dioxide evolution. The perturbation of the oxygen data by the large samples taken has already been mentioned. Also, in several cases oxygen was essentially completely depleted, indicating that the amount of oxygen available in the container was insufficient to saturate the sample. In the case of carbon dioxide, those materials which were the most prolific sources (EN-7, DAP, and 91 LD) appeared to evolve the gas at an approximately linear rate versus time after an initial period of rapid evolution. This linear rate with time precluded any prediction of total quantity.

Although the predictive objective was not fully achieved, the gas analysis study has been of considerable value. For perhaps the first time, the very important role that organic components in sealed systems may have with respect to oxygen depletion and carbon dioxide and hydrogen evolution has been demonstrated. The study suggests that an examination of the outgassing behavior under thermally accelerated conditions of other commonly used organic materials would be useful.

In the case of physical properties, most of the materials showed no significant changes attributable to thermal aging. Only two, RTV silicone potting material and polysulfide sealant, demonstrated clearly observable degradative changes. In the case of RTV silicone potting material, the property most descriptive of the degradative process originally was not included in the test plan. Only in the case of polysulfide sealant could a prediction of future changes be made. Perhaps the lesson to be learned from these results is that more quantitative properties such as tensile strength should be substituted for the less quantitatively useful measurements such as TMA.

FUTURE WORK

No further work is planned on this aging study; however, to achieve predictive results, some changes should be made for future studies of this type.

Certainly one important change would be to assure that gas samples withdrawn are not so large as to perturb the system. This could be accomplished in at least two different ways. One is to use many more of the small gas sample containers, withdrawing one periodically for only one gas sample per container. A second approach would be to use larger containers with greater free volumes, such that any given sampling would withdraw no more than 1 to 2 percent of the total gas from the container.

A second change required would be to increase the number of gas samples taken versus time. For example, the number of points available from this study was insufficient to distinguish between first and second order for hydrogen evolution from polysulfide. Even if an entirely empirical fit versus time were used, more points would be needed to produce a parametric equation of the necessary precision for predictive purposes.

Finally, the question of oxygen consumption must be addressed. Of the 10 materials tested, seven reacted with oxygen, some quite rapidly with complete depletion of the oxygen available. To carefully characterize these reactions, sufficient oxygen would

need to be available to allow the reaction to be studied for a longer time. This need would argue in favor of a large container possessing a greater volume-to-sample weight ratio.

Appendix A
GAS ANALYSES

1. GLASS MICROBALLOON-FILLED EPOXY

Containers: A-1, C-29, D-43, E-57

Average Sample Weight: 12.2 g

The analytical data are shown in Table A-1. GMB epoxy reacts slowly with oxygen. Small amounts of CO_2 were observed, but the quantity is not stoichiometric with the quantity of oxygen consumed. Trace quantities of CO and CH_4 were evolved at 60 and 70°C, but none was present at 50°C.

Water and acetaldehyde were the predominant species evolved in the "other" category. Acetone was present at 70 and 60°C but not at 50°C. Trace amounts of siloxane were observed at all three temperatures.

Table A-1. GMB Epoxy Gas Analysis

Time	Total Quantity (cm ³ -atm)	Amount (Percent)						
		N ₂	O ₂	CO ₂	CO	CH ₄	H ₂	Other*
Matrix E (70°C)								
Start	64.93	78.63	21.37					
2 Weeks	71.69	73.44	18.90	0.11				7.55
1 Month	62.26	78.10	19.96	0.23				1.71
3 Months	52.68	81.42	18.51	0.49	0.12			
6 Months	44.53	82.79	15.06	0.67	0.33	0.03		1.12
1 Year	37.03	85.67	9.61	1.56		0.06		3.10
Matrix EE (70°C)								
Start		78.63	21.37					
1 Year	66.68	86.47	13.48	1.53	0.84	0.06		
Matrix D (70°C)								
Start	68.64	78.63	21.37					
6 Months	69.52	83.63	13.98	0.90	0.48	0.03		0.98
Matrix C (60°C)								
Start	105.42	78.63	21.37					
1 Year	105.56	81.77	17.49	0.62	0.18	0.02		
Matrix A (50°C)								
Start	70.70	78.63	21.37					
1 Year	71.39	81.62	19.76	0.27				
*Others (in descending order): water, acetaldehyde, acetone, siloxanes, dichloro- propane, ethane, propane, and ethylene.								

2. EN-7 AND WHITE PIGMENT

Containers: A-2, C-30, D-44, E-58

Average Sample Weight: 14.7 g

The analytical data for EN-7 are shown in Table A-2. EN-7 reacts with oxygen rapidly, decreasing the oxygen concentration by more than 95 percent in 1 month at 70°C. Residual oxygen concentration was very small at all three temperatures after 1 year; therefore, estimating the activation energy of the reaction was not possible.

Carbon dioxide was the major gas evolved at all three temperatures. At 70°C (E matrix), the initial rate was approximately 0.3 cm³/g/mo for the first month. Thereafter, the rate was a linear 0.04 cm³/g/mo, and showed no decrease at the end of one year at 70°C. Because oxygen was essentially depleted after 1 month at 70°C, the continuing CO₂ production could be from the reaction of water with unreacted isocyanate groups.

Small quantities of carbon monoxide were detected at all three temperatures. The amount of CO evolved appeared to be temperature independent.

Perhaps the most surprising result was the detection of small amounts of evolved hydrogen. At 70°C (E matrix), approximately 0.5 cm³ was seen at 1 month and did not increase thereafter. Smaller amounts were observed at 60 and 50°C. The source of the hydrogen is unknown.

Water and acetaldehyde were the principal gases observed in the "other" category. Acetaldehyde may be caused by oxidative attack on the residual unsaturation of the polybutadiene backbone of the resin.

Table A-2. EN-7 Polyurethane Gas Analysis

Time	Total Quantity (cm ³ -atm)	Amount (Percent)						
		N ₂	O ₂	CO ₂	CO	CH ₄	H ₂	Other*
Matrix E (70°C)								
Start	67.44	78.63	21.37					
2 Weeks	62.92	83.02	1.04	4.28	0.30			11.36
1 Month	55.87	90.84	0.64	5.97	0.36		0.95	1.24
3 Months	50.45	81.19	0.49	8.38	0.28		0.75	8.91
6 Months	45.83	84.09	0.75	12.36			0.97	1.83
1 Year	42.09	77.19	0.31	20.72			0.60	1.18
Matrix EE (70°C)								
Start		78.63	21.37					
1 Year	69.50	82.98		10.42	0.32		0.76	5.52
Matrix D (70°C)								
Start	67.30	78.63	21.37					
6 Months	64.55	85.94	0.36	9.53	0.36		1.00	2.81
Matrix C (60°C)								
Start	101.70	78.63	21.37					
1 Year	92.45	91.78	0.46	7.18	0.35		0.09	0.14
Matrix A (50°C)								
Start	72.42	78.63	21.37					
1 Year	65.11	93.15	0.25	5.88	0.34		0.31	0.07
*Others (in descending order): water, acetaldehyde, acetone, propanol, ethane, propane, toluene, trichloroethylene, and ethylene.								

3. PHENOLIC MICROBALLOON FILLED POLYSULFIDE

Containers: A-3, C-31, D-45, E-59

Average Sample Weight: 22.2 g

The results for the gas sampling tests for polysulfide/phenolic microballoons are given in Table A-3. This material also reacts rapidly with oxygen, although not quite as fast as does EN-7. At 70°C (E matrix), approximately 94 percent of the oxygen was reacted in the first month. At the end of 1 year, only trace amounts remained at all three aging temperatures. The reaction of oxygen was not accompanied by large quantities of CO₂ or CO. Both gases were evolved in only small amounts.

At 70°C (E matrix), hydrogen was generated at an almost linear, but small, rate. A total of 1.1 cm³-atm was formed after one year at 70°C, and smaller amounts were found at 60 and 50°C.

Water and toluene were the predominant gases observed in the "other" category, but significant quantities of trichloroethylene, propene, acetaldehyde, ethene, and methanol also were found.

Table A-3. Polysulfide/Phenolic Microballoon Gas Analysis

Time	Total Quantity (cm ³ -atm)	Amount (Percent)						
		N ₂	O ₂	CO ₂	CO	CH ₄	H ₂	Other*
Matrix E (70°C)								
Start	67.21	78.63	21.37					
2 Weeks	61.69	91.14	4.57	0.18	0.33			3.78
1 Month	52.21	96.39	0.72	0.25	0.37		0.41	1.86
3 Months	46.31	97.09	0.60	0.24	0.42		0.78	0.87
6 Months	41.54	94.48	0.67	0.27	0.44		1.31	2.83
1 Year	37.95	91.17	0.44	1.13	0.61		2.50	4.15
Matrix EE (70°C)								
Start		78.63	21.37					
1 Year	64.18	91.54		1.60	0.48		1.08	5.30
Matrix D (70°C)								
Start	67.16	78.63	21.37					
6 Months	61.41	94.01	0.51	0.07	0.44		1.34	3.63
Matrix C (60°C)								
Start	103.25	78.63	21.37					
1 Year	89.63	97.10	0.15	0.11	0.45		0.49	1.70
Matrix A (50°C)								
Start	73.58	78.63	21.37					
1 Year	62.06	98.96	0.18	0.05	0.39		0.31	0.11
*Others (in descending order): water, toluene, trichloroethylene, propylene, acetaldehyde, ethylene, methanol, acetone, butene, siloxane, xylene, and ethane.								

4. SILICONE RTV POTTING MATERIAL AND CATALYST

Containers: A-4, C-32, D-46, E-60

Average Sample Weight: 17.7 g

The sampling data for RTV silicone potting material are listed in Table A-4. RTV silicone potting material was characterized by essentially no reactivity with oxygen, and only very small quantities of CO₂ were observed.

The principal gases evolved were water, low molecular weight siloxanes, and ethanol. None of these species were unexpected. Water is known to be present to bring about the cure, and ethanol is an elimination product of the cure reaction. The other organic materials detected are shown in the data table.

Table A-4. Silicone RTV Potting Material Gas Analysis

Time	Total Quantity (cm ³ -atm)	Amount (Percent)						
		N ₂	O ₂	CO ₂	CO	CH ₄	H ₂	Other*
Matrix E (70°C)								
Start	66.36	78.63	21.37					
2 Weeks	68.41	75.54	20.64	0.26				3.56
1 Month	60.18	78.08	20.57	0.27				1.08
3 Months	52.96	78.76	20.25	0.33				0.66
6 Months	46.65	79.85	20.14	0.35				
1 Year	40.94	79.06	19.47	0.60				0.87
Matrix EE (70°C)								
Start		78.63	21.37					
1 Year	78.49	77.29	21.37	0.28				1.06
Matrix D (70°C)								
Start	67.21	78.63	21.37					
6 Months	70.87	78.32	20.33	0.29				1.06
Matrix C (60°C)								
Start	104.85	78.63	21.37					
1 Year	107.69	78.89	20.87	0.25				
Matrix A (50°C)								
Start	71.19	78.63	21.37					
1 Year	73.00	80.01	20.97	0.14				
*Others (in descending order): water, siloxanes, ethanol, acetone, 1-butene, butanal- dehyde, and butanol.								

5. DIALLYL PHTHALATE

Containers: A-5, C-33, D-47, E-61

Average Sample Weight: 26.7 g

Diallyl Phthalate (DAP) was the most unusual material included in the aging study from the perspective of gas sampling. In both the oxygen reaction and in the rich variety of organic gases evolved, DAP differs from the other materials examined.

Oxygen reaction at 70°C (D and E matrices) appeared to be linear with time (zero-order). Assuming the same to be true at 60 and 50°C and thus calculating rates at these temperature based on the gas analysis at 1 year aging, an excellent Arrhenius plot was obtained with an activation energy of approximately 13 kcal/mol. Because an oxygen concentration-independent mechanism is difficult to rationalize, a similar analysis was made assuming first order kinetics. Although the Arrhenius plot was not nearly as good a fit of the data, the calculated activation energy was near 12 kcal/mol. Thus, whichever rate law is the more correct, the low activation energies suggest a diffusion-controlled reaction rather than one in which thermoxidation is the rate controlling step.

Carbon dioxide generation from DAP at 70°C resembled that from EN-7, in that the initial rate was high for approximately the first month, and thereafter was much slower and essentially linear for the remainder of the 1 year aging. The appearance of CO₂ does not correlate with the disappearance of O₂, and thus suggests that the source may be the reaction or decomposition of some substance such as residual peroxide catalyst. The CO₂ evolution showed no signs of diminishing at 12 months aging time.

Also, DAP was the only material studied that evolved any significant amounts of carbon monoxide and methane. At 70 and 60°C, the quantities of the two gases evolved were almost the same; at 50°C, more methane than CO was liberated.

DAP is also unique in this study in regard to the variety of organic gases observed during gas sampling. The species are shown in Table A-5. With the exception of water and solvents such as acetone and toluene, the origin of most of these substances is not known.

Table A-5. Diallyl Pthalate Gas Analysis

Time	Total Quantity (cm ³ -atm)	Amount (Percent)						
		N ₂	O ₂	CO ₂	CO	CH ₄	H ₂	Other*
Matrix E (70°C)								
Start	65.44	78.63	21.37					
2 Weeks	76.64	73.87	16.49	3.96	0.75	1.50		3.43
1 Month	67.28	75.49	14.60	5.46	1.21	2.39	0.05	0.80
3 Months	57.83	74.43	6.35	7.08	2.42	3.51	0.11	6.10
6 Months	50.26	79.46	1.03	8.94	2.70	3.99	0.12	3.76
1 Year	45.14	76.01	0.30	11.99	5.10	4.89	0.12	1.59
Matrix EE (70°C)								
Start		78.63	21.37					
1 Year	71.89	83.76		4.00	3.62	1.41	0.18	7.03
Matrix D (70°C)								
Start	69.86	78.63	21.37					
6 Months	78.19	80.59	1.67	8.49	3.53	3.04	0.18	2.50
Matrix C (60°C)								
Start	107.58	78.63	21.37					
1 Year	113.26	82.18	6.48	6.55	2.68	2.64	0.13	
Matrix A (50°C)								
Start	70.54	78.63	21.37					
1 Year	74.38	80.42	9.02	6.70	2.17	3.61	0.12	
*Others (in descending order): water; acetone; chloromethane, methanol; α-methyl styrene; 1-butene, acetaldehyde; methylformate; butane; ethane; methyl acetate; benzene; propylene; isopropyl benzene; tetrachloroethylene; siloxane; trichloroethylene; acetophenone, crotonaldehyde; toluene; and ethyl benzene.								

6. POLYSULFIDE SEALANT

Containers: A-6, C-34, D-48, E-62

Average Sample Weight: 23.4 g

The gas analysis data for polysulfide sealant are shown in Table A-6. Next to DAP, polysulfide exhibited the most unexpected results with respect to the variety of gaseous species observed.

Oxygen consumption by polysulfide was relatively rapid, slightly slower than EN-7 polyurethane but much faster than epoxy or DAP. At 70°C, approximately 95 percent of the available oxygen in the container had been reacted within the first month. At 60 and 50°C, oxygen consumption was essentially complete when sampled at the end of 1 year aging. The oxygen reaction does not produce carbon dioxide, and only very small amounts of carbon monoxide were observed.

The most surprising result from polysulfide was the quantity of free hydrogen evolved. After 1 year at 70°C the quantity was 2.7 cm³-atm, or about 0.12 cm³-atm/g of material. Efforts were made to fit the data at 70°C to both first and second order rate expressions. With only four data points versus time, it was not possible to distinguish which was the better fit, as the correlation coefficients were both 0.98. By using the 1-year data at 50 and 60°C, it was calculated that the first order rate expression gave an activation energy of 31 kcal/mol, and the second order one an activation energy of 33 kcal/mol. Thus, while the correct rate order was not deduced, it does appear that the reaction producing hydrogen has a quite high activation energy and probably is not diffusion controlled. The first and second order analyses also indicated that the maximum hydrogen evolution possible was between 0.12 and 0.14 cm³-atm/g.

Table A-6 also lists the other substances observed in the gas phase over polysulfide. With the exception of water and the common solvents, their origin is not understood. It is interesting to note the complete absence of any sulfur compounds in the gas analysis.

Table A-6. Polysulfide Sealant Gas Analysis

Time	Total Quantity (cm ³ -atm)	Amount (Percent)						
		N ₂	O ₂	CO ₂	CO	CH ₄	H ₂	Other*
Matrix E (70°C)								
Start	67.55	78.63	21.37					
2 Weeks	61.50	91.54	3.23	0.05	0.17			5.01
1 Month	52.92	97.30	0.64	0.13	0.24		1.76	
3 Months	47.85	86.53	0.32	0.11	0.24		2.97	9.83
6 Months	43.53	92.00	0.45	0.04	0.32		4.22	2.97
1 Year	41.68	87.88	0.27	0.05	0.46		5.09	6.25
Matrix EE (70°C)								
Start		78.63	21.37					
1 Year	62.55	90.41		0.06	0.33		3.07	6.13
Matrix D (70°C)								
Start	67.82	78.63	21.37					
6 Months	67.19	91.57	0.47	0.01	0.30		3.76	3.89
Matrix C (60°C)								
Start	109.85	78.63	21.37					
1 Year	97.36	95.77	0.24		0.23		2.03	1.73
Matrix A (50°C)								
Start	69.59	78.63	21.37					
1 Year	79.39	98.82	0.70		0.24		0.71	
*Others (in descending order): water; ethane; propane; methanol; ethanol; ethylene; propylene; acetaldehyde, 1-butane; acetone; crotonaldehyde; butene; xylene; isopropanol; and trichloroethylene.								

7. SILICONE RTV 21 SPONGE

Containers: A-7, C-35, D-49, E-63

Average Sample Weight: 12.5 g

The data for silicone RTV 21 are given in Table A-7. This material was one of the most unreactive studied. The changes shown in nitrogen and oxygen percentages appear to be caused mainly by the evolution of other materials. The principal compounds evolved were water, ethanol, and low molecular weight siloxanes, all of which can be expected from this material. Traces of acetaldehyde were also detected.

Table A-7. Silicone RTV 21 Gas Analysis

Time	Total Quantity (cm ³ -atm)	Amount (Percent)						
		N ₂	O ₂	CO ₂	CO	CH ₄	H ₂	Other*
Matrix E (70°C)								
Start	67.87	78.63	21.37					
2 Weeks	68.07	73.13	19.29	0.05				7.53
1 Month	59.84	78.36	20.26	0.15				1.23
3 Months	52.88	77.14	19.69	0.40			0.10	2.67
6 Months	46.68	79.35	19.85	0.23			0.11	0.46
1 Year	37.11	77.62	19.17	0.51			0.17	2.53
Matrix EE (70°C)								
Start		78.63	21.37					
1 Year	70.84	77.47	23.00	0.18			0.12	
Matrix D (70°C)								
Start	69.57	78.63	21.37					
6 Months	69.99	72.17	18.57	0.20			0.14	8.92
Matrix C (60°C)								
Start	108.14	78.63	21.37					
1 Year	109.24	79.07	20.68	0.14			0.03	0.08
Matrix A (50°C)								
Start	69.32	78.63	21.37					
1 Year	73.14	80.41	20.62	0.17			0.08	
*Others (in descending order): water, ethanol, siloxanes, acetone, acetaldehyde, 1-butene, trichloroethylene, methyl acetate, and ethylene.								

8. MICA-FILLED EPOXY

Containers: A-8, C-36, D-50, E-64

Average Sample Weight: 22.9 g

The data for mica-filled epoxy are shown in Table A-8. This epoxy, like GMB epoxy, is characterized principally by oxygen consumption and carbon dioxide evolution. However, both were greater for the mica-filled material than for the GMB system.

At 70°C, oxygen was down to approximately 6 percent at 6 months, and less than 1 percent after 1 year. Oxygen reaction was less, but significant, after 1 year at 50 and 60°C. CO₂ evolution followed a similar trend with regard to temperature. At all temperatures, the disappearance of oxygen was substantially greater than the evolution of carbon dioxide. Small amounts of carbon monoxide were observed at each temperature.

The other materials evolved from mica-filled epoxy also are shown in Table A-8. Those present in the greatest amounts were water, trichloroethylene, and acetaldehyde.

Table A-8. Mica-Filled Epoxy Gas Analysis

Time	Total Quantity (cm ³ -atm)	Amount (Percent)						
		N ₂	O ₂	CO ₂	CO	CH ₄	H ₂	Other*
Matrix E (70°C)								
Start	69.12	78.63	21.37					
2 Weeks	77.16	74.79	17.45	0.50	0.09			7.17
1 Month	66.67	80.44	17.32	0.95	0.15			1.14
3 Months	55.54	83.12	11.06	2.41	0.42			2.99
6 Months	47.41	89.86	6.10	4.05				
1 Year	40.30	88.49	0.91	6.66	1.00			2.94
Matrix EE (70°C)								
Start		78.63	21.37					
1 Year	69.47	87.31	0.52	5.18	0.52			6.47
Matrix D (70°C)								
Start	66.15	78.63	21.37					
6 Months	67.26	86.31	5.73	3.99	0.68			3.29
Matrix C (60°C)								
Start	108.43	78.63	21.37					
1 Year	107.75	85.83	9.87	3.48	0.53			0.29
Matrix A (50°C)								
Start	78.71	78.63	21.37					
1 Year	74.90	87.92	11.30	2.43	0.41			
*Others (in descending order): water, trichloroethylene, acetaldehyde, siloxane, methyl acetate, methyl isobutyl ketone, propene, xylene, toluene, and ethylene.								

9. POLYOLEFIN HEAT-SHRINK TUBING

Containers: A-9, C-37, D-51, E-65

Average Sample Weight: 1.1 g

The gas analysis results are given in Table A-9. This material was the most inert of the 10 materials studied. Oxygen consumption was nil, and only traces of carbon dioxide were observed. No carbon monoxide was detected at any temperature.

Some organic gases were evolved, but the amounts seen were extremely small compared to the other nine materials studied.

Table A-9. Polyolefin Heat-Shrink Tubing Gas Analysis

Time	Total Quantity (cm ³ -atm)	Amount (Percent)						Other*
		N ₂	O ₂	CO ₂	CO	CH ₄	H ₂	
Matrix E (70°C)								
Start	82.41	78.63	21.37					
2 Weeks	83.53	78.46	21.17	0.02				0.35
1 Month	73.79	78.72	21.07	0.11				0.10
3 Months	65.41	78.71	21.11	0.08				0.10
6 Months	57.77	78.95	21.00	0.08				
1 Year	51.65	78.22	21.30	0.33				0.15
Matrix EE (70°C)								
Start		78.63	21.37					
1 Year	81.40	77.40	21.37	0.12				1.11
Matrix D (70°C)								
Start	81.84	78.63	21.37					
6 Months	82.62	77.87	21.10	0.07				0.96
Matrix C (60°C)								
Start	114.06	78.63	21.37					
1 Year	114.10	78.60	21.30	0.10				
Matrix A (50°C)								
Start	82.90	78.63	21.37					
1 Year	82.78	78.75	21.29	0.06				
*Others (in descending order): 1-butene, T-butyl isobutyl ether, 2-chloropropene, acetone, isobutylene, water, propylene, ethanol, and trichloroethylene.								

10. 91 LD PHENOLIC

Containers: A-10, C-38, D-52, E-66

Average Sample Weight: 30.1 g

The gas analysis results for 91 LD phenolic are given in Table A-10. As expected, this material does react with oxygen, although the rate is slower than with EN-7 polyurethane and polysulfide. At 70°C, oxygen is essentially depleted at 6 months aging. Oxygen depletion was also essentially complete after 1 year at 50 and 60°C.

The only permanent gas evolved in significant amounts was carbon dioxide. As with most of the other materials which evolved CO₂, the amount did not show any stoichiometric relation to the amount of oxygen reacted. The amount of CO₂ observed decreased as the aging temperature was lowered. Very small amounts of carbon monoxide were detected at all three temperatures.

As expected, water was the largest of the other gases evolved. Isopropanol, ethanol, and methanol also were present in greater than trace amounts.

Table A-10. 91 LD Gas Analysis

Time	Total Quantity (cm ³ -atm)	Amount (Percent)						
		N ₂	O ₂	CO ₂	CO	CH ₄	H ₂	Other*
Matrix E (70°C)								
Start	69.33	78.63	21.37					
2 Weeks	77.52	78.16	13.98	1.49	0.05			6.32
1 Month	66.18	85.58	10.46	2.72	0.12			1.12
3 Months	55.68	93.87	1.83	5.84	0.22			
6 Months	50.19	90.56	0.66	6.69				2.09
1 Year	46.76	88.26	0.54	8.59	0.18			2.43
Matrix EE (70°C)								
Start		78.63	21.37					
1 Year	60.08	87.33		6.30	0.23			6.14
Matrix D (70°C)								
Start	67.54	78.63	21.37					
6 Months	70.07	90.51	0.37	5.79	0.23			3.10
Matrix C (60°C)								
Start	108.93	78.63	21.37					
1 Year	103.55	93.24	0.21	5.83	0.33			0.39
Matrix A (50°C)								
Start	72.20	78.63	21.37					
1 Year	64.29	96.84	0.39	4.04	0.32			
*Others (in descending order): water, isopropanol, ethanol, methanol, siloxanes, trichloroethylene, methyl isobutyl ketone, 1-butene, and acetaldehyde.								

PAIR COMBINATION A: EN-7 AND DAP

Containers: A-11, C-39, D-53, E-67

Average Sample Weights:	EN-7:	14.7 g
	DAP:	26.7 g

The analytical data for this pair are summarized in Table A-11. As anticipated from the analytical results on the two individual materials, oxygen depletion was very rapid and carbon dioxide evolution very large. In fact, CO₂ evolution clearly exceeded oxygen availability, thus indicating that oxidative reactions are certainly not the only source for CO₂. The amount of CO₂ observed was essentially equal to the sum of the amounts found for the two separate materials, and this may suggest that oxidative reactions are not a very significant source. The amount of CO₂ decreased at the lower temperatures.

Carbon monoxide evolution was significant, but interestingly was only about half the amount seen from the DAP alone. This suggests some interaction between EN-7 and CO. This is the only evidence of any synergistic effects for this pair combination.

Methane evolution from the pair was the same as for DAP alone. Similarly, the amount of free hydrogen detected matched well with that found for EN-7 separately.

The organic vapors detected are a combination of those seen for the individual materials; they are listed in Table A-11.

Table A-11. EN-7/DAP (Material Pair A) Gas Analysis

Time	Total Quantity (cm ³ -atm)	Amount (Percent)						
		N ₂	O ₂	CO ₂	CO	CH ₄	H ₂	Other*
Matrix E (70°C)								
Start	54.55	78.63	21.37					
2 Weeks	57.25	83.58	0.70	9.18	0.94	2.03		3.57
1 Month	50.81	81.60	0.45	11.83	1.04	3.13	0.83	1.12
3 Months	47.00	77.53	0.30	15.87	1.19	4.46	0.71	
6 Months	42.83	71.17	0.23	19.58	1.37	4.31	0.69	2.65
1 Year	41.08	61.65	0.28	31.32	2.06	4.69	0.57	
Matrix EE (70°C)								
Start		78.63	21.37					
1 Year	61.54	75.87		13.51	1.37		0.76	8.49
Matrix D (70°C)								
Start	57.93	78.63	21.37					
6 Months	65.62	76.84	0.36	15.12	1.38	3.29	0.78	2.23
Matrix C (60°C)								
Start	94.22	78.63	21.37					
1 Year	93.94	84.92	0.22	10.65	1.04	2.51	0.99	
Matrix A (50°C)								
Start	58.74	78.63	21.37					
1 Year	59.26	83.90	0.23	10.85	1.15	4.42	1.22	
*Others (in descending order): water; chloromethane, methanol; ethane; acetone; methyl acetate; methylformate; propylene; trichloroethylene; acetaldehyde; 1-butene; benzene; α-methyl styrene; siloxanes; toluene; and ethylene.								

PAIR COMBINATION B: EN-7 AND 91 LD PHENOLIC

Containers: A-12, C-40, D-54, E-68

Average Sample Weights:	EN-7:	14.7 g
	91 LD:	30.1 g

The gas sampling results are shown in Table A-12. At 70°C, oxygen depletion is rapid, more than 95 percent complete within the first month. The oxygen concentration remaining after 1 year at 50 and at 60°C was less than 0.5 percent. This is consistent with the individual behavior of the two materials.

Carbon dioxide evolution was quite large, as expected, but did not equal the sum of the amounts seen in the individual material containers. This may indicate some synergism. Because CO₂ evolution in pair combination A, which also contained EN-7, did approximately equal the sum for the individual materials, it must be assumed that EN-7 was not affected. Therefore, it seems probable that CO₂ evolution from the other material, 91 LD, is somewhat suppressed by additional CO₂ in the atmosphere. The amount of carbon monoxide observed was essentially the same as that for 91 LD alone, with no contribution from the EN-7. Likewise, the hydrogen apparently came from EN-7 only. No methane was detected.

The organic gases observed were consistent with those seen from the separate materials.

Table A-12. EN-7/91 LD Phenolic (Material Pair B) Gas Analysis

Time	Total Quantity (cm ³ -atm)	Amount (Percent)						
		N ₂	O ₂	CO ₂	CO	CH ₄	H ₂	Other*
Matrix E (70°C)								
Start	53.25	78.63	21.37					
2 Weeks	53.92	No Data						
1 Month	46.92	89.06	0.50	7.46	0.26		0.51	2.21
3 Months	42.23	84.24	0.25	11.41	0.26		0.43	3.41
6 Months	38.57	80.75	0.67	15.88	0.21		0.50	1.99
1 Year	36.89	70.97	0.47	27.92	0.22		0.42	
Matrix EE (70°C)								
Start		78.63	21.37					
1 Year	66.23	78.20		14.62	0.27		0.61	6.30
Matrix D (70°C)								
Start	55.81	78.63	21.37					
6 Months	61.22	84.68	0.41	11.66	0.26		0.62	2.37
Matrix C (60°C)								
Start	89.35	78.63	21.37					
1 Year	86.54	89.79	0.31	8.70	0.26		0.66	0.28
Matrix A (50°C)								
Start	65.05	78.63	21.37					
1 Year	61.85	95.28	0.43	5.51	0.27		0.77	
*Others (in descending order): water; isopropanol; ethanol; acetone; 1-butene, acetaldehyde; methanol; ethane; siloxane; propene; trichloroethylene; toluene; and ethylene.								

PAIR COMBINATION C: SILICONE RTV POTTING MATERIAL AND DAP

Containers: A-13, C-41, D-55, E-69

Average Sample Weight:	Silicone RTV Potting Material:	17.7 g
	DAP:	26.7 g

The gas sampling data for the RTV silicone potting material/DAP pair combination are shown in Table A-13. Oxygen consumption was approximately the same as for DAP alone, and this is consistent with the observation that the RTV silicone potting material has little or no reactivity with oxygen. Carbon dioxide evolution is also the same as with DAP individually, with very little contribution from RTV silicone potting material.

Carbon monoxide, methane, and trace amounts of hydrogen are also near the same as was observed with DAP. No evidence of any interaction or synergism between these two materials exists from the gas analyses.

The organic gases detected are also given in Table A-13. Most of these also appear to be evolved from the DAP.

Table A-13. Silicone RTV Potting Material/DAP (Material Pair C)
Gas Analysis

Time	Total Quantity (cm ³ -atm)	Amount (Percent)						
		N ₂	O ₂	CO ₂	CO	CH ₄	H ₂	Other*
Matrix E (70°C)								
Start	53.93	78.63	21.37					
2 Weeks	62.09	No Data						
1 Month	53.39	76.02	13.83	5.16	1.29	2.43	0.07	1.20
3 Months	45.11	80.22	5.35	7.66	2.72	3.78	0.11	0.16
6 Months	39.07	78.01	0.54	9.05		3.91	0.08	8.41
1 Year	35.16	74.17	0.36	12.81	4.26	4.90	0.08	3.42
Matrix EE (70°C)								
Start		78.63	21.37					
1 Year	57.60	84.07		3.97	3.65	1.56	0.14	6.61
Matrix D (70°C)								
Start	56.26	78.63	21.37					
6 Months	62.00	80.67	1.07	7.65	3.40	3.30	0.15	3.76
Matrix C (60°C)								
Start	94.47	78.63	21.37					
1 Year	96.50	83.46	5.50	6.06	2.81	2.61	0.16	
Matrix A (50°C)								
Start	60.08	78.63	21.37					
1 Year	61.14	82.28	6.88	5.88	2.53	4.10	0.12	

*Others (in descending order): water; siloxane; ethanol; chloromethane, methanol; acetone; 1-butene; ethane; butanal; propylene; acetaldehyde; propane; methyl styrene; ethylene; crotonaldehyde; toluene; and isopropanol.

PAIR COMBINATION D: DAP AND POLYSULFIDE SEALANT

Containers: A-14, C-42, D-56, E-70

Average Sample Weights:	DAP:	26.7 g
	Polysulfide:	28.4 g

The results are given in Table A-14. At 70°C, oxygen depletion was almost complete after only 2 weeks. After 1 year at 50 and 60°C, oxygen depletion was also essentially complete.

This pair combination provided the most striking example of synergistic interaction observed in the matter of carbon dioxide evolution. It will be recalled that DAP was observed to be a material which evolved large amounts of CO₂ when tested individually, and that polysulfide evolved none. The data in Table A-14 show that for the pair CO₂ was barely detectable, clearly indicating that CO₂ reacts with polysulfide strongly. The chemical nature of this reaction is not presently known. It also was observed that the carbon monoxide evolved from DAP appears to react with polysulfide, although not to the extent that CO₂ does. Again, the nature of the reaction is not known.

The amount of methane detected was equivalent to that from DAP alone, with no evidence of any interaction occurring. However, the amount of hydrogen for the pair was somewhat greater than the sum of that from the two materials individually, indicating a possibility of some interaction.

The organics found also are given in Table A-14. They are a combination of those observed in the individual material tests.

Table A-14. DAP/Polysulfide Sealant (Material Pair D) Gas Analysis

Time	Total Quantity (cm ³ -atm)	Amount (Percent)						
		N ₂	O ₂	CO ₂	CO	CH ₄	H ₂	Other*
Matrix E (70°C)								
Start	55.86	78.63	21.37					
2 Weeks	52.68	89.39	0.09	0.08	1.06	1.97		7.41
1 Month	46.16	90.65	0.55	0.10	1.08	3.09	2.06	2.47
3 Months	41.90	85.78	0.46	0.05	1.33	4.26	4.20	3.92
6 Months	37.65	83.43	0.48	0.02	1.83	4.34	5.69	4.21
1 Year	34.56	77.11	0.47	0.03	3.19	5.10	8.29	5.81
Matrix EE (70°C)								
Start		78.63	21.37					
1 Year	55.27	85.79		0.05	1.66	1.48	4.22	6.80
Matrix D (70°C)								
Start	56.01	78.63	21.37					
6 Months	58.33	84.34	0.42	0.01	1.64	3.93	4.80	4.86
Matrix C (60°C)								
Start	94.88	78.63	21.37					
1 Year	87.96	92.20	0.32		1.16	3.06	2.25	1.01
Matrix A (50°C)								
Start	61.48	78.63	21.37					
1 Year	55.58	85.30	0.34		1.10	3.93	1.11	8.22
*Others (in descending order): water; 1-butene, acetaldehyde; chloromethane, methanol; ethane; acetone; propylene; crotonaldehyde; benzene; methyl acetone; butanal; siloxane; propane; toluene; ethylene; ethanol; α-methyl styrene; benzene, trichloroethylene; crotonaldehyde; methyl formate; methylethyl ketone; and methyl acetate.								

NUMERIC CONTAINERS

Containers: N-1 through N-7

As described in the text of this report, the numeric matrix consisted of eight larger containers, each of which accommodated samples of every individual material in the same weights used in the alpha matrix, as well as all pair combinations, also in the same weights used in the alpha matrix. The polysulfide sealant and phenolic microballoon-filled polysulfide samples were encapsulated in glass microballoon-filled epoxy to more nearly simulate their actual use condition in the fireset. It may be assumed, therefore, that these two materials did not contribute their full potential to the gas phase above the samples.

Numeric containers N-1, N-6, N-7, and N-8 were aged at 70°C for 3 months, 6 months, 1 year, and 2 years, respectively. Containers N-2 and N-3 were held at 50°C for 6 months and 1 year, respectively, and containers N-4 and N-5 were aged at 60°C for 6 months and 1 year, respectively. The gas analysis data are summarized in Table A-15. The data for N-8, 2 years at 70°C, are not included in Table A-15 because of a failure of the GC detector during the gas sampling.

In light of the data obtained on the individual materials, there were no unexpected results from the numeric matrix. Oxygen was depleted rapidly and almost completely at all temperatures. Carbon dioxide evolution increased with both time and temperature. At 70°C, the rate after 3 months is approximately linear, following an initially higher rate. This form of CO₂ evolution was observed individually with EN-7, DAP, and 91 LD. The data clearly indicate that the limit of CO₂ evolution was not reached within 1 year at 70°C.

The results are somewhat different with carbon monoxide and methane. It will be noticed from Table A-15 that the observed concentrations of these two gases do not vary greatly with either time or temperature of aging. The only significant source for both is DAP, and the data clearly indicate that the levels observed are near, if not equal to, the total quantity to be expected.

A similar condition was observed for hydrogen evolution. In particular, there is no difference between the hydrogen concentrations seen at 6 months and one year at 70°C. The limiting evolution had apparently been achieved.

The organics detected in the gas phase appear to have come mainly from DAP and the silicone samples. There does not appear to be any evidence of material interactions in the organic data.

Table A-15. Numeric Containers (All Materials) Gas Analysis

Time	Total Quantity (cm ³ -atm)	Amount (Percent)						
		N ₂	O ₂	CO ₂	CO	CH ₄	H ₂	Other
N-1 (70°C)								
Start	480.14	78.63	21.37					
3 Months	453.44	86.99	0.30	5.36	0.63	1.24	0.95	4.53
Others: ethanol; siloxanes; acetone; butene, acetaldehyde; ethane; methanol; water; propylene; chloromethane; ethylene; dimethyl styrene.								
N-2 (50°C)								
Start	484.03	78.63	21.37					
6 Months	408.67	88.69	0.67	1.62	0.53	1.12	0.78	6.59
Others: ethane, ethylene; siloxanes; ethanol; acetaldehyde; acetone; propylene; water; trichloroethylene.								
N-3 (50°C)								
Start	482.43	78.63	21.37					
1 Year	419.24	86.76	0.21	3.08	0.66	1.38	0.76	7.15
Others: ethanol; ethane, ethylene; siloxanes; acetone; 1-butene; water; methanol; isopropanol.								
N-4 (60°C)								
Start	464.82	78.63	21.37					
6 Months	418.63	84.93	0.34	4.03	0.61	1.42	0.75	7.92
Others: ethanol; siloxanes; ethane, ethylene; acetaldehyde; acetone; methanol; propylene; water.								
N-5 (60°C)								
Start	464.91	78.63	21.37					
1 Year	420.08	83.92	0.20	4.81	0.73	1.63	0.81	7.90
Others: ethanol; ethane; siloxanes; acetone; butene, butane; methanol, chloromethane; water; isopropanol.								
N-6 (70°C)								
Start	447.19	78.63	21.37					
6 Months	432.45	82.17	0.14	6.23	0.70	1.39	1.27	8.10
Others; ethanol, siloxanes, acetone, acetaldehyde, ethane, methanol, propylene, water.								
N-7 (70°C)								
Start	467.42	78.63	21.37					
1 Year	450.70	82.68	0.17	9.33	0.87	1.47	1.26	4.22
Others: siloxanes; ethanol; acetone; butene, butane; ethane; methanol, chloromethane; water; propylene; isopropanol.								

Appendix B
PHYSICAL PROPERTIES

1. GLASS MICROBALLOON-FILLED EPOXY

Tests: Flexural modulus, TMA, weight change, and density

The test data are shown in Tables B-1 through B-4. The only significant change noted was the increase in glass transition temperature as determined by TMA analysis. The change in T_g , caused by additional curing of the epoxy during thermal aging, is commonly observed for most epoxy systems under similar conditions. The small variations noted in density stem from the fact that the samples were cut from WR test block castings, which normally differ in density slightly. No changes were observed which would indicate that the material was degrading.

Table B-1. GMB Epoxy: Flexural Modulus and Flexural Strength

Temperature (°C)	Time	Container	Modulus (psi x 10 ⁻³)		Stress (psi x 10 ⁻³)	
			Mean	Standard Deviation	Mean	Standard Deviation
Ambient	0		470	12	8.95	0.26
Ambient	3 Months		477	6	9.18	0.22
70	3 Months	N-1	437	10	8.12	0.23
Ambient	6 Months		454	7	8.67	0.35
50	6 Months	N-2	446	6	8.59	0.17
60	6 Months	N-4	439	9	7.84	0.19
70	6 Months	N-6	410	4	7.46	0.20
70	6 Months	D-43	427	13	7.90	0.22
Ambient	1 Year		458	11	8.38	0.28
50	1 Year	N-3	462	7	8.70	0.21
50	1 Year	A-1	476	19	8.23	0.44
60	1 Year	N-5	445	10	7.69	0.18
60	1 Year	C-29	452	7	8.42	0.22
70	1 Year	N-7	425	6	7.71	0.15
70	1 Year	E-57	436	2	8.33	0.31
Ambient	2 Years		465	4	8.48	0.52
70	2 Years	N-8	439	6	7.37	0.14

Table B-2. GMB Epoxy: T_g by TMA

Temperature (°C)	Time	Container	T_g (°C)
Ambient	0		77
Ambient	3 Months		75
70	3 Months	N-1	90
Ambient	6 Months		73
50	6 Months	N-2	83
60	6 Months	N-4	92
70	6 Months	N-6	94
70	6 Months	D-43	93
Ambient	1 Year		82
50	1 Year	N-3	91
50	1 Year	A-1	88
60	1 Year	N-5	88
60	1 Year	C-29	92
70	1 Year	N-7	101
70	1 Year	E-57	95
Ambient	2 Years		79
70	2 Years	N-8	100

Table B-3. GMB Epoxy: Weight Change

Temperature (°C)	Time	Container	Weight Change (Percent)
70	3 Months	N-1	+0.40
50	6 Months	N-2	+0.41
60	6 Months	N-4	+0.44
70	6 Months	N-6	+0.43
70	6 Months	D-43	+0.57
50	1 Year	N-3	+0.33
50	1 Year	A-1	+0.44
60	1 Year	N-5	+0.43
60	1 Year	C-29	+0.49
70	1 Year	N-7	-2.20
70	1 Year	E-57	+0.36
50	2 Years	B-15	+0.62
70	2 Years	N-8	+0.58

Table B-4. GMB Epoxy: Density

Temperature (°C)	Time	Container	Mean (g/cm ³)	Standard Deviation
Ambient	3 Months		0.811	0.001
70	3 Months	N-1	0.810	0.000
Ambient	6 Months		0.814	0.005
50	6 Months	N-2	0.807	0.001
60	6 Months	N-4	0.806	0.002
70	6 Months	N-6	0.813	0.001
70	6 Months	D-43	0.814	0.001
Ambient	1 Year		0.806	0.004
50	1 Year	N-3	0.810	0.004
50	1 Year	A-1	0.815	0.001
60	1 Year	N-5	0.811	0.001
60	1 Year	C-29	0.807	0.002
70	1 Year	N-7	0.806	0.002
70	1 Year	E-57	0.813	0.002
Ambient	2 Years		0.804	0.001
70	2 Years	N-8	0.805	0.002

2. EN-7 POLYURETHANE

Tests: Dynamic Shear Modulus, Weight Change, and Density

The data are given in Tables B-5 through B-9. The dynamic shear modulus versus temperature data for zero time, 2 year unaged (ambient), and 2 year aged at 70°C are given as representative of the very large number of shear modulus measurements actually taken. Virtually all the measurements taken gave identical results, and no changes with aging were observed. Similarly, no significant changes in weight or density occurred with aging. Visually, the samples changed color from an off-white to a caramel color, but otherwise were not changed.

Table B-5. EN-7: Zero Time Shear Modulus

Temperature (°C)	Shear Modulus, G' (MPa)	Loss Modulus, G'' (MPa)
-140	1336	52
-120	1189	40
-100	1091	30
-80	894	61
-70	409	102
-60	188	41
-40	94.5	10
-20	74.1	4.5
0	60.5	6.1
20	35.5	5.9
40	10.2	4.2
60	1.47	0.64
80	0.60	0.26
100	0.29	0.02
120	0.29	0.01
140	0.26	0.02

Table B-6. EN-7: Ambient 2-Year Shear Modulus

Temperature (°C)	Shear Modulus, G' (MPa)	Loss Modulus, G'' (MPa)
-140	1294	39
-120	1187	31
-100	1150	22
-90	1111	23
-85	1071	31
-80	1000	53
-75	816	58
-70	580	117
-65	359	88
-60	237	54
-55	177	35
-50	137	21
-45	118	15
-40	104	11
-20	76	5.1
0	60	5.1
20	42	5.7
30	28	5.7
40	17	4.3
50	6.7	2.5
60	2.1	0.9
70	1.6	0.7

Table B-7. EN-7: 70°C, 2-Year Shear
Modulus (Container N-8)

Temperature (°C)	Shear Modulus, G' (MPa)	Loss Modulus, G'' (MPa)
-140	1341	51
-120	1228	39
-100	1182	26
-90	1147	26
-85	1124	37
-80	1094	47
-75	896	95
-70	592	122
-65	361	91
-60	233	55
-55	179	35
-50	144	24
-45	121	17
-40	105	13
-20	76	6.0
0	56	5.5
20	36	5.5
30	25	5.1
40	15	4.0
50	5.8	2.4
60	2.7	0.8
70	0.8	0.3

Table B-8. EN-7: Weight Change

Temperature (°C)	Time	Container	Weight Change (Percent)
70	3 Months	N-1	+0.66
70	3 Months	N-1, Combination A	+0.45
70	3 Months	N-1, Combination B	+0.37
50	6 Months	N-2	+0.60
50	6 Months	N-2, Combination A	+0.37
50	6 Months	N-2, Combination B	+0.32
60	6 Months	N-4	+0.47
60	6 Months	N-4, Combination A	+0.65
60	6 Months	N-4, Combination B	+0.74
70	6 Months	N-6	+0.83
70	6 Months	N-6, Combination A	+0.73
70	6 Months	N-6, Combination B	+0.67
70	6 Months	D-44	+0.25
70	6 Months	D-53, Combination A	+0.25
70	6 Months	D-54, Combination B	+0.26
50	1 Year	N-3	+0.78
50	1 Year	N-3, Combination A	+0.28
50	1 Year	N-3, Combination B	+0.32
50	1 Year	A-2	+0.17
50	1 Year	A-11, Combination A	+0.18
50	1 Year	A-12, Combination B	+0.18
60	1 Year	N-5	+0.91
60	1 Year	N-5, Combination A	+0.61
60	1 Year	N-5, Combination B	+0.43
60	1 Year	C-30	+0.18
60	1 Year	C-39, Combination A	+0.19
60	1 Year	C-40, Combination B	+0.17
70	1 Year	N-7	+0.96
70	1 Year	N-7, Combination A	+1.26
70	1 Year	N-7, Combination B	+0.91
70	1 Year	E-58	+0.09
70	1 Year	E-67, Combination A	+0.11
70	1 Year	E-68, Combination B	+0.12
70	2 Years	N-8	+1.29
70	2 Years	N-8, Combination A	+1.25
70	2 Years	N-8, Combination B	+1.25
50	2 Years	B-16	+0.21
50	2 Years	B-25, Combination A	+0.21
50	2 Years	B-26, Combination B	+0.18

Table B-9. EN-7: Density

Temperature (°C)	Time	Container	Mean (g/cm ³)	Standard Deviation
Ambient	3 Months		1.01	0.000
70	3 Months	N-1	1.02	0.006
70	3 Months	N-1, Combination A	1.02	0.000
70	3 Months	N-1, Combination B	1.02	0.010
Ambient	6 Months		1.01	0.000
50	6 Months	N-2	1.02	0.006
50	6 Months	N-2, Combination A	1.02	0.000
50	6 Months	N-2, Combination B	1.02	0.000
60	6 Months	N-4	1.02	0.000
60	6 Months	N-4, Combination A	1.02	0.000
60	6 Months	N-4, Combination B	1.02	0.000
70	6 Months	N-6	1.02	0.000
70	6 Months	N-6, Combination A	1.02	0.000
70	6 Months	N-6, Combination B	1.02	0.000
70	6 Months	D-44	1.01	0.006
70	6 Months	D-53, Combination A	1.02	0.006
70	6 Months	D-54, Combination B	1.01	0.006
Ambient	1 Year		1.01	0.000
50	1 Year	N-3	1.02	0.006
50	1 Year	N-3, Combination A	1.02	0.006
50	1 Year	N-3, Combination B	1.02	0.006
50	1 Year	A-2	1.01	0.000
50	1 Year	A-11, Combination A	1.01	0.000
50	1 Year	A-12, Combination B	1.01	0.000
60	1 Year	N-5	1.01	0.000
60	1 Year	N-5, Combination A	1.01	0.006
60	1 Year	N-5, Combination B	1.02	0.006
60	1 Year	C-30	1.02	0.000
60	1 Year	C-39, Combination A	1.02	0.006
60	1 Year	C-40, Combination B	1.02	0.006
70	1 Year	N-7	1.01	0.000
70	1 Year	N-7, Combination A	1.01	0.006
70	1 Year	N-7, Combination B	1.02	0.000
70	1 Year	E-58	1.02	0.000
70	1 Year	E-67, Combination A	1.02	0.000
70	1 Year	E-68, Combination B	1.02	0.006
Ambient	2 Years		1.01	0.000
70	2 Years	N-8	1.01	0.000
70	2 Years	N-8, Combination A	1.01	0.000
70	2 Years	N-8, Combination B	1.01	0.006

3. PHENOLIC MICROBALLOON-FILLED POLYSULFIDE

Tests: Compression-deflection testing, TMA, weight change,
 and density

The data are given in Tables B-10 through B-13. The compression-deflection values shown in Table B-10 are the stress in psi required to produce a compression of the sample of 15 percent, and are the mean of three samples. Each of the three samples used for the mean at each aging condition was cycled three times through the test, and the value reported is that measured for the third compression cycle. The results listed in Table B-10 indicate considerable sample-to-sample variation, but show no systematic trend with thermal aging. The observed variations apparently are caused by fabrication rather than degradation.

Table B-11 lists the glass transition temperature (T_g) and softening temperatures (T_s) as determined by TMA. Although there is again considerable scatter among the measurements, there is a general trend to higher values for both T_g and T_s with increasing age. This probably is caused by some additional curing, as well as loss of solvent with time and temperature. It is interesting to note that the increase in T_g appears to be time dependent but not temperature dependent, whereas T_s is primarily temperature dependent.

The weight change and density data given in Tables B-12 and B-13 reflect little change. The weight losses are small and probably caused by solvent loss. The density showed no change with time or temperature.

Table B-10. Polysulfide/Phenolic Microballoon:
Compression-Deflection Testing

Temperature (°C)	Time	Container	Mean (psi)	Standard Deviation
Ambient	0		303	36.54
Ambient	3 Months		238	32.20
70	3 Months	N-1	206	39.00
Ambient	6 Months		303	35.12
50	6 Months	N-2	308	2.89
60	6 Months	N-4	288	2.89
70	6 Months	N-6	242	20.21
Ambient	1 Year		322	10.41
50	1 Year	N-3	218	23.09
60	1 Year	N-5	258	12.58
70	1 Year	N-7	247	30.55
Ambient	2 Years		282	50.55
70	2 Years	N-8	266	18.04

Table B-11. Polysulfide/Phenolic Microballoon:
 T_g and T_s by TMA

Temperature (°C)	Time	Container	T_g (°C)	T_s (°C)
Ambient	0		-52	116
Ambient	3 Months		-57	96
70	3 Months	N-1	-58	115
Ambient	6 Months		-52	100
50	6 Months	N-2	-51	111
60	6 Months	N-4	-50	108
70	6 Months	N-6	-46	156
70	6 Months	D-45	-52	144
Ambient	1 Year		-47	113
50	1 Year	N-3	-48	123
50	1 Year	A-3	-45	125
60	1 Year	N-5	-47	126
60	1 Year	C-31	-48	143
70	1 Year	N-7	-46	153
70	1 Year	E-59	-47	155
Ambient	2 Years		-46	117
70	2 Years	N-8	-47	138

Table B-12. Polysulfide/Phenolic Microballoon:
Weight Change

Temperature (°C)	Time	Container	Weight Change (Percent)
70	3 Months	N-1	-0.50
50	6 Months	N-2	-0.17
60	6 Months	N-4	-0.46
70	6 Months	N-6	-2.0
70	6 Months	D-45	-0.69
50	1 Year	N-3	-0.29
50	1 Year	A-3	-0.06
60	1 Year	N-5	-0.86
60	1 Year	C-31	+0.04
70	1 Year	N-7	-0.73
70	1 Year	E-59	-0.18
70	2 Years	N-8	-2.7
50	2 Years	B-17	-0.04

Table B-13. Polysulfide/Phenolic Microballoon:
Density

Temperature (°C)	Time	Container	Mean (g/cm ³)	Standard Deviation
Ambient	3 Months		1.65	0.006
70	3 Months	N-1	1.64	0.008
Ambient	6 Months		1.64	0.022
50	6 Months	N-2	1.65	0.019
60	6 Months	N-4	1.65	0.015
70	6 Months	N-6	1.65	0.019
70	6 Months	D-45		
Ambient	1 Year		1.64	0.018
50	1 Year	N-3	1.64	0.028
50	1 Year	A-3	1.64	0.013
60	1 Year	N-5	1.65	0.025
60	1 Year	C-31	1.64	0.016
70	1 Year	N-7	1.65	0.017
70	1 Year	E-59	1.65	0.009
Ambient	2 Years		1.65	0.021
70	2 Years	N-8	1.64	0.023

4. SILICONE RTV POTTING MATERIAL

Tests: Shore A hardness, TMA, weight change, and density

RTV silicone potting material is one of only two materials included in this study which showed any significant change in physical properties as a result of thermally-accelerated aging. Unfortunately, the tests chosen do not reflect the real changes occurring. The data taken are given in Tables B-14 through B-17. The Shore A hardness results listed in Table B-14 indicate no change except in the samples aged for 2 years at 70°C, which show approximately a 15 percent decrease. The T_g as determined by TMA indicates considerable scatter but no trend toward degradation with aging. Weight loss measurements gave a small decrease, probably because of the vaporization of ethanol which is a product of the cure reaction. Density determinations showed no change with time or temperature.

The evidence obtained for degradation was qualitative in nature. It was observed during disassembly of the 6-months specimens that the tear or tensile strength of the material had dropped noticeably, and that the effect was worse with increasing temperature. Similar changes were noted in the 1-year and 2-year samples, but attempts to perform quantitative tensile strength measurements were not successful because of sample geometry. However, Robert Martinez of Sandia National Laboratories Albuquerque, upon learning of these qualitative observations, did fabricate and age tensile specimens in air and in argon.

The results at SNLA clearly showed a drop in tensile strength in both atmospheres after 1 year at 70°C. The decrease was approximately 30 percent in argon and almost 50 percent for those samples aged in air. No visual evidence of reversion was observed at Bendix or Sandia.

Although no visual evidence of reversion was obvious, the data from Bendix and Sandia clearly indicate that some degradative process is underway. Oxidative attack is unlikely, because all the crosslinks in the cured resin are of the

type. Furthermore, the gas analyses described in Appendix A show very little oxygen consumption by RTV silicone potting material. Additional crosslinking also seems an unlikely explanation, because this should tend to increase rather than decrease both tensile strength and hardness. By elimination, it would appear that a reversion process is the most probable degradative mechanism, possibly a hydrolysis of the crosslink bonds caused by water vapor and a still-active catalyst. The data certainly suggest that the long-term chemical stability of this material should be viewed with suspicion.

Table B-14. RTV Silicone Potting Material: Durometer Hardness

Temperature (°C)	Time	Container	Shore A Hardness
Ambient	0		46.0
Ambient	3 Months		50.8
70	3 Months	N-1	48.8
70	3 Months	N-1, Combination C	45.4
Ambient	6 Months		49.5
50	6 Months	N-2	45.0
50	6 Months	N-2, Combination C	43.5
60	6 Months	N-4	51.5
60	6 Months	N-4, Combination C	47.0
70	6 Months	N-6	44.0
70	6 Months	N-6, Combination C	47.5
70	6 Months	D-46	46.0
70	6 Months	D-55, Combination C	48.5
Ambient	1 Year		48.5
50	1 Year	N-3	45.0
50	1 Year	N-3, Combination C	50.0
50	1 Year	A-4	45.0
50	1 Year	A-13, Combination C	55.0
60	1 Year	N-5	46.5
60	1 Year	N-5, Combination C	45.5
60	1 Year	C-32	42.5
60	1 Year	C-41, Combination c	46.5
70	1 Year	N-7	45.5
70	1 Year	N-7, Combination C	43.0
70	1 Year	E-60	40.0
70	1 Year	E-69, Combination C	46.5
Ambient	2 Years		43.6
70	2 Years	N-8	37.4
70	2 Years	N-8, Combination C	36.0

Table B-15. RTV Silicone Potting Material: T_g by TMA

Temperature (°C)	Time	Container	T _g (°C)
Ambient	0		-97
Ambient	3 Months		-94
70	3 Months	N-1	-95
70	3 Months	N-1, Combination C	-100
Ambient	6 Months		-102
50	6 Months	N-2	-104
50	6 Months	N-2, Combination C	-105
60	6 Months	N-4	-105
60	6 Months	N-4, Combination C	-104
70	6 Months	N-6	-105
70	6 Months	N-6, Combination C	-106
70	6 Months	D-46	-104
70	6 Months	D-55, Combination C	-104
Ambient	1 Year		-103
50	1 Year	N-3	-108
50	1 Year	N-3, Combination C	-110
50	1 Year	A-4	-103
50	1 Year	A-13, Combination C	-99
60	1 Year	N-5	-101
60	1 Year	N-5, Combination C	-105
60	1 Year	C-32	-107
60	1 Year	C-41, Combination C	-100
70	1 Year	N-7	-111
70	1 Year	N-7, Combination C	-106
70	1 Year	E-60	-100
70	1 Year	E-69, Combination C	-102
Ambient	2 Years		-99
70	2 Years	N-8	-97
70	2 Years	N-8, Combination C	-99

Table B-16. RTV Silicone Potting Material: Weight Change

Temperature (°C)	Time	Container	Weight Change (Percent)
70	3 Months	N-1	-1.14
70	3 Months	N-1, Combination C	-0.81
50	6 Months	N-2	-0.29
50	6 Months	N-2, Combination C	-0.38
60	6 Months	N-4	-0.57
60	6 Months	N-4, Combination C	-1.27
70	6 Months	N-6	-1.36
70	6 Months	N-6, Combination C	-1.18
70	6 Months	D-46	-0.19
70	6 Months	D-55, Combination C	-0.16
50	1 Year	N-3	-0.55
50	1 Year	N-3, Combination C	-0.78
50	1 Year	A-4	-0.07
50	1 Year	A-13, Combination C	-0.14
60	1 Year	N-5	-1.09
60	1 Year	N-5, Combination C	-1.31
60	1 Year	C-32	-0.03
60	1 Year	C-41, Combination C	-0.09
70	1 Year	N-7	-2.18
70	1 Year	N-7, Combination C	-2.05
70	1 Year	E-60	-0.79
70	1 Year	E-69, Combination C	+0.03
50	2 Years	B-18	-0.04
50	2 Years	B-27, Combination C	-0.05
70	2 Years	N-8	-2.34
70	2 Years	N-8, Combination C	-2.69

Table B-17. RTV Silicone Potting Material: Density

Temperature (°C)	Time	Container	Mean (g/cm ³)	Standard Deviation
Ambient	3 Months		1.22	0.000
70	3 Months	N-1	1.23	0.006
70	3 Months	N-1, Combination C	1.23	0.000
Ambient	6 Months		1.24	0.009
50	6 Months	N-2	1.23	0.009
50	6 Months	N-2, Combination C	1.23	0.004
60	6 Months	N-4	1.25	0.011
60	6 Months	N-4, Combination C	1.23	0.004
70	6 Months	N-6	1.24	0.005
70	6 Months	N-6, Combination C	1.25	0.022
70	6 Months	D-46	1.24	0.005
70	6 Months	D-55, Combination C	1.23	0.004
Ambient	1 Year		1.24	0.004
50	1 Year	N-3	1.23	0.005
50	1 Year	N-3, Combination C	1.23	0.005
50	1 Year	A-4	1.23	0.004
50	1 Year	A-13, Combination C	1.22	0.005
60	1 Year	N-5	1.22	0.005
60	1 Year	N-5, Combination C	1.22	0.004
60	1 Year	C-32	1.22	0.004
60	1 Year	C-41, Combination C	1.23	0.007
70	1 Year	N-7	1.24	0.004
70	1 Year	N-7, Combination C	1.23	0.005
70	1 Year	E-60	1.24	0.005
70	1 Year	E-69, Combination C	1.23	0.008
Ambient	2 Years		1.23	0.010
70	2 Years	N-8	1.23	0.005
70	2 Years	N-8, Combination C	1.24	0.004

5. DIALLYL PHTHALATE

Tests: Flexural modulus, weight change, and density

The data are shown in Tables B-18 through B-20. The flexural modulus and strength values given are each the mean of five samples per aging condition. The modulus values are directly proportional to the slope of the stress-strain plot, and the strength values are the stress in psi at which failure occurs.

While the gas analysis data on DAP provided some interesting and even surprising results, the same is not true for its measured physical properties. An inspection of the data shows that no discernable physical changes occurred with aging. Furthermore, no color change or other visual alteration was observed.

Table B-18. DAP: Flexural Modulus and Flexural Strength

Temperature (°C)	Time	Container	Modulus (psi x 10 ⁻⁶)		Stress (psi x 10 ⁻³)	
			Mean	Standard Deviation	Mean	Standard Deviation
Ambient	0		1.42	0.14	9.36	1.10
Ambient	3 Months		1.35	0.02	11.01	1.45
70	3 Months	N-1	1.32	0.15	9.45	1.39
70	3 Months	N-1, Combination A	1.32	0.10	10.26	1.83
70	3 Months	N-1, Combination C	1.41	0.02	10.45	2.14
70	3 Months	N-1, Combination D	1.32	0.12	9.03	0.92
Ambient	6 Months		1.28	0.07	9.91	1.17
50	6 Months	N-2	1.28	0.08	9.39	2.63
50	6 Months	N-2, Combination A	1.29	0.13	10.05	1.66
50	6 Months	N-2, Combination C	1.24	0.09	9.20	1.65
50	6 Months	N-2, Combination D	1.25	0.07	10.08	2.54
60	6 Months	N-4	1.37	0.07	10.38	1.67
60	6 Months	N-4, Combination A	1.28	0.10	9.12	0.87
60	6 Months	N-4, Combination C	1.38	0.10	10.87	1.49
60	6 Months	N-4, Combination D	1.29	0.10	10.23	1.84
70	6 Months	N-6	1.29	0.08	10.35	1.99
70	6 Months	N-6, Combination A	1.29	0.15	10.63	1.37
70	6 Months	N-6, Combination C	1.25	0.07	8.04	0.99
70	6 Months	N-6, Combination D	1.25	0.11	10.16	0.91
70	6 Months	D-47	1.28	0.10	9.04	0.74
70	6 Months	D-53, Combination A	1.33	0.12	9.67	1.31
70	6 Months	D-55, Combination C	1.29	0.05	9.60	1.15
70	6 Months	D-46, Combination D	1.27	0.11	8.93	1.67

Table B-18 Continued. DAP: Flexural Modulus and Flexural Strength

Temperature (°C)	Time	Container	Modulus (psi x 10 ⁻⁶)		Stress (psi x 10 ⁻³)	
			Mean	Standard Deviation	Mean	Standard Deviation
Ambient	1 Year		1.34	0.11	10.36	1.73
50	1 Year	N-3	1.22	0.02	9.55	0.76
50	1 Year	N-3, Combination A	1.27	0.08	10.73	2.04
50	1 Year	N-3, Combination C	1.29	0.07	9.86	1.29
50	1 Year	N-3, Combination D	1.19	0.20	8.89	0.67
50	1 Year	A-5	1.26	0.08	10.15	1.23
50	1 Year	A-11, Combination A	1.30	0.02	9.84	1.29
50	1 Year	A-13, Combination C	1.27	0.08	9.87	3.12
50	1 Year	A-14, Combination D	1.26	0.01	10.75	2.14
60	1 Year	N-5	1.26	0.09	10.38	2.29
60	1 Year	N-5, Combination A	1.30	0.06	10.82	1.38
60	1 Year	N-5, Combination C	1.27	0.04	11.12	1.72
60	1 Year	N-5, Combination D	1.31	0.02	9.42	1.97
60	1 Year	C-33	1.31	0.06	10.87	2.25
60	1 Year	C-39, Combination A	1.30	0.07	10.95	1.47
60	1 Year	C-41, Combination C	1.30	0.08	10.65	1.65
60	1 Year	C-42, Combination D	1.23	0.06	8.49	0.93
70	1 Year	N-7	1.37	0.23	10.90	1.87
70	1 Year	N-7, Combination A	1.34	0.09	10.85	1.76
70	1 Year	N-7, Combination C	1.24	0.07	9.56	1.04
70	1 Year	N-7, Combination D	1.21	0.06	8.90	1.15

Table B-18 Continued. DAP: Flexural Modulus and Flexural Strength

Temperature (°C)	Time	Container	Modulus (psi x 10 ⁻⁶)		Stress (psi x 10 ⁻³)	
			Mean	Standard Deviation	Mean	Standard Deviation
70	1 Year	E-61	1.23	0.06	9.19	1.70
70	1 Year	E-67, Combination A	1.21	0.95	8.95	1.11
70	1 Year	E-69, Combination C	1.26	0.11	9.42	1.53
70	1 Year	E-70, Combination D	1.32	0.06	9.58	2.06
Ambient	2 Years		1.38	0.16	10.52	2.11
70	2 Years	N-8	1.36	0.08	8.95	1.25
70	2 Years	N-8, Combination A	1.36	0.04	8.77	1.07
70	2 Years	N-8, Combination C	1.45	0.10	11.36	1.47
70	2 Years	N-8, Combination D	1.29	0.04	8.30	1.56

Table B-19. DAP: Weight Change

Temperature (°C)	Time	Container	Weight Change (Percent)
70	3 Months	N-1	-0.06
70	3 Months	N-1, Combination A	-0.01
70	3 Months	N-1, Combination C	-0.06
70	3 Months	N-1, Combination D	-0.14
50	6 Months	N-2	+0.17
50	6 Months	N-2, Combination A	-0.08
50	6 Months	N-2, Combination C	-0.01
50	6 Months	N-2, Combination D	+0.05
60	6 Months	N-4	-0.04
60	6 Months	N-4, Combination A	-0.03
60	6 Months	N-4, Combination C	-0.04
60	6 Months	N-4, Combination D	-0.25
70	6 Months	N-6	-0.08
70	6 Months	N-6, Combination A	-0.05
70	6 Months	N-6, Combination C	-0.01
70	6 Months	N-6, Combination D	+0.05
70	6 Months	D-47	+0.16
70	6 Months	D-53, Combination A	-0.12
70	6 Months	D-55, Combination C	-0.07
70	6 Months	D-56, Combination D	-0.03
50	1 Year	N-3	-0.06
50	1 Year	N-3, Combination A	-0.06
50	1 Year	N-3, Combination C	-0.05
50	1 Year	N-3, Combination D	+0.03
50	1 Year	A-5	+0.08
50	1 Year	A-11, Combination A	-0.17
50	1 Year	A-13, Combination C	-0.12
50	1 Year	A-14, Combination D	-0.16
60	1 Year	N-5	-0.09
60	1 Year	N-5, Combination A	-0.08
60	1 Year	N-5, Combination C	-0.09
60	1 Year	N-5, Combination D	-0.01
60	1 Year	C-33	+0.06
60	1 Year	C-39, Combination A	-0.22
60	1 Year	C-41, Combination C	-0.16
60	1 Year	C-42, Combination D	-0.17

Table B-19 Continued. DAP: Weight Change

Temperature (°C)	Time	Container	Weight Change (Percent)
70	1 Year	N-7	-0.09
70	1 Year	N-7, Combination A	-0.09
70	1 Year	N-7, Combination C	-0.13
70	1 Year	N-7, Combination D	+0.16
70	1 Year	E-61	+0.01
70	1 Year	E-67, Combination A	-0.27
70	1 Year	E-69, Combination C	-3.35
70	1 Year	E-70, Combination D	-0.25
70	2 Years	N-8	-0.15
70	2 Years	N-8, Combination A	-0.17
70	2 Years	N-8, Combination C	-0.15
70	2 Years	N-8, Combination D	+0.09

Table B-20. DAP: Density

Temperature (°C)	Time	Container	Mean (g/cm ³)	Standard Deviation
Ambient	3 Months		1.68	0.006
70	3 Months	N-1	1.67	0.012
70	3 Months	N-1, Combination A	1.67	0.006
70	3 Months	N-1, Combination C	1.66	0.010
70	3 Months	N-1, Combination D	1.66	0.006
Ambient	6 Months		1.67	0.007
50	6 Months	N-2	1.68	0.004
50	6 Months	N-2, Combination A	1.70	0.008
50	6 Months	N-2, Combination C	1.70	0.009
50	6 Months	N-2, Combination D	1.72	0.005
60	6 Months	N-4	1.67	0.004
60	6 Months	N-4, Combination A	1.67	0.012
60	6 Months	N-4, Combination C	1.67	0.004
60	6 Months	N-4, Combination D	1.68	0.015
70	6 Months	N-6	1.64	0.023
70	6 Months	N-6, Combination A	1.67	0.005
70	6 Months	N-6, Combination C	1.66	0.004
70	6 Months	N-6, Combination D	1.66	0.009
70	6 Months	D-47	1.67	0.015
70	6 Months	D-53, Combination A	1.66	0.005
70	6 Months	D-55, Combination C	1.66	0.004
70	6 Months	D-56, Combination D	1.66	0.005
Ambient	1 Year		1.68	0.008
50	1 Year	N-3	1.67	0.008
50	1 Year	N-3, Combination A	1.66	0.004
50	1 Year	N-3, Combination C	1.67	0.007
50	1 Year	N-3, Combination D	1.67	0.007
50	1 Year	A-5	1.67	0.006
50	1 Year	A-11, Combination A	1.67	0.004
50	1 Year	A-13, Combination C	1.67	0.008
50	1 Year	A-14, Combination D	1.67	0.004
60	1 Year	N-5	1.67	0.004
60	1 Year	N-5, Combination A	1.67	0.004
60	1 Year	N-5, Combination C	1.67	0.008
60	1 Year	N-5, Combination D	1.67	0.008

Table B-20 Continued. DAP: Density

Temperature (°C)	Time	Container	Mean (g/cm ³)	Standard Deviation
60	1 Year	C-33	1.67	0.000
60	1 Year	C-39, Combination A	1.67	0.010
60	1 Year	C-41, Combination C	1.67	0.005
60	1 Year	C-42, Combination D	1.66	0.006
70	1 Year	N-7	1.66	0.005
70	1 Year	N-7, Combination A	1.66	0.017
70	1 Year	N-7, Combination C	1.66	0.004
70	1 Year	N-7, Combination D	1.66	0.004
70	1 Year	E-61	1.66	0.009
70	1 Year	E-67, Combination A	1.66	0.010
70	1 Year	E-69, Combination C	1.67	0.005
70	1 Year	E-70, Combination D	1.66	0.007
Ambient	2 Years		1.68	0.006
70	2 Years	N-8	1.66	0.000
70	2 Years	N-8, Combination A	1.66	0.011
70	2 Years	N-8, Combination C	1.66	0.000
70	2 Years	N-8, Combination D	1.66	0.006

6. POLYSULFIDE SEALANT

Tests: Volume resistivity, TMA, Shore A hardness, weight change, and density

Polysulfide sealant was the only material other than silicone RTV Potting Material that showed significant changes in physical properties as a result of aging. The data are given in Tables B-21 through B-25.

The volume resistivity data are shown in Table B-21. The measurements were made on 2.00 by 0.125 in. disc samples between copper electrodes. Six measurements were made on each individual sample, and between the measurements the sample was removed from the electrodes and repositioned for the next determination. The data table gives the high, low, and average of the six measurements on each sample in megohms. Comparing the data at zero time with that for the samples aged 6 months and 1 year at 70°C indicates that the thermally aged specimens have suffered a dramatic decrease in resistivity. However, this change may have been caused by the samples adhering strongly to the spacers placed between them during aging; consequently, severe pullout of sample material occurred when these spacers were removed, resulting in pitting on the faces of the discs. To check for this effect, 6 samples which had been stored at ambient conditions for 2 years were measured. The results showed that the volume resistivity had increased with ambient temperature aging, probably because of a loss of solvent from the material. It is improbable that aging at temperatures such as 70°C would produce changes diametrically opposite to those observed for ambient temperature aging; therefore, it was concluded that the sharp decrease in resistivity seen for the thermally-aged samples was caused by surface damage (pitting) that occurred after aging rather than by chemical changes in the material.

The T_g as determined by TMA showed a slight increase with aging, probably because of loss of residual solvent from the material. A similar effect was observed for the phenolic microballoon filled polysulfide.

The Shore A hardness values given in Table B-23 showed a linear decline with aging at all three temperatures. Solving for the linear rate constants, and using these in an Arrhenius plot of $\ln K$ versus $1/T$, gave an activation energy of 22.6 kcal/mol, and a calculated rate constant at 35°C of 0.26 hardness units per year decrease. Thus, in 25 years at 35°C, the hardness would be predicted to drop to approximately 46 to 47 from an initial value of 53.2. While this progressive softening with time and temperature certainly suggests chain scission at the disulfide and polysulfide linkages, the process is relatively slow at the

Table B-21. Polysulfide Sealant: Volume Resistivity

Temperature (°C)	Time	Volume Resistivity (MΩ)		
		High	Low	Average
Ambient	0	25,500	20,000	23,000
Ambient	0	26,500	18,500	22,500
Ambient	0	26,500	22,000	24,300
Ambient	0	25,000	19,500	22,700
Ambient	0	19,000	17,500	18,250
Ambient	0	21,500	20,000	20,900
Ambient	0	30,500	27,000	29,000
Ambient	0	20,500	17,000	19,250
70	6 Months	5,100	4,200	4,733
70	6 Months	11,500	9,750	10,583
70	6 Months	4,850	4,350	4,683
70	1 Year	5,350	3,750	4,566
70	1 Year	2,575	1,900	2,246
70	1 Year	4,900	4,150	4,550
Ambient	2 Years	33,000	29,250	30,917
Ambient	2 Years	37,500	30,750	33,333
Ambient	2 Years	39,000	33,500	34,833
Ambient	2 Years	38,000	31,500	34,792
Ambient	2 Years	40,500	33,000	37,458
Ambient	2 Years	57,500	43,000	52,333

expected stockpile temperatures; in view of its use as a potting material, softening of this material should offer no threat to the fireset functionality.

Weight loss data were quite scattered, because of adhesion of the polysulfide to the spacers used. Density values showed no change with aging.

Table B-22. Polysulfide Sealant: T_g by TMA

Temperature (°C)	Time	Container	T_g (°C)
Ambient	0		-51
Ambient	3 Months		-48
70	3 Months	N-1	-50
70	3 Months	N-1, Combination D	-50
Ambient	6 Months		-48
50	6 Months	N-2	-48
50	6 Months	N-2, Combination D	-48
60	6 Months	N-4	-49
60	6 Months	N-4, Combination D	-49
70	6 Months	N-6	-48
70	6 Months	N-6, Combination D	-47
70	6 Months	D-48	-50
70	6 Months	D-56, Combination D	-50
Ambient	1 Year		-42
50	1 Year	N-3	-43
50	1 Year	N-3, Combination D	-44
50	1 Year	A-6	-42
50	1 Year	A-14, Combination D	-42
60	1 Year	N-5	-47
60	1 Year	N-5, Combination D	-43
60	1 Year	C-34	-43
60	1 Year	C-42, Combination D	-43
70	1 Year	N-7	-45
70	1 Year	N-7, Combination D	-44
70	1 Year	E-62	-42
70	1 Year	E-70, Combination D	-44
Ambient	2 Years		-44
70	2 Years	N-8	-43
70	2 Years	N-8, Combination D	-43

Table B-23. Polysulfide Sealant: Durometer Hardness

Temperature (°C)	Time	Container	Shore A Hardness
Ambient	0		54.0
Ambient	3 Months		55.7
70	3 Months	N-1	50.0
70	3 Months	N-1, Combination D	50.9
Ambient	6 Months		52.0
50	6 Months	N-2	52.5
50	6 Months	N-2, Combination D	52.5
60	6 Months	N-4	49.0
60	6 Months	N-4, Combination D	49.0
70	6 Months	N-6	42.5
70	6 Months	N-6, Combination D	44.5
70	6 Months	D-48	46.0
70	6 Months	D-56, Combination D	49.0
Ambient	1 Year		55.5
50	1 Year	N-3	52.0
50	1 Year	N-3, Combination D	52.5
50	1 Year	A-6	55.0
50	1 Year	A-14, Combination D	52.0
60	1 Year	N-5	48.0
60	1 Year	N-5, Combination D	49.0
60	1 Year	C-34	49.0
60	1 Year	C-42, Combination D	51.5
70	1 Year	N-7	39.5
70	1 Year	N-7, Combination D	40.5
70	1 Year	E-62	43.0
70	1 Year	E-70, Combination D	45.0
Ambient	2 Years		51.4
70	2 Years	N-8	30.2
70	2 Years	N-8, Combination D	33.0

Table B-24. Polysulfide Sealant: Weight Change

Temperature (°C)	Time	Container	Weight Change (Percent)
70	3 Months	N-1	-0.49
70	3 Months	N-1, Combination D	-0.89
50	6 Months	N-2	-0.26
50	6 Months	N-2, Combination D	-0.36
60	6 Months	N-4	-0.40
60	6 Months	N-4, Combination D	-0.55
70	6 Months	N-6	-2.47
70	6 Months	N-6, Combination D	-2.31
70	6 Months	D-48	-1.10
70	6 Months	D-56, Combination D	-0.12
50	1 Year	N-3	-0.39
50	1 Year	N-3, Combination D	-0.44
50	1 Year	A-6	-0.17
50	1 Year	A-14, Combination D	-0.04
60	1 Year	N-5	-1.02
60	1 Year	N-5, Combination D	-0.87
60	1 Year	C-34	-0.85
60	1 Year	C-42, Combination D	+0.06
70	1 Year	N-7	-6.92
70	1 Year	N-7, Combination D	-5.72
70	1 Year	E-62	-0.56
70	1 Year	E-70, Combination D	-0.16
50	2 Years	B-20	-0.18
50	2 Years	B-28, Combination D	+0.12
70	2 Years	N-8	-6.51
70	2 Years	N-8, Combination D	-2.85

Table B-25. Polysulfide Sealant: Density

Temperature (°C)	Time	Container	Mean (g/cm ³)	Standard Deviation
Ambient	3 Months		1.89	0.000
70	3 Months	N-1	1.88	0.006
70	3 Months	N-1, Combination D	1.88	0.000
Ambient	6 Months		1.89	0.005
50	6 Months	N-2	1.89	0.005
50	6 Months	N-2, Combination D	1.89	0.000
60	6 Months	N-4	1.89	0.000
60	6 Months	N-4, Combination D	1.89	0.004
70	6 Months	N-6	1.89	0.000
70	6 Months	N-6, Combination D	1.89	0.004
70	6 Months	D-48	1.89	0.000
70	6 Months	D-56, Combination D	1.90	0.006
Ambient	1 Year		1.89	0.011
50	1 Year	N-3	1.88	0.007
50	1 Year	N-3, Combination D	1.88	0.013
50	1 Year	A-6	1.88	0.013
50	1 Year	A-14, Combination D	1.87	0.009
60	1 Year	N-5	1.88	0.000
60	1 Year	N-5, Combination D	1.88	0.008
60	1 Year	C-34	1.86	0.000
60	1 Year	C-42, Combination D	1.88	0.007
70	1 Year	N-7	1.86	0.007
70	1 Year	N-7, Combination D	1.88	0.015
70	1 Year	E-62	1.88	0.018
70	1 Year	E-70, Combination D	1.89	0.007
Ambient	2 Years		1.91	0.006
70	2 Years	N-8	1.88	0.000
70	2 Years	N-8, Combination D	1.89	0.006

7. SILICONE RTV 21 SPONGE

Tests: Compression-deflection testing, weight change, and density

Physical testing on this material proved difficult because of the great variability between samples as fabricated. The material was prepared as a free-rise foam between parallel plates, and it was found to be impossible to reproduce properties from one sample to the next.

The compression-deflection test data are given in Table B-26. Because of the sample-to-sample variability, each sample had to be tested before and after aging rather than the usual method of comparing identical unaged versus aged samples. The test method was the same as that used for the phenolic microballoon-filled polysulfide. Each value in Table B-26 is the mean of six samples, and each sample was cycled three times through the compression test before recording the measurement on the third cycle. The data show no significant change with aging at any of the times and temperatures used.

The weight change data (Table B-27) show no significant change. This is consistent with the gas analysis results, which showed little change in composition.

The density results in Table B-28 show a large scatter, consistent with the large sample variability. Even if some change had occurred, it would not be detectable from the density measurements.

Within the limits imposed by the sample variability, this material showed no changes in physical properties with thermal aging.

Table B-26. Silicone RTV 21 Sponge: Compression-Deflection Testing

Temperature (°C)	Time	Container	Stress (psi)			
			Before		Aged	
			Mean	Standard Deviation	Mean	Standard Deviation
70	3 Months	N-1	31.8	1.103	30.4	1.744
50	6 Months	N-2	31.2	9.282	34.3	16.073
60	6 Months	N-4	29.9	7.968	30.5	8.620
70	6 Months	N-6	30.7	6.451	30.3	5.354
50	1 Year	N-3	33.4	7.643	32.8	5.950
60	1 Year	N-5	33.8	5.927	32.2	6.494
70	1 Year	N-7	28.8	7.333	27.3	6.653
70	2 Years	N-8	31.9	8.814	30.2	6.539

Table B-27. Silicone RTV 21 Sponge:
Weight Change

Temperature (°C)	Time	Container	Weight Change (Percent)
70	3 Months	N-1	+0.50
50	6 Months	N-2	+0.15
60	6 Months	N-4	+0.22
70	6 Months	N-6	+0.73
50	1 Year	N-3	+0.33
50	1 Year	A-7	-0.04
60	1 Year	N-5	+0.13
60	1 Year	C-35	+0.07
70	1 Year	N-7	+0.60
70	1 Year	E-63	0.00
50	2 Years	B-21	+0.05
70	2 Years	N-8	+0.99

Table B-28. Silicone RTV 21 Sponge: Density

Temperature (°C)	Time	Container	Mean (g/cm ³)	Standard Deviation
Ambient	3 Months		0.907	0.006
70	3 Months	N-1	0.920	0.005
Ambient	6 Months		0.899	0.012
50	6 Months	N-2	0.898	0.009
60	6 Months	N-4	0.898	0.010
70	6 Months	N-6	0.900	0.011
70	6 Months	D-44	0.901	0.006
Ambient	1 Year		0.895	0.007
50	1 Year	N-3	0.897	0.004
50	1 Year	A-7	0.890	0.016
60	1 Year	N-5	0.889	0.011
60	1 Year	C-35	0.888	0.014
70	1 Year	N-7	0.890	0.009
70	1 Year	E-63	0.881	0.008
Ambient	2 Years		0.898	0.009
70	2 Years	N-8	0.917	0.007

8. MICA-FILLED EPOXY

Tests: Flexural modulus, TMA, weight change, and density

The test data are shown in Tables B-29 through B-32. The only changes observed were those associated with the increased curing which occurred during aging. The flexural modulus increased slightly with aging, although flexural strength did not. The T_g increased with thermal aging, again consistent with an increase in the degree of cure. Weight changes were very small, corresponding to a slight degree of oxygen attack, as indicated by the gas analysis. No significant changes in density were observed.

Table B-29. Mica-Filled Epoxy: Flexural Modulus and Flextural Strength

Temperature (°C)	Time	Container	Modulus (psi x 10 ⁻⁶)		Stress (psi x 10 ⁻³)	
			Mean	Standard Deviation	Mean	Standard Deviation
Ambient	0		0.717	0.11	13.14	0.72
Ambient	3 Months		0.701	0.04	12.48	1.04
70	3 Months	N-1	0.711	0.05	13.04	0.76
Ambient	6 Months		0.685	0.04	11.07	3.04
50	6 Months	N-2	0.670	0.03	12.26	1.88
60	6 Months	N-4	0.687	0.02	13.02	0.83
70	6 Months	N-6	0.686	0.02	13.30	0.64
70	6 Months	D-50	0.696	0.02	12.39	0.76
Ambient	1 Year		0.710	0.02	13.51	1.00
50	1 Year	N-3	0.727	0.01	13.33	0.29
50	1 Year	A-8	0.711	0.07	12.60	0.76
60	1 Year	N-5	0.730	0.03	13.05	0.87
60	1 Year	C-36	0.754	0.03	12.23	1.75
70	1 Year	N-7	0.715	0.06	13.20	1.04
70	1 Year	E-64	0.734	0.04	13.05	0.25
Ambient	2 Years		0.865	0.02	13.90	0.18
70	2 Years	N-8	0.840	0.006	13.70	0.61

Table B-30. Mica-Filled Epoxy: T_g by TMA

Temperature (°C)	Time	Container	T_g (°C)
Ambient	0		119
Ambient	3 Months		125
70	3 Months	N-1	134
Ambient	6 Months		131
50	6 Months	N-2	142
60	6 Months	N-4	133
70	6 Months	N-6	132
70	6 Months	D-50	130
Ambient	1 Year		134
50	1 Year	N-3	132
50	1 Year	A-8	132
60	1 Year	N-5	136
60	1 Year	C-36	131
70	1 Year	N-7	137
70	1 Year	E-64	136
Ambient	2 Years		133
70	2 Years	N-8	139

Table B-31. Mica-Filled Epoxy: Weight Change

Temperature (°C)	Time	Container	Weight Change (Percent)
70	3 Months	N-1	+0.24
50	6 Months	N-2	+0.29
60	6 Months	N-4	+0.27
70	6 Months	N-6	+0.30
70	6 Months	D-50	+0.51
50	1 Year	N-3	+0.24
50	1 Year	A-8	+0.37
60	1 Year	N-5	+0.25
60	1 Year	C-36	+0.40
70	1 Year	N-7	+0.25
70	1 Year	E-64	+0.36
50	2 Years	B-22	+0.25
70	2 Years	N-8	+0.46

Table B-32. Mica-Filled Epoxy: Density

Temperature (°C)	Time	Container	Mean (g/cm ³)	Standard Deviation
Ambient	3 Months		1.51	0.006
70	3 Months	N-1	1.50	0.000
Ambient	6 Months		1.56	0.015
50	6 Months	N-2	1.56	0.005
60	6 Months	N-4	1.55	0.009
70	6 Months	N-6	1.55	0.009
70	6 Months	D-50	1.52	0.005
Ambient	1 Year		1.50	0.005
50	1 Year	N-3	1.52	0.000
50	1 Year	A-8	1.50	0.005
60	1 Year	N-5	1.50	0.007
60	1 Year	C-36	1.51	0.004
70	1 Year	N-7	1.50	0.008
70	1 Year	E-64	1.50	0.005
Ambient	2 Years		1.50	0.004
70	2 Years	N-8	1.50	0.005

10. 91 LD PHENOLIC

Tests: Flexural modulus, weight change, and density

The test data are given in Tables B-33 through B-35. The flexural modulus and strength indicate no change with aging. The weight changes observed were negligible, and the density showed no variation with age.

Table B-33. 91 LD Phenolic: Flexural Modulus and Flexural Strength

Temperature (°C)	Time	Container	Modulus (psi x 10 ⁻⁶)		Stress (psi x 10 ⁻³)	
			Mean	Standard Deviation	Mean	Standard Deviation
Ambient	0		2.51	0.10	36.82	3.10
Ambient	3 Months		2.64	0.17	36.84	5.89
70	3 Months	N-1	2.42	0.13	36.36	3.21
70	3 Months	N-1, Combination B	2.55	0.17	38.22	4.99
Ambient	6 Months		2.50	0.14	38.54	2.37
50	6 Months	N-2	2.37	0.10	34.50	3.70
50	6 Months	N-2, Combination B	2.45	0.16	34.76	4.84
60	6 Months	N-4	2.42	0.22	35.00	3.48
60	6 Months	N-4, Combination B	2.54	0.31	33.18	6.08
70	6 Months	N-6	2.45	0.12	36.44	4.87
70	6 Months	N-6, Combination B	2.48	0.21	36.12	7.05
70	6 Months	D-52	2.47	0.19	34.91	5.23
70	6 Months	D-54, Combination B	2.54	0.22	35.58	4.75
Ambient	1 Year		2.64	0.06	35.74	2.81
50	1 Year	N-3	2.67	0.14	36.72	3.64
50	1 Year	N-3, Combination B	2.72	0.29	34.05	6.31
50	1 Year	A-10	2.61	0.17	34.76	3.20
50	1 Year	A-12, Combination B	2.62	0.21	34.15	3.81
60	1 Year	N-5	2.70	0.17	36.01	3.64
60	1 Year	N-5, Combination B	2.59	0.34	34.59	9.72
60	1 Year	C-38	2.66	0.18	33.93	4.42
60	1 Year	C-40, Combination B	2.66	0.19	32.10	3.87

Table B-33 Continued. 91 LD Phenolic: Flexural Modulus and Flexural Strength

Temperature (°C)	Time	Container	Modulus (psi x 10 ⁻⁶)		Stress (psi x 10 ⁻³)	
			Mean	Standard Deviation	Mean	Standard Deviation
70	1 Year	N-7	2.51	0.26	37.02	3.90
70	1 Year	N-7, Combination B	2.76	0.21	36.15	1.77
70	1 Year	E-66	2.67	0.12	34.10	3.58
70	1 Year	E-68, Combination B	2.57	0.26	27.38	6.64
Ambient	2 Years		2.75	0.09	36.17	2.20
70	2 Years	N-8	2.63	0.09	38.09	2.33
70	2 Years	N-8, Combination B	2.76	0.08	36.25	7.40

Table B-34. 91 LD Phenolic: Weight Change

Temperature (°C)	Time	Container	Weight Change (Percent)
70	3 Months	N-1	-0.09
70	3 Months	N-1, Combination B	+0.03
50	6 Months	N-2	+0.22
50	6 Months	N-2, Combination B	+0.19
60	6 Months	N-4	+0.07
60	6 Months	N-4, Combination B	+0.04
70	6 Months	N-6	+0.12
70	6 Months	N-6, Combination B	-0.18
70	6 Months	D-52	+0.70
70	6 Months	D-54, Combination B	+0.55
50	1 Year	N-3	+0.07
50	1 Year	N-3, Combination B	-0.14
50	1 Year	A-10	+0.60
50	1 Year	A-12, Combination B	+0.18
60	1 Year	N-5	-0.15
60	1 Year	N-5, Combination B	-0.12
60	1 Year	C-38	+0.76
60	1 Year	C-40, Combination B	+0.38
70	1 Year	N-7	-0.31
70	1 Year	N-7, Combination B	-0.06
70	1 Year	E-66	+0.43
70	1 Year	E-68, Combination B	+0.31
50	2 Years	B-24	+0.77
50	2 Years	B-26, Combination B	+0.55
70	2 Years	N-8	-0.37
70	2 Years	N-8, Combination B	-0.35

Table B-35. 91 LD Phenolic: Density

Temperature (°C)	Time	Container	Mean (g/cm ³)	Standard Deviation
Ambient	3 Months		1.86	0.000
70	3 Months	N-1	1.86	0.000
70	3 Months	N-1, Combination B	1.86	0.000
Ambient	6 Months		1.90	0.005
50	6 Months	N-2	1.92	0.005
50	6 Months	N-2, Combination B	1.92	0.005
60	6 Months	N-4	1.92	0.011
60	6 Months	N-4, Combination B	1.92	0.013
70	6 Months	N-6	1.90	0.004
70	6 Months	N-6, Combination B	1.91	0.008
70	6 Months	D-52	1.86	0.004
70	6 Months	D-54, Combination B	1.88	0.013
Ambient	1 Year		1.86	0.004
50	1 Year	N-3	1.87	0.008
50	1 Year	N-3, Combination B	1.86	0.004
50	1 Year	A-10	1.86	0.004
50	1 Year	A-12, Combination B	1.86	0.005
60	1 Year	N-5	1.85	0.005
60	1 Year	N-5, Combination B	1.85	0.005
60	1 Year	C-38	1.86	0.004
60	1 Year	C-40, Combination B	1.86	0.004
70	1 Year	N-7	1.86	0.000
70	1 Year	N-7, Combination B	1.86	0.005
70	1 Year	E-66	1.86	0.000
70	1 Year	E-68, Combination B	1.86	0.000
Ambient	2 Years		1.84	0.005
70	2 Years	N-8	1.85	0.013
70	2 Years	N-8, Combination B	1.85	0.005