NOV 1 1966

MASTER

ALO-3633-2

UC 33

AEC RESEARCH AND DEVELOPMENT REPORT
SPECIAL

CPSTI PRICES

H.C. \$ 2.00 MN 0.50

AT(30-1)-3633
DEVELOP 1800F-400F FIBROUS-TYPE INSULATION
FOR RADIOISOTOPE POWER SYSTEMS

Second Quarterly Progress Report
Report No. ALO-3633-2

October 3, 1966

Report Period: July 1, 1966 to September 30, 1966

J. O. Collins

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

There is no objection from the patent point of view to the publication or dissemination of this document:

Patent Group (Brookhaven)

By.....*gpc*.....

10/27.1966

DISCLAIMER

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

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above "person acting on behalf of the Commission" includes any employee or Contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment or contract with the Commission, or his employment with such Contractor.

Printed in U.S.A. Price Available from
The Office of Technical Services, Department of
Commerce, Washington 25, D.C.

ALO-3633-2

UC 33

AEC RESEARCH AND DEVELOPMENT REPORT
SPECIAL

iii

DISTRIBUTION

L. W. Otoski, Area Manager
Sandia Area Office
U. S. Atomic Energy Commission
Albuquerque Operations Office
Albuquerque, New Mexico 87115 (2 cys)

A. J. Clark, Manager
Isotope Power Department
Department 9330
Sandia Corporation
Post Office Box 5800
Albuquerque, New Mexico 87115 (1 cy)

R. T. Carpenter, Chief
Isotopic Power Branch
Division of Space Nuclear
Systems
U. S. Atomic Energy Commission
Washington, D.C. 20545 (1 cy)

S. J. Seiken
Division of Reactor Development
and Technology
U. S. Atomic Energy Commission
Washington, D.C. 20545 (1 cy)

J. E. Konklin, Acting Chief
Technology Development Branch
Special Projects Division
U. S. Atomic Energy Commission
New York Operations Office
376 Hudson Street
New York, New York 10014 (1 cy)

L. Sisler, Isotope Power
Laboratory
Minnesota Mining & Manufacturing
Company
Space Center, 2501 Walnut Street
Roseville, Minnesota 55119 (2 cys)

J. F. O'Brien
Martin Marietta Corporation
Nuclear Products
Baltimore, Maryland 21203 (1 cy)

D. G. Harvey
Martin Marietta Corporation
Nuclear Products
Baltimore, Maryland 21203 (1 cy)

E. Ray
General Electric Company
Missile & Space Development
Valley Forge Space Technology
Center, P. O. Box 8555
Philadelphia, Pennsylvania 19101 (2 cys)

William Botts
Atomics International
Division of North American Aviation
P. O. Box 309
Canoga Park, California 91304 (2 cys)

P. Underhill, Project Manager
Large Milliwatt Program
Aerojet-General Nucleonics
Post Office Box 77
San Ramon, California (1 cy)

F. Hittman, General Manager
Hittman Associates, Inc.
4715 E. Wabash Avenue
Baltimore, Maryland 21215 (1 cy)

ALO-3633-2

UC 33

AEC RESEARCH AND DEVELOPMENT REPORT
SPECIAL

iv

J. Kenney, Program Manager
Compact Thermoelectric Converter
Westinghouse Electric Corporation
P. O. Box 10864
Pittsburgh, Pennsylvania 15213

(1 cy)

W. Kortier
Battelle Memorial Institute
505 King Avenue
Columbus, Ohio 43201

(1 cy)

J. Epstein
Goddard Space Flight Center
Greenbelt, Maryland

(1 cy)

Capt. Morrow
Wright-Patterson Air Force Base
Dayton, Ohio 45433

(1 cy)

J. O. Collins
Johns-Manville Research &
Engineering Center
Manville, New Jersey 08835

(2 cys)

W. DeWitt
Union Carbide Corporation
Linde Division
P. O. Box 44
Tonawanda, New York 14152

(2 cys)

G. Rose
Radio Corporation of America
415 South Fifth Street
Building 10-2
Harrison, New Jersey

(1 cy)

H. S. Potter, Chief
New York Patents Group
U. S. Atomic Energy Commission
Brookhaven Area Office
Upton, New York 11973

(1 cy)

J. Dunlay
Thermo Electron Engineering Corp.
Post Office Box 482
Waltham, Massachusetts 02154

(2 cys)

Harold Garber
NUMEC
609 North Warren Avenue
Apollo, Pennsylvania 15613

(1 cy)

U. S. Atomic Energy Commission
New York Operations Office
376 Hudson Street
New York, New York 10014
Attn: Reports Library

(1 cy)

U. S. Atomic Energy Commission
Division of Technical Information
Extension
Post Office Box 62
Oak Ridge, Tennessee 37831
and one reproducible copy)

(3 cys

ALO-3633-2

UC 33

AEC RESEARCH AND DEVELOPMENT REPORT
SPECIAL

v

ABSTRACT

by

J. O. Collins

This is the Second Quarterly Report for AEC Contract AT(30-1)-3633 covering the period July 1966 through September 1966.

Eleven experimental MIN-K formulations were investigated for processing technique, strength and moldability. Two formulations have been tentatively chosen as suitable for 1400F continuous service, one for bulk insulation application with good strength characteristics, and one for intricate T/E module application.

The status of the equipment required for the Detailed Evaluation phase is presented.

TABLE OF CONTENTS

	<u>Page</u>
Legal Notice	ii
Distribution	iii
Abstract	v
I. Introduction	1
II. Initial Screening	2
III. Material and Process Development	9
IV. Equipment	26
V. Conclusions	31
VI. Third Quarter Effort	32
VII. References	33
VIII. Appendix	34

LIST OF FIGURES

	<u>Page</u>
Figure 1. Electron Micrograph of the Silica Particles in MICROTHERM	3
Figure 2. MICROTHERM at 500X Magnification Showing Chromic Oxide (Black Specs) and Amosite Fiber	4
Figure 3. MICROTHERM at 500X Magnification Showing Chromic Oxide (Black Specs) and Glassy Fiber	5
Figure 4. TGA of MICROTHERM	7
Figure 5. Module Insulation Made with Formulation 1999	12
Figure 6. Stress-Strain Relationship of Formulation 2002 at Various Thicknesses	16
Figure 7. Stress-Strain Relationship of Formulation 2002 after Various Thermal Histories	17
Figure 8. Permanent Strain - Maximum Strain Relationship of Formulation 2002	18
Figure 9. Results of Machining Formulation 1999, Blocks 5 and 6. .	21
Figure 10. Results of Machining Formulation 1999, Blocks 8 and 9. .	22
Figure 11. Results of Machining Formulation 2002, Blocks 25 and 26	23
Figure 12. Results of Machining Formulation 2002, Blocks 27 and 28	24
Figure 13. Compression-Relaxation Units	27
Figure 14. Vacuum/Gas Furnaces	28
Figure 15. Johns-Manville Vacuum Thermal Conductivity Apparatus . .	30

LIST OF TABLES

	<u>Page</u>
Table 1. Spectrographic Analysis of MICROTHERM	6
Table 2. Spectrographic Analysis of Glassy Fiber and Shot in MICROTHERM	6
Table 3. Second Quarter Experimental MIN-K Formulations	10
Table 4. Comparison of Average Strength of Formulations Made in the Papenmeier and Henschel Mixers	11
Table 5. Modulus of Rupture of Formulation 1999	13
Table 6. Modulus of Rupture of 1/2-in. Thick Formulation 2002 Specimens	14
Table 7. Thermal Stability of Formulation 2002	14
Table 8. Modulus of Rupture of Formulation 2003	19

1. INTRODUCTION

The First Quarterly Report⁽¹⁾ described the Initial Screening of potential candidate insulations for RTG applications, and the preliminary development and evaluation of experimental MIN-K formulations for 1400F service.

The current report describes in detail the chemical and physical nature of MICROTHERM, a product developed in England which is very similar to MIN-K. Sample size did not permit an evaluation of its thermal conductivity, strength, thermal stability, or similar properties. However, additional material is on order.

The current report also describes what is tentatively considered to be the two formulations which will be recommended for 1400F service. Neither formulation contains an organic binder, and each has only small amounts of chemically bound water which is essentially removed by the short, 1400F firing cycle recommended as part of the manufacturing cycle.

The equipment required for compression-deflection tests, outgassing and compatibility tests, and thermal conductivity measurements are presented, and the results of their initial startups are discussed.

⁽¹⁾Numbers in parenthesis refer to references in Section VII.

II. INITIAL SCREENING

A 6-in. diameter by 1-in. thick sample of MICROTHERM made by Boucher and Company, Kidderminster, England, was analyzed by microscopic, X-ray diffraction, spectrographic and thermogravimetric methods. MICROTHERM is a development of Boucher and Company, and is reported to be similar in thermal efficiency to the MIN-K family of products. This particular form of MICROTHERM was molded to 20 pcf.

A. MICROSCOPIC ANALYSIS

Petrographic examination of the sample as received showed the following:

Bulky Silica	Major
Chromic Oxide	Minor
Amosite Fiber	Approximately 5 per cent
Glassy Fiber and Shot	Approximately 5 per cent

(Shot = unfiberized glassy material)

The amosite fiber showed a brown coloration, and an elevated refractive index typical of amosite which had been heated to 760C.

The ultimate particle size of the silica was approximately 0.03 microns as shown by the electron micrograph in Figure 1.

The chromic oxide had an average particle size of 1 micron with an approximate minimum of <0.3 microns and an approximate maximum of 6 microns. This oxide shows as black specks in Figures 2 and 3.

The amosite fiber ranged in diameter from <0.3 microns to 37 microns with an average of 2 microns. The length was from <10 microns to 1430 microns with an average of 200 microns. Figure 2 shows a typical example of an amosite fiber.

The glassy fibers ranged in diameter from 5.6 to 31 microns with an average of about 14 microns. A glassy fiber may be seen in Figure 3.

B. X-RAY DIFFRACTION

The X-ray diffractometer diagrams and the Debye-Scherrer films indicated a strong pattern of Cr_2O_3 . Additionally, the X-ray diagram of the dark brown fiber indicated it to be oxyamosite, or amosite which had been decomposed at temperatures between 500C and 800C.

FIGURE 1.

ELECTRON MICROGRAPH OF THE SILICA PARTICLES
IN MICROTHERM (36,000X MAG.)

No. 463C

JOHNS-MANVILLE RESEARCH AND ENGINEERING CENTER

FIGURE 2.

MICROTHERM AT 500X MAGNIFICATION SHOWING CHROMIC OXIDE
(BLACK SPECKS) AND AMOSITE FIBER

No. E-3497B

JOHNS-MANVILLE RESEARCH AND ENGINEERING CENTER

FIGURE 3.

MICROTHERM AT 500X MAGNIFICATION SHOWING CHROMIC OXIDE
(BLACK SPECKS) AND GLASSY FIBER

No. E-3497A

C. SPECTROGRAPHIC ANALYSIS

The results of the spectrographic analysis are given in Table 1 below.

TABLE 1.
SPECTROGRAPHIC ANALYSIS OF MICROTHERM*

SiO ₂ (by difference)	62 ±2 per cent
Cr ₂ O ₃	32 ±2 per cent
Al ₂ O ₃	3.7
Fe ₂ O ₃	1.8
TiO ₂	0.26
MgO	0.24
Na ₂ O	<0.1

Total Ignition Loss at 1800F - 1.9 per cent

---

*All elements expressed as oxides on the ignited basis

A spectrographic analysis of the glassy fiber and shot extracted from the MICROTHERM gave the qualitative analysis shown in Table 2.

TABLE 2.
SPECTROGRAPHIC ANALYSIS OF THE GLASSY FIBER
AND SHOT IN MICROTHERM

Al and Si	Major
Zr	Small
Ti	Trace
Fe	Not Detected
Na	Not Detected
B	Not Detected

D. THERMOGRAVIMETRIC ANALYSIS

The thermogravimetric curve for MICROTHERM is given in Figure 4. The sample was preconditioned in the same manner as the TGA examinations reported in the First Quarterly Report⁽¹⁾, i.e., 20 hr at 54 per cent RH and room temperature. An initial weight loss of 1.3 per cent at 120C represented adsorbed moisture, while the balance of the loss (up to 1.8 per cent) probably represented water chemically combined with silica. This curve is similar to those for the experimental MIN-K formulation published in Figure 21, page 49 of the First Quarterly Report⁽¹⁾.

FIGURE 4.

THERMOGRAVIMETRIC ANALYSIS OF MICROTHERM
(in air)

A further qualitative examination indicated that an organic binder was not present in quantities greater than a few tenths of one per cent.

E. MICROTHERM SUMMARY

MICROTHERM is definitely similar to MIN-K and consists of a very finely divided silica, opacified with about 32 per cent chromic oxide, and reinforced with both amosite and alumina-silica fibers. It cannot be established definitely whether the amosite was fired prior to mixing with the other ingredients, or the MICROTHERM was fired after molding. The TGA curve would lead one to suspect the former, however, due to the loss in weight above 120C.

The small sample appeared to have considerable less integrity and handling strength than the MIN-K formulations. This may be due to any one or a combination of the following:

1. High opacifier content and hence lower silica content;
2. Poor fiber distribution and/or low fiber reinforcing efficiency per unit weight due to the large diameters;
3. A different silica material.

Thermal conductivity data have been verbally quoted as being slightly higher than MIN-K in air, but lower than MIN-K in vacuum. The specific values are presently suspect due to the nature of the test method, and hence will not be reported here. A thermal conductivity vs mean temperature curve will be developed by this laboratory upon receipt of additional material.

III. MATERIAL AND PROCESS DEVELOPMENT

A. REVIEW SUMMARY

The first quarterly effort resulted in a tentative choice of raw materials, formulation, and processing technique. CAB-O-SIL M5 silica, MICRO-QUARTZ, and ASTROQUARTZ fibers, and titanium dioxide opacifier were considered worthy of additional investigation. Formulation 1979 provided excellent strength, handleability, and machineability, although lacked the molding characteristics considered necessary for the forming of intricately shaped parts. The Henschel mixer greatly increased the uniformity of the MIN-K mix over the standard processing methods, although it was considered pertinent to investigate the Papenmeier mixer since its design differed slightly from the Henschel.

Table 3 lists the formulations investigated during the second quarter.

B. PROCESSING TECHNIQUES

Formulation 1993 duplicated Formulation 1979 except that the MICRO-QUARTZ fiber was pre-fired at 1500F for 2 hours, and premilled in the Henschel for one minute prior to blending with the other ingredients. Previous efforts had indicated that such pretreatments might increase the strength of the formulation over 1979.

Thirty-two 1/2-in. thick specimens of Formulation 1993 were tested for modulus of rupture with an average result of 72.8 psi. Since Formulation 1979 averaged 69.8 psi by the same test, it was concluded that the pretreatment of the MICRO-QUARTZ did not sufficiently improve the strength of the formulation to warrant its inclusion as part of the manufacturing process.

Formulations 1994 through 1997, which were duplications of Formulations 1991, 1992, 1973 and 1979, respectively, were devised to establish a comparison between the Henschel and the Papenmeier mixers. Two basic differences between these mixers were:

1. The Papenmeier was conical in shape having its smaller diameter at the top, whereas the Henschel had vertical sides.
2. The Papenmeier had a choice of several blade designs, whereas the Henschel mixers at the Research and Engineering Center had only the one type.

It appeared that the Papenmeier did a slightly less efficient job of opening the MICRO-QUARTZ fiber, particularly during the premilling operations in Formulations 1994 and 1995. Fiber hangup in and around the blade was also somewhat more evident, resulting in fiber clumps in the finished mix.

TABLE 3.
SECOND QUARTER EXPERIMENTAL MIN-K FORMULATIONS*

Number	Silica	Fiber			Opacifier		Comments
	CAB-O-SIL M5	MICRO-QUARTZ	ASTROQUARTZ 1/2-in.	ASTROQUARTZ 1/4-in.	Silicon	TAM -5 μ TiO ₂	
1993	75	4**	5		16		MICRO-QUARTZ premilled 1 minute in Henschel
1994	75	9			16		Papenmeier evaluation: fiber premilled in Papenmeier
1995	75	9**			16		Papenmeier evaluation: fiber premilled in Papenmeier
1996	79			5	16		Papenmeier evaluation
1997	75	4	5		16		Papenmeier evaluation
1999	75	8		1		16	Henschel: moldability evaluation
2000	75	7		2		16	Henschel: moldability evaluation
2001	75	6		3		16	Henschel: moldability evaluation
2002	75	4	5			16	Henschel: Similar to 1979
2003	67	4	5			24	Henschel: Conductivity - strength trade off

*All numbers represent per cent by weight.

**Heat treated 2 hr at 1500F.

Table 4 below summarizes the modulus of rupture tests, and compares these results with the averages of the same mixes made in the Henschel.

TABLE 4.
COMPARISON OF AVERAGE STRENGTH OF FORMULATIONS
MADE IN THE PAPENMEIER AND HENSCHEL MIXERS

<u>Papenmeier</u>		<u>Henschel</u>	
<u>Formulation</u>	<u>MR (psi)</u>	<u>Formulation</u>	<u>MR (psi)</u>
1994	32.5	1991	46.5
1995	37.5	1992	47.3
1996	35.0	1973	41.0
1997	67.4	1979	69.8

Based upon both visual examination of the mixes during the various process stages, and the average modulus of rupture of the products, it was concluded that the Henschel mixer outperformed the Papenmeier with regard to opening and uniformly distributing the fibers within the formulation. This conclusion should in no way be construed to indicate the relative merits of these two machines when used for the purpose for which they were designed, that of dry blending fiber and powdered resins.

C. FORMULATIONS

Moldability

As previously reported⁽¹⁾, the moldability of the stronger formulations such as 1979 did not appear adequate when used to form small, intricate shapes. This was believed to be caused by the relative lack of flow of the mix within the mold due to the presence of the 1/2-in. long staple ASTROQUARTZ fiber. To improve the flow, Formulations 1999, 2000 and 2001 were devised. These formulations contained primarily MICRO-QUARTZ fiber with small amounts of 1/4-in. ASTROQUARTZ staple fiber added. Molding trials centered primarily upon the SNAP 19 T/E module insulation configuration.

Formulation 1999 containing 8 per cent MICRO-QUARTZ and only 1 per cent 1/4 in. ASTROQUARTZ was considered the best compromise. Figure 5 shows a photograph of the SNAP 19 module insulation molded with Formulation 1999. In comparison to the molding depicted in Figure 20, page 48 of the First Quarterly Report⁽¹⁾, the single large shear crack along the bottom edge has now been reduced in size considerably. Likewise, the lip along the top edge is considerably firmer than in the earlier molding.

FIGURE 5.

MODULE INSULATION MADE WITH FORMULATION 1999

It should be pointed out that a modified tool design may alleviate the shear cracks, but that very small cross-sectional areas such as the top lip will always be susceptible to handling damage regardless of the formulation used. Subsequent designs should, if at all possible, minimize or eliminate such areas.

The strength (modulus of rupture) of Formulation 1999 was definitely lower as anticipated due to the greatly reduced staple fiber content. Table 5 summarizes these results.

TABLE 5.

MODULUS OF RUPTURE OF FORMULATION 1999

<u>Exposure</u>	<u>MR, psi</u>
No thermal history	39.9
Exposed 2 hr to 1400F	61.9

Because of the increased strength, and the removal of chemically combined water within the CAB-O-SIL M5 and the MICRO-QUARTZ fiber, it is recommended that the manufacturing procedure for intricate shapes (using Formulation 1999) include a 2 hr exposure to 1400F. Since no binder exists in the molded part, this firing can be accomplished by inserting it into, and removing it from a furnace operating at 1400F. This would eliminate the slow heatup and firing schedule presently undertaken by the PbTe generator manufacturers.

Bulk Insulation

Formulation 2002 represents a duplication of Formulation 1979, except that TAM* -5 μ TiO_2 was substituted for silicon as the opacifier.

The modulus of rupture of Formulation 2002 was determined in the as-molded state (no thermal history), after 2 hr at 1000F and after 2 hr at 1400F. Sixteen specimens were tested in the as-molded state, while eight were tested following each of the two thermal conditionings. Table 6 summarizes the results.

*Titanium Alloy Metals Division, National Lead Company.

TABLE 6.

MODULUS OF RUPTURE OF 1/2-IN. THICK FORMULATION 2002 SPECIMENS

<u>Condition</u>	<u>MR, psi</u>
As molded	71.0
2 Hr at 1000F	92.4
2 Hr at 1400F	102.0

Previously reported values for Formulation 1979⁽¹⁾ were 69.8 psi and 86.1 psi for the as-molded and 1000F conditions, respectively, indicating as expected that the substitution of opacifier would not alter the strength properties.

Formulation 2002, which was developed for 1400F continuous hot face service, showed exceptional improvement in thermal stability over standard MIN-K 1301 currently used for this service. Nine specimens, with no previous thermal history, were subjected in groups of three to isothermal conditions of 1400F for 168 hrs, 1500F for 100 hr, and 1600F for 48 hr. Table 7 below summarizes the results, and compares them with the results of the 24 hr exposures of MIN-K 1301 reported earlier⁽¹⁾.

TABLE 7.

THERMAL STABILITY OF FORMULATION 2002

<u>Time, hr</u>	<u>Temperature, °F</u>	<u>Shrinkage, %</u>	
		<u>Linear</u>	<u>Thickness</u>
168	1400	0.3	0.9
100	1500	0.3	1.2
48	1600	0.5	1.3
		<u>MIN-K 1301</u>	
24	1400	1.5	2.9
24	1500	5.6	9.7
24	1600	11.5	18.9

It is anticipated that the incorporation of a 2 hr, 1400F isothermal firing of Formulation 2002 into the manufacturing procedure would significantly reduce any subsequent shrinkage at these elevated temperatures. Thus, one

might expect the thickness shrinkage of Formulation 2002 to be approximately 0.3 and 0.4 per cent for the 1500F and 1600F exposures, respectively. This will be verified in the following quarter.

The room temperature stress-strain curves for Formulation 2002 are given in Figures 6 and 7. These tests were conducted on a Riehle Hydraulic Model KA-60 at a loading rate of approximately 60 psi per minute, and with a 0.001-in. deflection dial gage. The samples were 4-1/2 x 4-1/2-in. square (nominally) and loaded over their entire area. No lateral restraint was provided during the tests. A static preload of 0.34 psi was applied to each specimen.

For this preliminary work, readings were taken at 2 per cent deflection increments, although intermediate points will be obtained during more detailed evaluations of the product. The average of eight specimens was used for each curve, although all eight were not carried to maximum deflection (in this case, 15 per cent) in order that the permanent strain after various levels of deflection might be determined. For example, two specimens were deflected to 4 per cent, two to 8 per cent, two to 12 per cent, and two to 15 per cent. In all cases, data were accumulated up to the completion of the test. After releasing the load, the specimen was allowed to regain for 1 minute at which time the permanent strain reading was taken. (Actually, no further movement of the specimen could be detected after 30 seconds.) Figure 8 is a plot of the permanent strain vs the maximum strain for samples having no previous thermal history, and those having a thermal history either at 1000F or 1400F.

Figure 6 indicates that the stress-strain curve is sensitive to thickness up to about 1/2 in. This may be caused in part by nonuniformity of density which becomes more apparent in the thin cross-sections, due to the effect of the natural thickness regain tendency of the product after molding. The regain tendency can be predicted with reasonable accuracy and accounted for during the pressing of the product. However, it may also constitute a source of low compression resistance if, as predicted by the low end of the stress-strain curve, the regain is primarily a surface phenomenon and not uniformly distributed throughout the thickness of the part.

The modulus of elasticity of the 1/2 and 1-in. thick specimens having no thermal history averaged 1460 psi. There was considered insufficient data to establish 90 per cent confidence limits. Earlier work by Martin Company⁽²⁾ showed MIN-K 1301 to have an average modulus of elasticity of 5400 psi. Aside from the material composition changes, other factors such as sample configuration and loading rate may significantly alter the slope of the stress-strain curve. It is known, however, that for MIN-K products in general, the slope is quite sensitive to density. For example, the modulus of elasticity for MIN-K 2000 at 25 pcf (similar in nature to Formulation 2002) has been reported as high as 14,000 psi⁽³⁾.

Figure 7 shows the effect of thermal history upon the stress-strain curve, and hence upon the modulus of elasticity. Those specimens fired 2 hr at 1400F had an average value of $E = 2250$ psi. Although there was again insufficient

FIGURE 6.

STRESS-STRAIN RELATIONSHIP FOR VARIOUS
THICKNESSES OF FORMULATION 2002

All tests at room temperature

FIGURE 7.

STRESS-STRAIN RELATIONSHIP OF FORMULATION
2002 AFTER VARIOUS THERMAL HISTORIES

All tests at room temperature

FIGURE 8.

PERMANENT STRAIN - MAXIMUM STRAIN
RELATIONSHIP OF FORMULATION 2002

All tests at room temperature

data to establish 90 per cent confidence limits, the 1400F history is considered to have a significant effect upon the stress-strain characteristics of Formulation 2002.

Figure 8 depicts the relationship between the permanent strain and the maximum strain to which the specimen was subjected. The prefired specimens definitely showed less permanent strain than did the specimens (average of 1/2-in. and 1-in. thick) which had no thermal history. It also points out that despite the apparent ceramic nature of the material after firing, the resiliency generally attributed to MIN-K not only remains, but probably improves.

Previous work on MIN-K 1301⁽⁴⁾ indicated that the stress-strain curve plotted on log-log coordinates consisted of two straight lines, the first being relatively steep (the slope of which represented the modulus of elasticity), and the second of considerably lesser slope. The point of intersection was considered to represent the yield and/or failure point of the material. Reinforcing the theory regarding the significance of the intersection was the fact that the intersection occurred at the same level of strain for all densities from 20 to 40 pcf, this being approximately 0.08 to 0.09 in./in.

A similar plot of the present data indicated that the same occurrence might be expected. This is reflected in the permanent strain vs maximum strain curve (Figure 8) if the presently drawn curves are replaced with two sets of straight lines (shown as dotted), the intersections of which both fall around the 0.11 to 0.12 in./in. strain level. However, additional data points would be required to confirm this phenomenon.

Since it had been shown previously⁽¹⁾ that additional amounts of opacifier would lower the thermal conductivity of the product, Formulation 2003 containing 24 per cent -5 micron, TiO_2 was subjected to strength evaluations. Table 8 below summarizes these results.

TABLE 8.

MODULUS OF RUPTURE OF FORMULATION 2003

<u>Exposure</u>	<u>MR, psi</u>
No thermal history	41.1
Exposed 2 Hr to 1400F	66.4

Although Formulation 2003 represented only a 50 per cent increase in opacifier content (24 per cent TiO_2) rather than the 100 per cent previously measured for conductivity (32 per cent TiO_2), the strength characteristics dropped markedly from those achieved with Formulation 2002. Interpolation of the data presented in Table 14, page 50 of the First Quarterly Report⁽¹⁾ indicates that Formulation 2003 should have a thermal conductivity of about 0.22(5) Btu in./hr sq ft °F at 1000F mean temperature. This represents only a 6 per cent improvement over Formulation 2002, with a 35 per cent sacrifice in strength and handleability. In light of the anticipated handling, fabrication, assembly, and service conditions to which MIN-K would be subjected, the sacrifice of strength for improved thermal efficiency does not appear justified, and in certain instances, may not be tolerable.

Machinability

Photographs of Formulations 1999 and 2002 after machining by Martin Company are shown in Figures 9 through 12. The blocks were 1/4 and 1-1/2 in. thick. The report by the shop supervisor is given in the Appendix.

The report, and additional comments made by the shop supervisor, may be summarized as follows:

1. Formulations 1999 and 2002 (prefired to 1400F) have machining qualities far superior to those of MIN-K 1301 or 2000.
2. These formulations were slightly better than Formulation 1976 and 1979 previously machined and reported⁽¹⁾, except that more airborne dust was evident.
3. Blocks made from Formulations 1999 and 2002 were very uniform with respect to fiber distribution and hence machining characteristics.
4. Formulation 1999 machined equally as well as Formulation 2002, even though the former was considered to be weaker, and more brittle.

Conclusion 3 carries considerable significance. It will be noted from the photographs that the machining of a shape from each block was in each case carried to successful conclusion, with no "rejects" or losses due to fiber clumps being "pulled out" as is the frequent case with MIN-K 1301 or 2000. Thus, rejects, which currently run between 25 and 75 per cent for standard MIN-K, would be drastically reduced to a level which would be as much a function of the care of the operator as it would the material itself.

It is believed that machining is a considerably more severe test for product uniformity than thermal conductivity, strength, compression resistance, etc., since machining can "evaluate" or "compare" very small, localized areas. Consequently, the process development phase concerned with the mixing equipment and conditions can be considered successfully completed.

FIGURE 9.

RESULTS OF MACHINING FORMULATION 1999, BLOCKS 5 AND 6

FIGURE 10.

RESULTS OF MACHINING FORMULATION 1999, BLOCKS 8 AND 9

FIGURE 11.

RESULTS OF MACHINING FORMULATION 2002, BLOCKS 25 AND 26

FIGURE 12.

RESULTS OF MACHINING FORMULATION 2002, BLOCKS 27 AND 28

D. SUMMARY

Formulations 2002 and 1999 have been tentatively chosen as the improved materials for use in bulk and intricate configurations, respectively, for service temperatures up to 1400F. These products appear to represent the best compromise between thermal efficiency, strength, moldability, and outgassing (with respect to the raw materials). The 2 hr isothermal firing of these materials at 1400F should eliminate essentially all residual chemically combined moisture, thus requiring only the removal of adsorbed moisture and oxygen during the assembly of the RTG. Subsequent tests will be conducted on these two formulations unless some major deficiency is uncovered requiring further material and process development.

IV. EQUIPMENT

A. COMPRESSION-RELAXATION UNITS

The ten compression-relaxation units are shown in Figure 13. Each was heated to 1800F to check the control characteristics. Although not shown in the diagram (Figure 24, page 55, First Quarterly Report), the primary hot face temperature control is by a thermocouple placed between the heater plate and the silicon carbide plate (directly above the heater plate). A second couple, placed at the carbide plate-specimen interface, not only records the hot face temperature of the specimen, but also indicates if the temperature controller at the heater plate must be adjusted to achieve the desired hot face temperature. Generally, the controller temperature runs 25 to 100F above the hot face temperature.

Such an arraignment increases the sensitivity of the control, and minimizes the temperature variation at the hot face of the specimen. A cold face thermocouple is also used to obtain a complete thermal cross-section of the specimen under test.

Each furnace was calibrated for load-deflection characteristics both cold and hot (1900F hot face) in that order. For the most part, the calibrations were the same, although where small differences existed, the furnace always deflected less when hot.

Breakage of the heater plates (and hence a shorting of the heating elements) has occurred both following calibration, and also as a result of several preliminary stress-strain tests. Heavier heater plates for all units are on order, and should be in operation by the middle of October.

B. VACUUM/GAS FURNACES

A photograph of the vacuum/gas furnace setup showing a five tube furnace, and a one tube furnace is presented in Figure 14. Delivery of all vacuum equipment parts was completed the last part of September. Assembly and checkout was initiated immediately.

The first heatup and checkout (still in progress) involves the following:

1. Temperature measurement of the Viton gasket at the top of each tube.
2. Measurement of the temperature gradient at various depths both inside and outside each tube.
3. Determination of the effectiveness of a multifoil (Inconel) radiation shield mounted directly below the Viton gasket to lower the temperature at the gasket, and to improve the temperature distribution within the tube.

FIGURE 13.
COMPRESSION-RELAXATION UNITS

FIGURE 14.
VACUUM/GAS FURNACES

4. Measurement of the vacuum capability of the system.

The heatup has been conducted in 200F increments. At this writing, the temperature is up to 1200F. The ceramic tubes had not been preheated or outgassed prior to this startup.

Preliminary indications are that at a furnace temperature of 800F:

1. The Viton gasket is 175F in the tube with air at 1 atmosphere and no radiation shield.
2. The radiation shield reduces this temperature by about 35F, and vacuum reduces this temperature an additional 25F.
3. A nominal gradient exists between 0 and 6-in. from the bottom of the tube, but increases to a total of 100F between 0 and 12-in.
4. The radiation shield reduces this gradient by about 50F.
5. Vacuums in the order of 1 to 1.5×10^{-3} mm Hg (measured between the tube and the manifold) have been achieved consistently.

No major problems have been encountered with the vacuum/gas equipment as yet.

C. JOHNS-MANVILLE VACUUM THERMAL CONDUCTIVITY APPARATUS

Figure 15 shows the Guarded Hot Plate stack in detail with the many electrical and thermocouple leads, and the cooling shroud (right) which surrounds the stack. Installation of this stack involved more effort than anticipated, and hence the final calibration of the unit did not begin until after October 1.

FIGURE 15.

JOHNS-MANVILLE VACUUM THERMAL CONDUCTIVITY APPARATUS

V. CONCLUSIONS

A. INITIAL SCREENING

1. MICROTHERM, made by Boucher and Company, England, is similar to the MIN-K family of materials.
2. MICROTHERM consists of approximately 62 per cent silica (same class of silica as used in MIN-K), 32 per cent Cr_2O_3 opacifier, and approximately 5 per cent each of dehydrated amosite and a glassy alumina-silica fiber for reinforcement.
3. The thermal conductivity of MICROTHERM is probably about the same as MIN-K, although verification of this and other physical properties must await receipt of additional material.

B. MATERIAL AND PROCESS DEVELOPMENT

1. The Henschel mixer consistently gave a stronger, more uniform product than did the Papenmeier mixer.
2. Formulation 1999, containing 1 per cent 1/4-in. ASTROQUARTZ and 8 per cent MICRO-QUARTZ was considered to be the best compromise for intricate moldings up to 1400F service.
3. Formulation 2002 was considered to be the best for bulk insulation, and minor load bearing applications up to 1400F service.
4. Post firing both Formulations 1999 and 2002 for 2 hr at 1400F (isothermal) resulted in strength increases from 39.9 psi to 61.9 psi, and from 71.0 psi to 102.0 psi, respectively.
5. Post firing of these formulations should be included in the manufacturing procedure not only for the additional strength, but also to remove residual chemically combined moisture.
6. Preliminary data indicated that the modulus of elasticity of Formulation 2002 (normal to "laminar" structure) was 2250 psi.
7. Both Formulations 1999 and 2002 had excellent machining characteristics and uniformity of structure, particularly with respect to fiber openness and distribution.

VI. THIRD QUARTER EFFORT

1. Checkout of vacuum equipment will be completed, and long term (2000 hr) life tests will be initiated.
2. The cursory evaluation of candidate load bearing materials will be completed.
3. The effect of variables such as temperature, batches, moldings within batches, and material axis on the stress-strain characteristics of Formulation 2002 will be initiated.
4. The development of MIN-K formulations for 1800F continuous service will be initiated.

VII. REFERENCES

1. Develop 1800F-400F Fibrous-Type Insulation for Radioisotope Power Systems, First Quarterly Progress Report, Report No. AL0-3633-1, July 1, 1966, under AEC Contract AT(30-1)-3633.
2. Structural Evaluation of MIN-K 1301, Report No. MND-3169-45, January 1965, under AEC Contract AT(30-1)-3169.
3. Johns-Manville internal report dated January 1965.
4. Johns-Manville internal report dated November 1960.

VIII. APPENDIXREPORT OF VARIOUS MACHINING OPERATIONS ON FORMULATIONS 1999, 2002DRILLING AND COUNTERBORINGFormulation 1999, Blocks 5, 6, 8, 9

Showed slight breaking of edges top and bottom when backed up by predrilled template. Drill had to be removed often and cleaned with brush to remove dust that packed in flutes. Caution should be used when drilling close to wall or edge as flutes tend to load up and push through. Results were very good. There was no noticeable difference in doing the same type of operations on the various blocks.

Formulation 2002, Blocks 25, 26, 27, 28

No noticeable difference. Results same as above.

SAWING WITH BAND SAWFormulation 1999, Blocks 5, 6, 8, 9

Saws very well retaining sharp corners and edges. Sawed surface fairly smooth, with no fibers showing. No difference noticed with the various blocks.

Formulation 2002, Blocks 25, 26, 27, 28

No noticeable difference. Results same as above.

TURNING ON LATHEFormulation 1999, Blocks 5, 6, 8, 9

Machinability very good. Edges and corners stay sharp using sharp pointed tool. In machining groove next to another groove, material breaks through, if wall between grooves is less than 1/4 in. Material was backed, both sides with 1/2 plywood during all operations. Airborne dust greater in these operations than on previous test formulations 1976 and 1979. No noticeable difference in machining the various blocks.

Formulation 2002, Blocks 25, 26, 27, 28

No noticeable difference. Results same as above.

ROUTINGFormulation 1999, Blocks 5, 6, 8, 9

Routed a 1/4 slot x 3/16 deep with good results, except in areas of thin walls or near holes or edges. In these locations slot has a tendency to break out. Edges and corners remain fairly sharp. No difference in the various blocks.

Formulation 2002, Blocks 25, 26, 27, 28

Results same as above with little noticeable difference.

SHAVINGFormulation 1999, Blocks 5, 6, 8, 9

Shaving using sharp square edge shaver worked very well with good results in maintaining sharp corners and edges. There was no difference between the various blocks.

Formulation 2002, Blocks 25, 26, 27, 28

Results same as above with no noticeable difference.

MILLINGFormulation 1999, Blocks 5, 6, 8, 9

Milled edges backed up with plywood on top and bottom with good results. Retained sharp corners and edges. There appears to be no difference in face or roll milling 1/4 x 1/4 groove. Milled well without backing on top. No noticeable difference in milling the various blocks.

Formulation 2002, Blocks 25, 26, 27, 28

No noticeable difference. Results same as above.

SANDINGFormulation 1999, Blocks 5, 6, 8, 9

Sanding caused loading up of emery cloth. Sandpaper worked better, but still loaded up requiring cleaning and changing paper often. Otherwise, results were good with no difference encountered in the various blocks.

Formulation 2002, Blocks 25, 26, 27, 28

No noticeable difference. Results same as above.

Results of the machining operations indicated that the above listed formulations are far superior to the MIN-K 1301 and 2000. As the above results indicate, there was very little perceptible difference in the machining operations performed on the various blocks. A greater degree of airborne dust was evident with these formulations requiring a better degree of dust collection and control, to prevent health hazards and dust contamination of shop areas.