HIGH-TEMPERATURE PROTECTIVE RE-ENTRY COATINGS FOR EXPANDABLE STRUCTURES

by M. T. Conger and T. W. Chalmers

The Goodyear Tire & Rubber Co and its subsidiary, Goodyear Aerospace Corporation, were among the initial participants in the search for coatings that will make possible the successful re-entry of a structure rigidized by gases confined under pressure. This method of rigidization is not new. The list of commercially available products is long; e. g., tires, mattresses, beach balls, footballs, basketballs, toys, lighter-than-air vehicles of several types, and even an experimental heavier-than-air vehicle of the aeroplane geometry. You will notice immediately that most of these items are rubberized fabric products.

The portion of re-entry coating research that I wish to present to you is sponsored by the Research and Technology Division, Air Force Systems Command, United States Air Force, under Contract No. AF 33(657)-11257. One of the purposes of the work under this contract is to develop coatings for use in the manufacture of expandable structures. The structures of interest are those that, during re-entry, must be resistant to a peak skin temperature of 2000°F and are to be fabricated from a high-strength coated metal-fiber fabric composite. Only the coating portion of this composite and the application of the coating to the metal fabric are within the scope of this investigation. Such important tasks as the development of the metal-fiber fabric and the design and fabrication of the re-entry structure are not within the scope of this research program.

In this coatings research program, elevated temperature leak tests and visual inspection means were used as guides to coating quality. The type of coatings studied were inorganic coatings, chemical vapor-deposited coatings, coatings based upon elastomeric ablative insulation, and coatings containing silicone rubber in combination with fusible fillers. I will describe the techniques used in this program, and then summarize for you what has been discovered concerning the properties of the coatings.

A thermal screening apparatus (Figure 1) was used to determine the gross effect of re-entry heat on the coatings. Four specimens could be simultaneously subjected to a stagnant air re-entry heating cycle. The specimens, 1 x 8 inches, were held upon the metal frame using spring clamps. Radiant heat was supplied by two silicone carbide heating rods. The temperature was

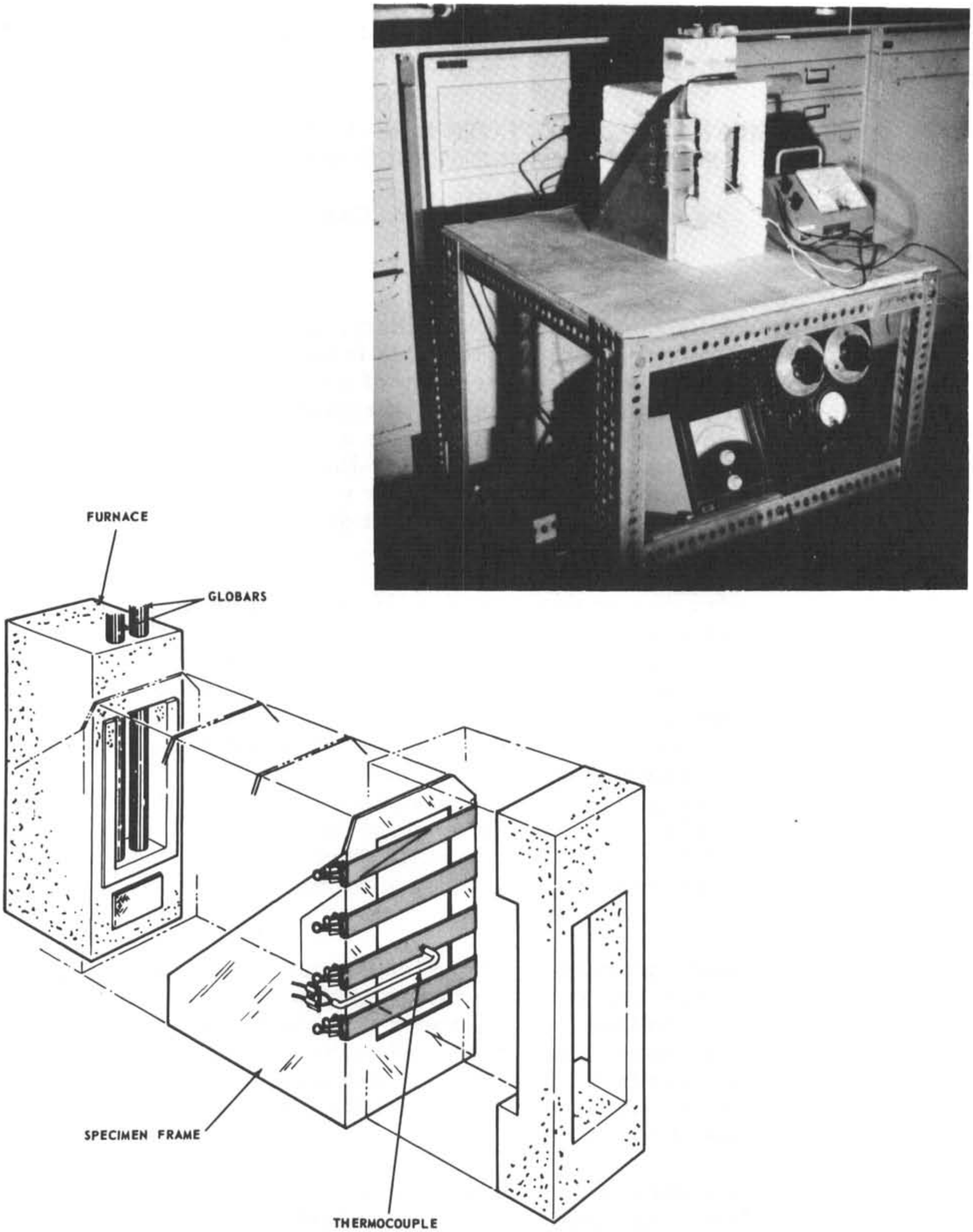


Figure 1. Thermal Screening Apparatus

varied in such a manner that there were 12-1/2 minutes from room temperature to 2000°F, 5 minutes at 2000°F, and 12-1/2 minutes from 2000°F to room temperature. Five specimens that have been subjected to this test are shown in Figure 2. If the coatings remained adhered to the substrate, were not visibly cracked, and were not visibly porous, they were judged to be worthy of further attention.

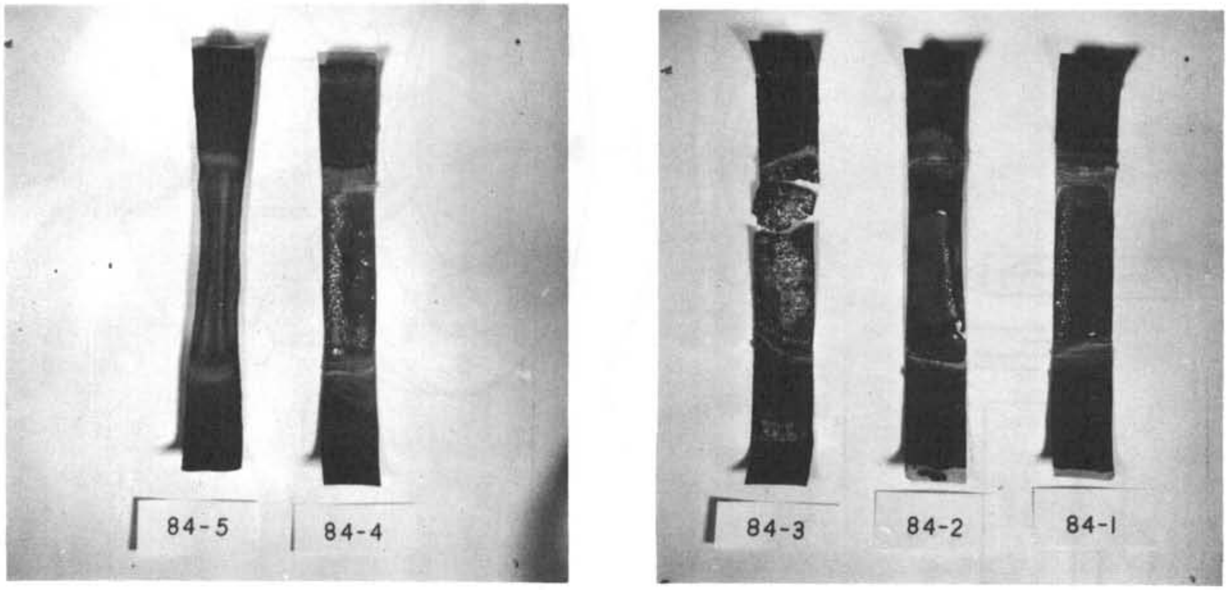
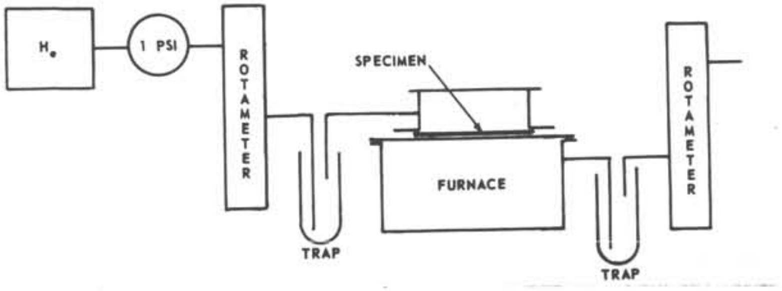


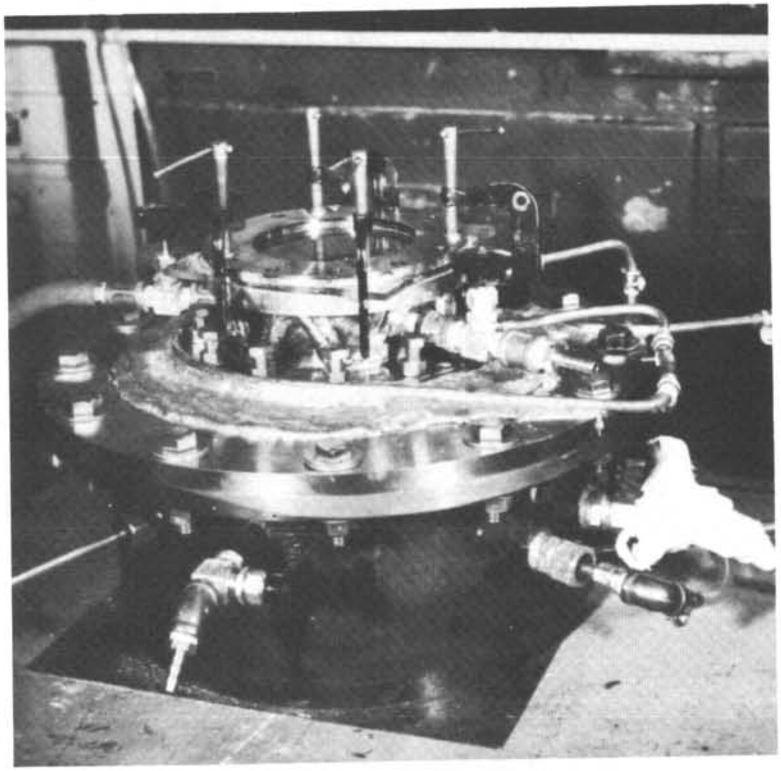
Figure 2. Specimens after Test

In most instances, further attention consisted of some form of leakage test conducted at high temperature and low inflation pressure. For this purpose, several apparatus designs were investigated. In the early work, these were used to determine the temperature at which coated metal fabric diaphragms from 1 to 6 inches in diameter leaked. The last of these designs was, at least in part, satisfactory (see Figure 3). Problems that arose in attempting to make gastight seals at the edge of the specimen during the high-temperature tests have been overcome through the use of focused radiant heating and water-cooled flanges.

However, instead of discussing diaphragm apparatus and tests further, I will discuss, in considerable detail, a much improved high-temperature test method that is now being used. This test is based on the testing of a 10-inch long by 3/8-inch diameter cylindrical specimen. Special features of this test are:

(1) The ability to measure the effect of folding and creasing of the type that is associated with the packaged vehicle prior to ejection for reentry.





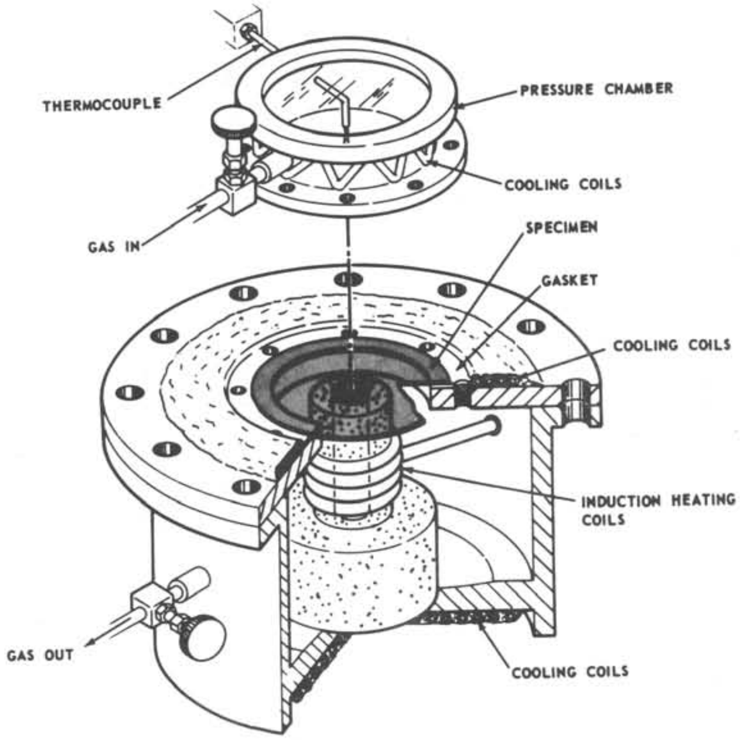


Figure 3. Diaphragm Leakage Apparatus

(2) The ability to measure the effect of tension or torsion forces applied during simulation of re-entry heating.

The assembled apparatus that is used is shown in Figure 4. Items depicted are the test chamber, helium reservoir, flow indicator, rotameter, leakage tester, water manometer, liquid-nitrogen cold trap, and the temperature recorder. This apparatus uses a very unsophisticated heating source - two ordinary oxygen-acetylene torches. The torches are mounted in an adjustable device through which the operator can continuously and simultaneously change the position of both torches with respect to the specimen chamber.

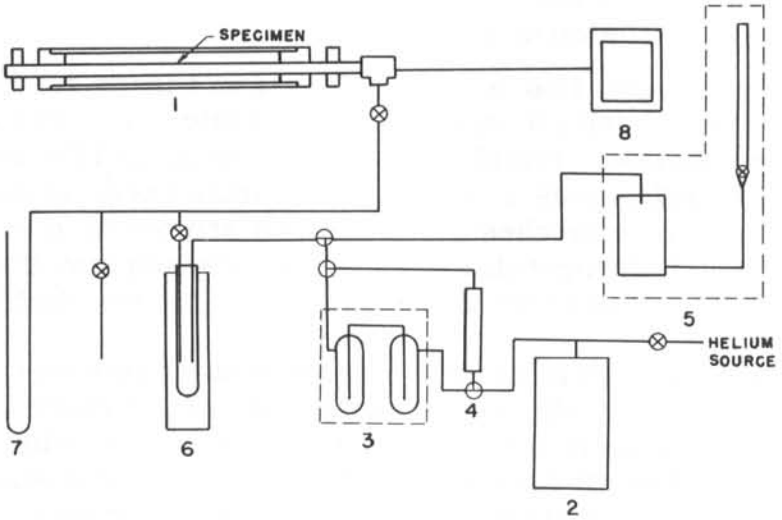
The test chamber itself is a one-inch stainless steel pipe with capped ends, which in turn have a centrally located hole 7/16 inch in diameter. A gas inlet tube in the chamber wall is used to introduce nitrogen or other gases to the space surrounding the test specimen. These gases, which simulate the re-entry atmosphere, escape from the chamber ends. Because of a large escape outlet, the pressure of the gas in the chamber is not measurably above atmospheric pressure at any time.

The stand that holds the test chamber also holds the specimen. This is possible because the specimen is several inches longer than the heating chamber, and this excess length projects through the holes in the capped ends. Devices that apply loads to the specimen can be readily attached to these projecting ends.

A bayonet-type chromel-alumel thermocouple inserted into the center of the specimen and terminating at the lengthwise center is assumed to measure the specimen temperature at that central point. Helium maintained at constant pressure is used inside the specimen. Suitable gages are provided to measure the rate at which the helium must be added to accomplish this. The last two items of the equipment are a liquid nitrogen trap for removal of volatile decomposition products and a device to determine the direction of flow of the inflation gas with respect to the specimen.

The test procedure normally used consists of two more or less independent operations, each of which investigates a separate property of the coating. In the first operation, the ability of the coating to withstand the stress imposed by the folds and creases in the preinflation package is investigated. To do this, the cylindrical test specimen is folded by bringing its ends together. Sufficient finger pressure is applied to the fold to exclude air from this area. The specimen is then unfolded and checked for leaks. If there are no leaks, it is assumed that the folding has caused no damage to the coating. Tensile tests after folding have shown considerable crease damage to the metal fabric substrate, however.

In the second operation, the ability of the coating to withstand re-entry heat while the cloth substrate is being subjected to cyclic distortions is investigated. To do this, the specimen is mounted in the heating chamber. Following



1. Test Chamber
2. Helium Reservoir
3. Flow Indicator
4. Rotameter
5. Leakage Tester
6. Cold Trap
7. Manometer
8. Temperature Recorder

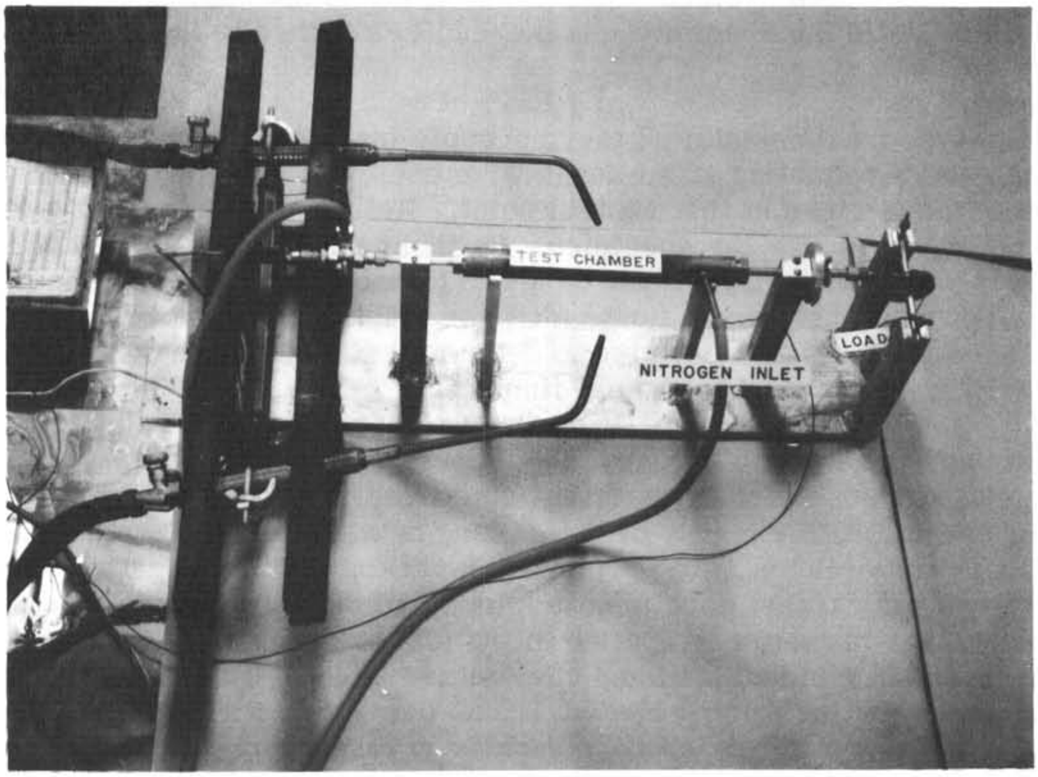


Figure 4. Cylinder Test Apparatus

purging of the specimen and the interconnected components with helium, the entire assembly is checked for leaks at one-psi helium pressure. After correcting leaks found, the cylindrical test specimen is heated to 2000°F in 12-1/2 minutes, held at 2000°F for 5 minutes, then cooled to room temperature in 12-1/2 minutes. During this time, the following steps are performed:

(1) Either nitrogen or air is continuously added to the space surrounding the heated portion of the test specimen.

(2) An axial load of 50 percent of the braking load of the cylinder is applied for 30 seconds of each minute.

(3) A one-psi gage inflation pressure is maintained within the test specimen and the interconnected assembly, using helium.

(4) The direction of the gas flow is observed, and the temperature at which the gas first flows into the cylinder is noted.

(5) The rate of flow of the gas to the cylinder is measured as necessary, and the time at which this is done is recorded.

We have used some of the many possible variations of this procedure to study the effects of (1) different peak temperatures, (2) different heating rates, (3) different inflation pressures, and (4) different tensile stresses. We can study, but have not studied, the effect of other types of loading such as torsional and compression and the combination of various loading means with each other and vibration. We believe that it is possible to study all the important conditions of re-entry with this single apparatus except those that are associated with the erosion of the coating caused by the vehicle's impingement upon the atmosphere at high velocity.

For those of you who are interested in some additional facts concerning the operating characteristics of this apparatus, your attention is directed to the fact that heating rates and cooling rates sufficiently high to change the temperature from between room temperature and 2000°F in 2-1/2 minutes can be achieved (see Figure 5). Your attention is also directed to Figure 6, a typical profile of temperatures that occurred at a particular instant along the length of the specimen. At the instant these temperatures occurred, the internally located thermocouple at the center had read 2000°F for 3 minutes. It will be noted that the 2000°F temperature is maintained only over a short length of the specimen and that the temperature decreases rapidly outside of this area. These data were obtained using a stainless steel tube as the test specimen. Due to the high rate of heat conduction along the length of this relatively thick walled stainless steel tube, the coated thin walled specimens used in the program will show a far greater lengthwise temperature variation. We have been told by aerodynamic experts that large, but not necessarily identical, temperature variations will exist on the surface of the re-entering structure.

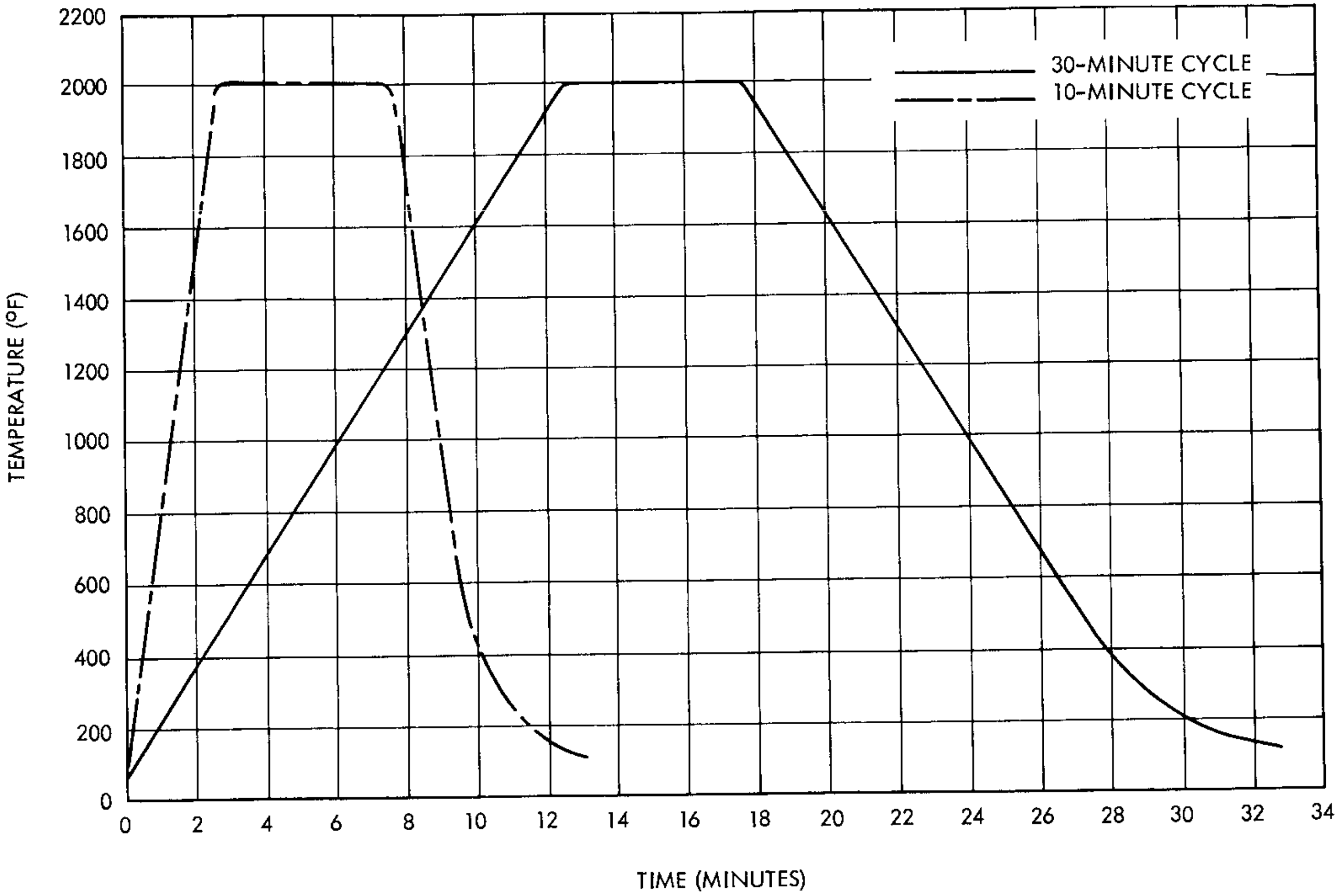


Figure 5. Heating Rate

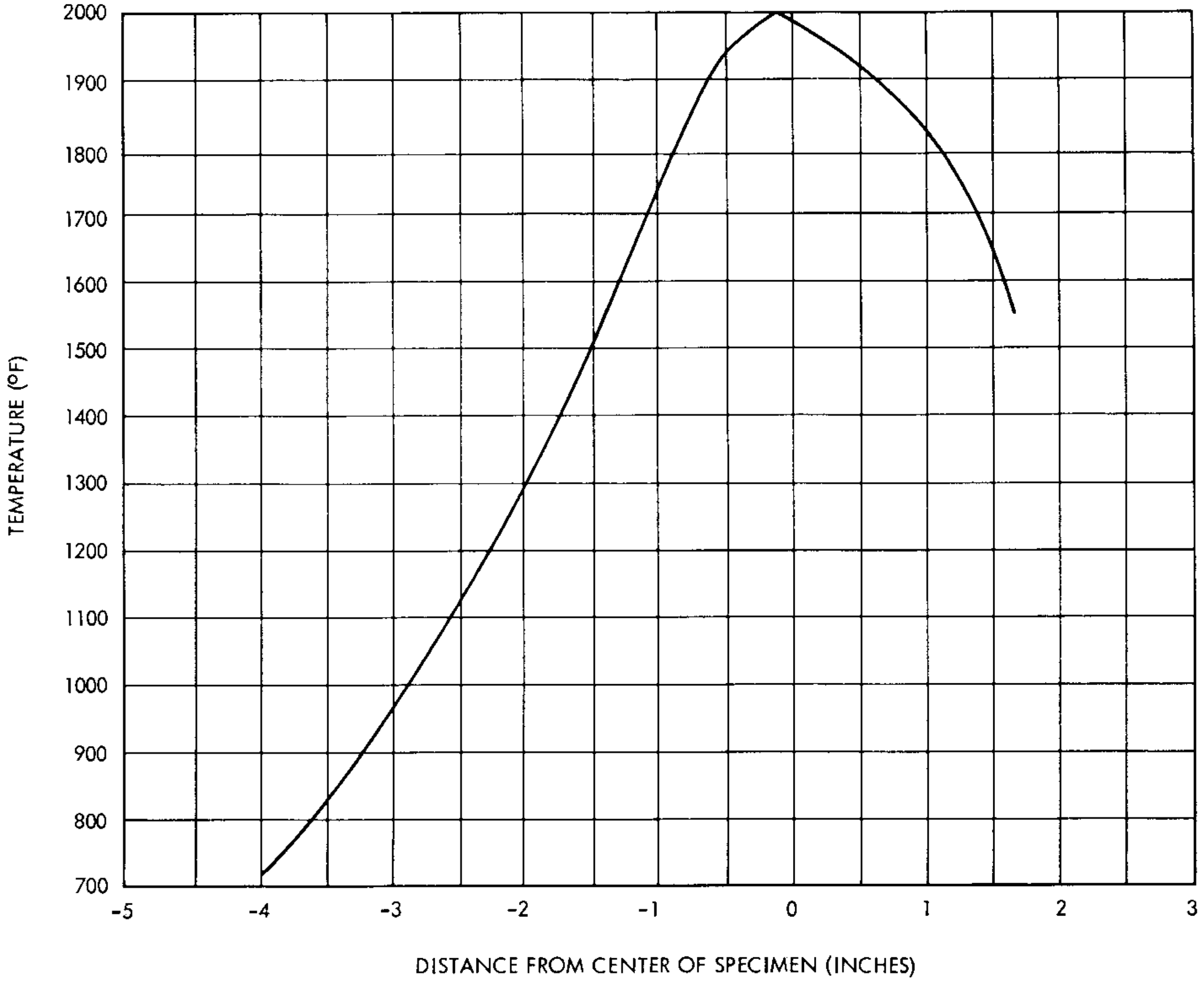


Figure 6. Temperature Profile

We have also been told that as heating occurs during re-entry, it may be necessary to remove inflation gases by special control mechanisms to maintain constant gage pressure. We know as a matter of experimental fact, that during a heating cycle in our apparatus at a constant pressure, it is necessary to bleed off some gas from the system because of the volume increase caused by thermal expansion of the gases. In the stainless steel tubing experiment previously described, the magnitude of the volume change due to thermal expansion was measured. The increase in volume was found to cause an outward flow of gas at a rate of 0.006 cc per second during the 12-1/2 minute heating cycle. If it is assumed that the 2000°F temperature is only that of the center one-inch length of the specimen and that the surface of this length is the entire surface of the test specimen, the point where the outward flow is observed to start during the re-entry cycle would identify the point where the leakage rate would be equal to the expansion rate of the gas; in other words, 0.006 cc/in.^{2}/sec.

During the cooling cycle, the contraction of the gases makes it appear that the specimen is leaking at an insignificantly higher rate than it actually is. While it is obvious that a true leak rate can be measured only when the temperature is constant, the error introduced by neglecting this effect is small in our apparatus due to the smallness of the thermal expansion in relation to the size of the leakage rate of interest.

Error from another source is possible. During the heating cycle, the coatings tested in our program give off volatile products. While it is easy to show that there is a volume increase in the inflation gases due to these volatile products, it is difficult to determine their quantitative effect on a time basis. It is believed that for the purposes of determining a leak temperature and the order of magnitude of the leakage rate, this effect can be neglected.

I would now like to tell you how the cylindrical test specimens are made (see Figure 7). The first step in their fabrication is the welding of metal cloth to

Figure 7. Uncoated Specimen

form a 3/8-inch diameter cylinder. This is accomplished using a jig designed and built by Goodyear Aerospace Corporation. While such factors are adjustable, we used a lapped seam having two weld lines 3/16 inch apart with each line consisting of 25 welds per inch.

In the second step of the cylinder fabrication, a 6-1/2 inch long piece of 3/8-inch diameter copper tubing is attached to each end of a 10-inch long piece of the metal cloth cylinder. A 1/2-inch long joining area is covered with a 1/4-inch length of 1/2-inch diameter copper tubing. This metal cover serves as a clamp to hold the cloth on the end of the 3/8-inch diameter copper tubing. It also acts as a heat sink during silver soldering. It would, in fact, be very difficult to make a gastight seal at the end joints and at the same time not burn a hole in the metal cloth if it were not for these external pieces of copper tubing.

After silver soldering, which is accomplished using an acetylene torch, excess soldering flux is removed with steam. The cleaning operation is completed with dichloroethylene degreasing solvent. After one hour in the solvent, the specimen is placed in a drying rack and allowed to air dry at ambient conditions.

The coating to be tested is applied by painting. Variable drying and vulcanization procedures were used that were dictated by the chemical nature of the coatings.

Figure 8 shows a finished specimen. The coating you see here is a 50/50 weight mixture of sodium silicate and silica.

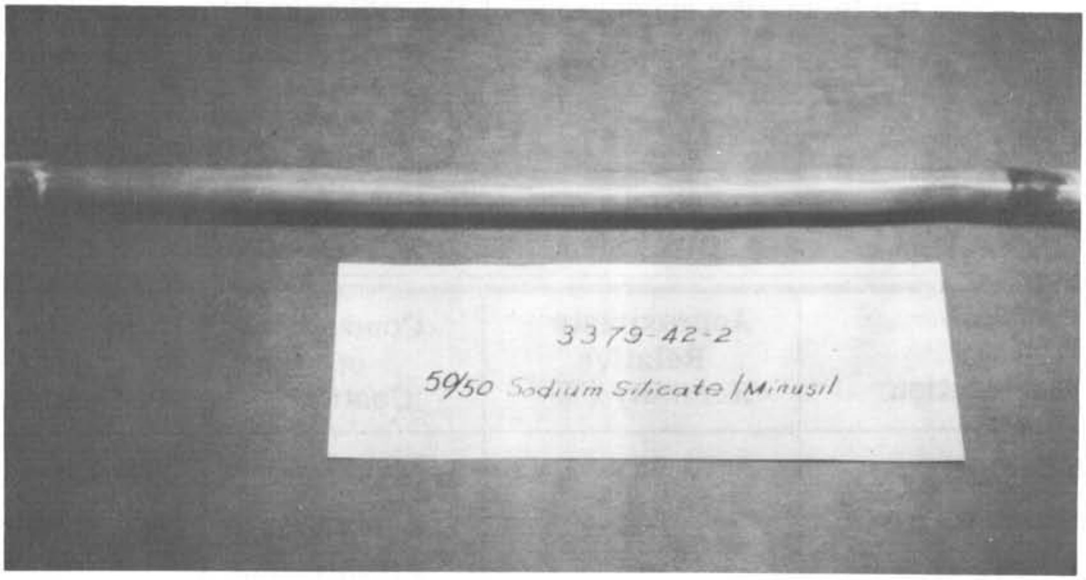


Figure 8. Coated Specimen

Using such test methods as have been described, more than 200 coatings have been evaluated, some of which were found to have interesting characteristics. These are coatings of sodium silicate reinforced with infusible fillers of several types, silicone rubber coatings containing fusible fillers, and coatings made from elastomeric ablative insulation containing fusible fillers.

A large amount of time was devoted to testing of coatings that used soluble silicates as binders. Such coatings attracted considerable attention because they were unique among the coatings; unique in that, neglecting the volatile water which is essential to achieving adequate flexibility, they were composed of materials that were chemically stable in the re-entry environment. It is now known that,unfortunately,the higher water solubility of these silicate coatings will restrict, if not completely prevent, their use.

The data in Table I shows the effect of various humidities upon a soluble sodium silicate coating at room temperature. The sodium silicate used is one that is commercially available and has a NaO_2: SiO_2 ratio of 1:2. In the re-entry environment, this silicate reinforced with various filaments fails at a variety of temperatures depending upon the moisture content of the coating and the degree of exposure of the cold coating areas of the specimen to moisture driven from the coating areas heated to temperatures above 212°F. Data illustrating this is given in Table II. You will note that the completely unprotected coating leaks abruptly at 212°F when the coating contains 12 percent or more water. The drier but brittle coatings fail at higher temperatures. A flexible coating protected in the cold areas by a silicone rubber coating fails at higher temperatures. Inspection indicated that the leakage was along a path between the silicone rubber coating and the silicate coating.

Figure 9 shows the foam-like appearance of the moisture-blown silicate coatings after testing.

TABLE I

EFFECT OF ATMOSPHERIC MOISTURE ON A SOLUBLE SILICATE COATING

Salt in Saturated Solution	Approximate Relative Humidity (%)	Condition of Coating	Moisture Content of Coating (%)
Sodium Sulfate	95	Liquid	Not measured
Ammonium Sulfate	81	Liquid	Not measured
Calcium Nitrate	51	Elastomeric	30
Calcium Chloride	31	Brittle	10

TABLE II

SODIUM SILICATE COATINGS CONTAINING SILICA FILLER

Description	Leakage Temperature (°F)
Dry to 30% moisture	210
Dry to 12% moisture	210
Dry to 7.5% moisture	320
Dry to 5% moisture	400
Dry to 2.5% moisture	520
Ends, moisture barrier coated	1120
Ends, moisture barrier coated	2000

Figure 9. Sodium Silicate Coating after Test

Elastomeric ablative insulation might offer special advantages if its use would delay the time that peak skin temperature is reached and/or lower the peak skin temperature. Such compositions can, we believe, be made to have high leak temperatures. Data supporting this point of view are given in Table III. The high leak temperatures were achieved by the use of glass frits. The large amount required for 2000°F protection causes the coating to be undesirably stiff, however.

Silicone rubber of a special type combined with glass frit has long been recognized as a combination that has promise for expandable re-entry structures. Such coatings have been investigated in this program. They are considered to be the most promising of the coatings studied. Some of the data that have been obtained are given in Table IV to illustrate two important properties of these coatings. The first is that the coating weight necessary to obtain low leakage may be as high as 15 oz per sq yd when this coating is used in combination with an open-weave cloth. The second fact is that for reasons as yet not completely understood, this coating leaked during the re-entry heating cycle when air was used as the test atmosphere rather than the non-oxidizing nitrogen atmosphere normally used in this test program.

It is unfortunate that I must stop this discussion here. The final chapter of the story must await the publication of the final report covering this research. I urge you to read this report when it is published as a TDR in October. That a superior coating composition will be disclosed in this report is a distinct possibility.

TABLE III

NITRILE RUBBER
ELASTOMERIC ABLATIVE INSULATION

Description	Coating Wt (oz/yd^2)	Leakage Temp (^oF)	Max Leak Rate (cc/sec)
Containing 75 % frit	11.6	>2000	0.13
Containing 50% frit	14.9	940	>7
Containing 25% frit	12.1	900	>7

TABLE IV

SILICONE RUBBER COATINGS* CONTAINING GLASS FRIT

Coating Wt (oz/yd^2)	Leakage Temp (°F)	Max Leakage Rate (cc/sec)	Test Atmosphere
11.9	After Folding	>7	Nitrogen
13.6	>2000	0.16	Nitrogen
15.1	>2000	0.24	Nitrogen
15.6	>2000	0.12	Nitrogen
17.3	>2000	0.06	Nitrogen
12.5	2000	>7	Air
18.4	2000	>7	Air
13.1	2000	>7	Nitrogen/Air

*Dow Corning S2077 with equal weight (dry basis) Harshaw Chemical AW-35 on 200-mesh stainless steel screen.

ACKNOWLEDGMENTS

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