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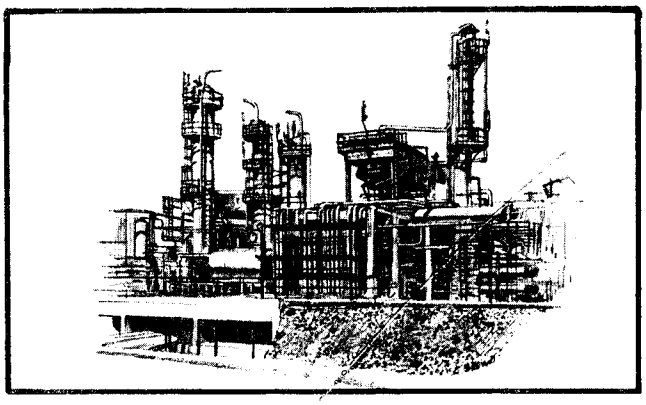

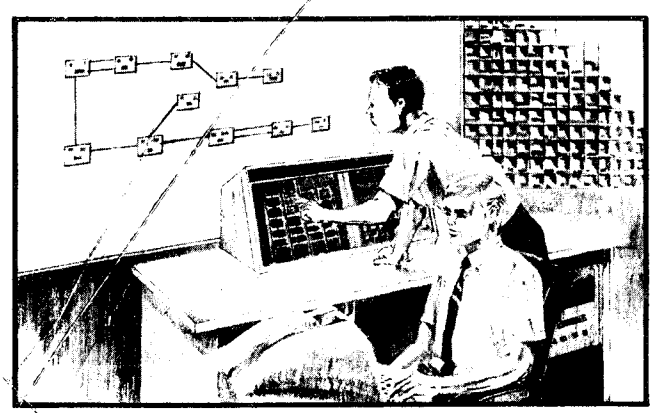

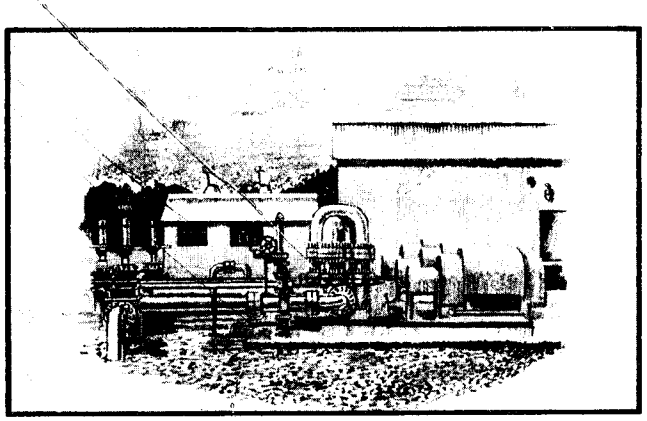

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FINAL REPORT

Task Order Number 21

Contract NAS 9-6698

Prepared by:

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July 24, 1972

for

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I

THERMAL CONDUCTIVITY OF FILLED RTV COMPOUNDS

(7010-210)

I. PURPOSE AND SCOPE

The following background information and work statement is taken from the task order.

> "In space applications, it is advantageous to use sealant materials which have high thermal conductivity so that heat can be conducted away from electrical components to adjacent heat-sinks and prevent over-heating. In addition, many applications require that the thermally conductive sealant material be electrically non-conductive to avoid the possibility of shorting vital circuitry. It is expected that a room temperature vulcanizing material, such as a silicone, heavily filled with alumina powder or other material could have the desired high thermal conductivity and low electrical conductivity.
>
> "It is directed that the thermal conductivity of alumina and other thermally conductive fillers milled into room temperature vulcanizing (RTV) compounds be explored. The effect of particle size, both narrow sieve cuts and broad size distributions, will be experimentally examined. Pretreatment of the filler, such as vacuum drying, and techniques of mixing will be considered, as will the ratio of filler to sealant compound.
>
> "For the most promising formulation, sheets 6" x 6" x 1/8" will be produced in sufficient amount for test specimens, as a minimum for ASTM tests D638, D695, D635, D257, and C177. Tests will be conducted by HR.
>
> "Equipment to measure the thermal conductivity will be assembled comparable to the Guarded Hot Plate apparatus. At the end of the task, the equipment will be submitted to the task monitor with the test samples for confirmation of the thermal conductivity measurements."

II. EXPERIMENTAL EQUIPMENT

A. Description

The guarded hot plate consists of an alundum plate 3/8" thick and 9" in diameter. A single spiral groove is formed in one face of the plate to a depth of slightly more than 3/16". The groove has a width of approximately 1/32" and starting from the center of the plate continues to the outer edge at the rate of approximately 11 turns per inch. The heating elements consist of No. 20 - 24 (awg.) Nichrom V resistance wire. The center heating element extends over the center 7-1/2" of the plate, with means for measuring the resistance of the wire contained in the center 6" area of the plate. A guard ring heating element 3/4" wide covers the remainder of the plate. This 3/4" width guard plus the 3/4" width to the beginning of the center test area gives an equivalent guard width of 1-1/2". The heating elements are cemented into the center of the heating plate with alundum cement.

The power leads of the heating element are brought through small holes and cemented into grooves about 1/16" deep in the back of the plate leading out to the edge of the plate. The power leads of the guard element are brought out through similar grooves in the back of the plate. Four thermocouples are also cemented in the back of the plate; the junctions of the couples are placed directly at the surface of the plate at a distance 1-7/8", 2-5/8", 3-3/8" and 4-1/8", respectively from the center of the plate. The same is duplicated on the opposite side and diametrically opposite. The thermocouples are iron-constantan, type J, instead of the chromel-alumel sometimes supplied. The manufacturer is Custom Scientific Instruments, Whippany, New Jersey.

The two inner thermocouples on each side of the hot plate are connected all four in parallel to a Compack II, which controls

the temperature of the central portion of the hot plate by time proportioning of the power to the central heating element. Similarly, the outer thermocouples are connected to an identical Compack II controlling the guard heater. Both controllers are 0-750°F. Because the resistance of the guard heater is considerably lower than that of the central heater, the voltage to the guard heater is dropped by a Powerstat variable autotransformer to 50% to maintain the guard power to an appropriate level.

The Compack II is a narrow control band (0.25-0.5%) taut-band meter with electrical cold-junction compensation and fail safe up-scale thermocouple break protection. Specifications are 2% accuracy, 5 seconds cycle time, 2% proportioning band, 0.5% set point resolution, 5 amp relay contacts, and thermocouple resistance compensation up to 10 ohms. Manufacturer is API Instruments Company of Chesterland, Ohio; sales and service in Houston by Quality Instruments Laboratory.

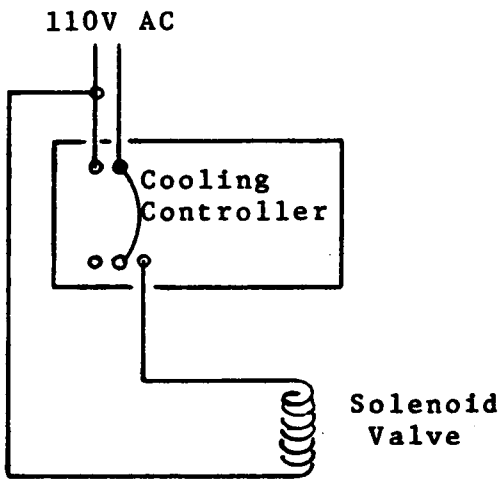
Electrical power level into the central heater is indicated by a Weston Model 432 Wattmeter, Catalog Number 9902010, 5 and 10 amps, 150 and 300 volts, 150/300/600 watts at 0.5% accuracy. The power dissipated in the central 6 inch diameter is apportioned by the resistance of the heating wire in the 6 inch diameter (measured through two holes in the hot plate) over the total resistance of the central heater.

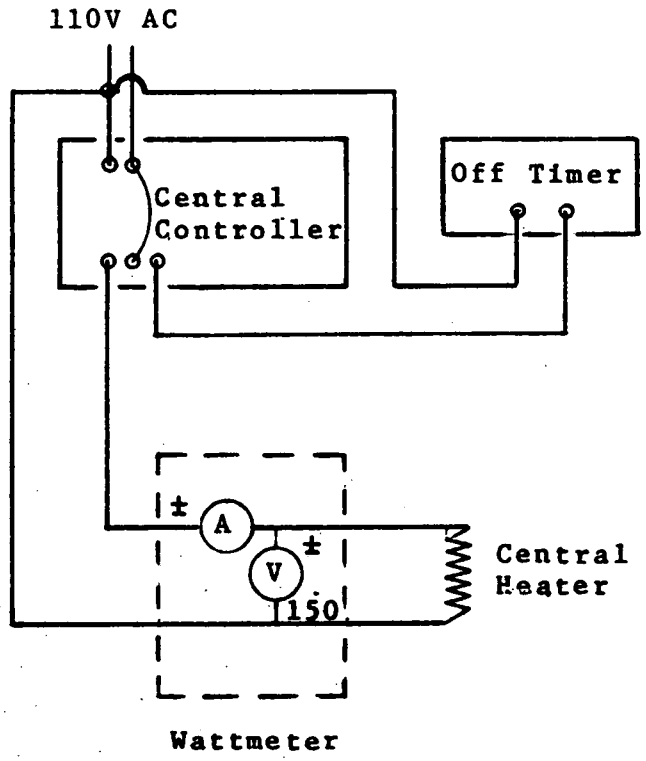
Two Lab-Chron timers indicating seconds and tenths are used. One is powered by the action of the control on the central heater so that the timer is on when there is no power to the heater. This timer therefore sums the amount of time that the heater is off during a total time period measured by the second timer.

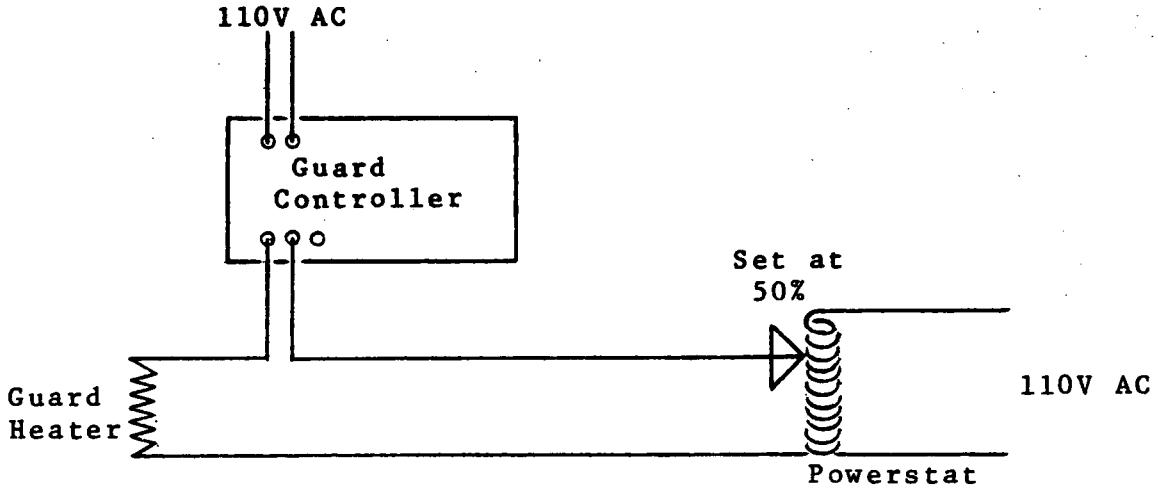
Two hollow cooling plates 9" diameter and 1" thick (inside dimensions 8.5" x 0.5") of cast bronze were also obtained from Custom Scientific. Each plate is connected by flexible, armored tubing to a solenoid valve and a tap water source, and to the drain. One side of each plate has two Iron-Constantan J thermocouples mounted in the surface. The two thermocouples of each cooling plate are connected in parallel to a Compack II controller, identical to those previously described, except having on-off control only. Each Compack II controls the solenoid valve supplying water to the corresponding cooling plate, so that water is allowed to flow when the plate becomes hotter than the set point.

Four copper plates nominally 9" diameter by 3/16" thick, each having a single Iron-Constantan J thermocouple mounted in the surface, were fabricated by HR.

An outer circular container of asbestos lumber 22" in diameter and 10" high was obtained from Custom Scientific. During assembly, half of the circumference is removed. The bottom cooling plate, thermocouple side up, is placed on the bottom of the container. A copper thermocouple plate, thermocouple side up, is stacked on the bottom cooling plate. This is followed by a sample slab, copper plate (thermocouple down), hot plate, copper plate (thermocouple up) second sample slab, copper plate (thermocouple down) and the upper cooling plate (thermocouple down). The thermocouples are attached to the proper controllers through connectors; each half of a connector set is marked with the same identification, and each connector set is marked uniquely. The guard and central heaters are connected to their respective controllers through similarly marked power plugs. The container is closed and filled with insulating powder. Although perlite was used, any other material electrically and thermally insulative to 750°F would be satisfactory.







ELECTRICAL SCHEMATICS

B. Operation

The two heating controllers are ganged to a single power cord, and the two cooling controllers are ganged to a single power cord. These two power cords are energized, power is supplied to the powerstat in the guard heater circuit and the powerstat set at 50%. All four controllers are set to 100°F. When the central and guard controller temperatures have advanced close enough to the set points so that both are cycling on and off, both set points are advanced by 50°F. This is repeated until the desired temperature level is reached, 400°F for this work. Care must be taken that the temperatures indicated on the central and guard controllers never differ from each other by more than 100°F to minimize danger of the hot plate cracking.

When controller temperatures seem to be stabilized, the set points are adjusted slightly to be sure that the guard and central controllers are controlling at exactly 400°F and to be sure that the cooling controllers are controlling at exactly 100°F. A manual valve in the water line ahead of the solenoid valves is used to restrict the water flow until the cooling plate temperature does not change significantly when the solenoid valve opens.

When the previous criteria appear to be satisfied, the temperatures of the copper thermocouple plates are monitored until steady state is reached and these temperatures no longer change. The effect of any slight variations in the temperatures of the hot plate and the cooling plates, will be dampened by the mass of the thermocouple plates. In the present work, the temperature gradient through each sample slab was recorded on a ten millivolt recorder as the difference in potential of the thermocouples in the copper thermocouple plates immediately above and below the sample, connected in series and with opposed potentials.

After steady state appears to be reached, both timers are started simultaneously and allowed to run until the "total" timer indicates 1000 sec. This is repeated until the "off" timer agrees with the previous "off" reading to within twice the time advanced by the "off" timer during a cycle of the central controller, 2 or 3 sec. per cycle. The final two values of the fraction time off are averaged and recorded.

The set point for the central controller is advanced just far enough so that the power stays on. The wattmeter is read and recorded, and any variations in the reading due to variations in the line voltage are noted. Power is cut off from the heating controllers, but not from the cooling controllers. The hot plate is allowed to cool down slowly to about 150°F before disassembly to prevent uneven cooling which might crack the hot plate.

III. EXPERIMENTATION

A. Sample Preparation

Filler material is weighed out in the amount required for a sample slab. Since the fillers are fine materials with large, specific surface areas, they adsorb water, oxygen, and nitrogen. The filler should therefore be degassed under vacuum (about 1 mm Hg absolute) at room temperature for about 20 minutes. The degassed filler is held under vacuum until the RTV is ready for mixing with filler.

The RTV is weighed into a plastic bucket. Plastic is used because the cured RTV is easily peeled from plastic or metal but cleanup from glass is difficult. The bucket should be large enough so that it is filled only about 1/3 full. An appropriate amount of curing agent or catalyst is weighed into the bucket and mixed thoroughly with a steel spatula, scraping the sides and bottom of the bucket frequently. The RTV is then transferred into a second bucket and mixed thoroughly. The filler is added and mixed in thoroughly. If the filler is added ahead of the catalyst, satisfactory mixing can not be achieved. The total mass is transferred back to the first bucket for a final, thorough mixing. The bucket of filled RTV is then placed into a vacuum chamber for deaeration.

As the pressure in the vacuum chamber is lowered, air bubbles trapped in the RTV expand, and the mass expands toward the top of the bucket. To break the bubbles, the pressure is raised, then lowered several times. If the filler has not previously been degassed, it is difficult to keep the mass from bubbling out of the bucket. Final absolute pressure of about 20 mm Hg is usually satisfactory when held about 20 minutes. If lower pressures are used, volatile components of the RTV are boiled out of the mass.

With a minimum of stirring, the deaerated mass is poured into the sample mold. The mold consists of two acrylic plastic sheets separated at the edge by four acrylic spacers and held together by "C" clamps to enclose a 10" x 10" x 0.5" sample slab. For very viscous silicone, such as RTV 30, the mold is pre-assembled with two spacers clamped to adjacent edges of each side. The mass is then poured onto the center of the bottom side and spread out with a spatula with as little stirring as possible. Recently entrapped air bubbles will slowly rise to the top where they must be manually broken. When bubbles are no longer apparent, the top side (with two spacers) is added to the mold, mashing the silicone mix flat, so that it fills out the mold and the excess is squeezed out through a partially open edge. The two sides are then clamped together. When the cure is completed, the mold is disassembled and the sample slab is peeled from the mold. For non-viscous silicone such as RTV 602, the mold is completely assembled and stood on edge; the sample is then poured in through the partially open upper edge. Although the RTV 600 series can be quickly cured by heat, it is better to use more catalyst and wait longer for the cure rather than distort the acrylic mold by heating. The sample slabs are tested just as they come from the mold without additional conditioning.

The appropriate amount of catalyst is difficult to define because the filler appears to contribute some catalytic effect, particularly when the filler is a fine powder. This is complicated by an immediate thickening or stiffening of the RTV as a fine powder is mixed in, in contrast to the catalytic effect which begins to be felt in about half an hour. This can be serious with a very viscous silicone, such as RTV 30. The safest approach is to always use the minimum catalyst recommended by the manufacturer. This has the disadvantage that complete curing may take 24 or more hours and delay testing. An alternate

approach is to advance mix several small batches with various amounts of catalyst and to select the final formulation which has the most appropriate final working consistency.

A very non-viscous silicone such as RTV 602, tends to allow the filler to settle out before being thickened by curing. For this situation, the maximum recommended catalyst should be used.

B. Data Analysis

Thermal conductivity is calculated from

$$k = \frac{(q/A)}{(\Delta t/L)}$$

where q is the heat flowing through the cross sectional area, A, and Δt is the corresponding temperature difference across a thickness of material, L.

Because of the symmetry in the sample loading, half of the heat generated by the central heater of the hot plate passes through each sample slab. Of the total electrical energy dissipated by the central heater, only that portion generated in the central six inch diameter of the hot plate is of interest. The fraction of electrical energy of interest is therefore,

$$F_c = \frac{\text{Resistance of heating wire in central 6" diameter}}{\text{Total resistance of central heater}}$$

$$F_c = \frac{28 \text{ ohm}}{48 \text{ ohm}} = 0.583$$

Since the power to the central heater is not supplied continuously, the effective power used is a fraction of the total power level corresponding to the fraction of time that the power is on,

$$F_t = \frac{\text{Total time - time off}}{\text{Total Time}}$$

typically F_t = (1000 sec-520 sec)/1000 sec = 0.480. The heat through the central area of one slab is typically

$$q = \frac{285 \text{ watts}}{2 \text{ directions}} \times \frac{28 \text{ ohm}}{48 \text{ ohm}} \times 0.480 \times \frac{\text{BTU/hr}}{0.293 \text{ watts}} = 136 \frac{\text{BTU}}{\text{hr}}$$

The effective area in the central 6" diameter of the hot plate is given by

$$A = \pi a^2 \left[1 + \frac{1}{12}\left(\frac{b}{a}\right)^2\right]$$

where b is the spacing of the heating wire windings (1/11 inch) and a is the radius to the tap of the central section (3 inch).

$$A = \pi 3^2[1 + \frac{1}{12}(\frac{1/11}{3})^2] = 28.3 \text{ in}^2 = 0.1965 \text{ ft}^2$$

The temperature difference from hot plate to cooling plate (400°F-100°F = 300°F) corresponds to 9.112 millivolts, from thermocouple tables. The temperature span is proportioned according to the potential difference of the thermocouples on opposite sides of the sample slab, typically 5.45 mv, as

$$\Delta t = 5.45 \text{ mv} \times \frac{300°F}{9.112 \text{ mv}} = 179.3°F$$

Although the sample thickness, L, is nominally one half inch because of the spacers between the mold sides, this is not exact or reproducible and should be checked for each sample. A micrometer is used to measure the sample thickness at eight points and an average is used. Typically L = 0.470 inch.

A typical thermal conductivity can now be calculated as

$$k = \frac{(q/A)}{(\Delta t/L)} = \frac{136/0.1965}{179.3/0.470} = \frac{1.82 \text{ BTU-inch}}{\text{hr-ft}^2\text{-°F}}$$

RMS Error

The wattmeter has 0.5% accuracy, but fluctuations in power level occur due to fluctuations in line voltage at about 3 watts out of 300 watts, or a total possible error of 1.5%.

Error in F_c is possible because resistance was measured to only two figures. If the resistance ratio should have been 29 ohm/47 ohm = 0.617 instead of 28 ohm/48 ohm = 0.583, the error would be (0.617-0.583)/0.583 x 100% = 5.8%. If the resistances were measured to a fraction of an ohm instead of one ohm, this error would practically vanish. It should be noted that although this is a random error in the determination of absolute thermal conductivity values, comparisons among k values will not be affected by this error since each k will be biased in the same direction and by the same amount.

The "time off" value might be in error by twice the time increment per cycle, about 4 sec out of 500 sec or 0.8%.

The radius of the central 6" diameter area of the central heater might be in error by 1/64 inch in 3 inch, or 0.5%, giving an area error of about 1%.

Possible error in the millivolt recorder is about one half a chart unit, 0.05 mv out of 5.45 mv, or 1%.

Although the sample thickness, L, is measured by micrometer to 0.001", the sample is elastic and might be squeezed up by 0.01" out of 0.5", or 2%.

The RMS error is the squre root of the sums of the squares of these errors,

$$(1.5^2 + 5.8^2 + 0.8^2 + 1.0^2 + 1.0^2 + 2.0^2)^{0.5} = 6.5\%$$

IV. RESULTS AND DISCUSSION

The results of the thermal conductivity testing in accordance with ASTM C177 are summarized below.

RTV		Filler		Thermal Conductivity BTU-inch/hr-ft^2-°F	
Type	Grams	Type	Grams	Replicates	Average
30	1400	none	-	1.75, 1.91 1.82, 1.85	1.8 (2.2)*
		fine	236	1.19, 1.49	1.3
		fine	336	2.10, 1.76	1.9
		80/200	336	1.47, 1.55	1.5
		60	336	1.48, 1.43	1.5
		8/14	336	1.43, 1.57	1.5
		8/14	500	1.94, 1.48	1.7
30	1400	Magnesia	236	2.38, 2.48 2.30, 2.45	2.4
602	1000	none	-	1.00, 1.07	1.0 (1.2)*
	900	fine	900	3.00, 2.24, 2.00, 1.85	2.0

Material Identification

Fine is Baker reagent aluminum oxide powder (27% through 200 mesh).
80/200 is Alcoa F-20 activated alumina through 80 mesh on 200 mesh.
60 is Norton Alumina RR (alundum) through 60 mesh, 99.8% on 200 mesh.
8/14 is Alcoa F-1 activated alumina through 8 mesh on 14 mesh.
Magnesia is Curtin USP magnesium oxide, heavy powder (95.4% through 200 mesh).
RTV-30 is a General Electric dimethyl silicone catalyzed with dibutyl tin dilaurate.
RTV-602 is a General Electric dimethyl silicone catalyzed with SRC-05.

Duplicate sample slabs were run at the same time, so the thermal conductivity (k) values occur in pairs, and in addition, some repeat runs were made. For the unfilled RTV 30, the second pair

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* Value in parenthesis from manufacturer's literature.

of k values were obtained several days after the first pair, with other runs made in between. For the magnesia filled RTV 30, the second pair of k values were obtained from a run immediately after the first pair, with only the top sample slab rotated 90° from its position during the first run. For the fine alumina filled RTV 602, the second pair of k values were obtained during the next run after the first pair, but the upper and lower sample slabs were reversed in position between runs.

The data indicate that the equipment is capable of reproducibility to about 5% on homogeneous samples. Absolute values of k appear to be consistently nearly 20% lower than the manufacturer's reported value. In addition, it appears possible to have data discrepancies of 50% because of non-homogeneous sample slabs. However, regardless of its shortcomings, the data validly indicate trends and some interesting conclusions are drawn in the next section.

The most promising formulation, 1400 gm RTV 30 with 236 gm magnesium oxide powder, was selected by the MSC Task Manager on the basis of the ASTM C177 thermal conductivity testing. The following additional testing for this formulation was performed on samples as taken from the mold without preconditioning.

ASTM D635-Flammability

Ten strips cut from a 1/8" thick sheet were all found to be self extinguishing by this test. Burning continued less than a minute after the ignition flame was withdrawn and was limited to the region which was substantially heated by the ignition flame. Extent of burning was 1/2" to 5/8" from the ignited end, and the material could not be re-ignited after burning ceased.

ASTM D638 - Tensile

Tensile strength of the most promising formulation was found to be 395.61 psi on a test piece cut from a 1/8" sheet. For unfilled RTV 30, the manufacturer reports 750 psi.

ASTM D257-DC Resistance

Volume resistivity was found to be 1.8×10^{14} ohm-cm for a 1/8" thick sheet of the most promising formulation. The manufacturer reports 2.9×10^{15} ohm-cm for unfilled RTV 30, and resistivity of magnesium oxide is reported as 1.05×10^{4} ohm-cm.

ASTM D695 - Compressive

Compressive strength of the most promising formulation was found to be 108.75 psi on a one inch thick test piece.

V. CONCLUSIONS AND RECOMMENDATIONS

1. Magnesium oxide is significantly better than aluminum oxide as a filler for enhancing thermal conductivity of RTV.
2. The crystalline structure of the filler seems to have little effect on the thermal conductivity as indicated by the similar results using porous activated alumina and using fused alundum.
3. RTV must be filled until the maximum allowable working viscosity is reached before significant enhancement of thermal conductivity results.
4. Use of fine particles of filler result in better thermal conductivity than does the use of coarse particles for the case of filling to equal final viscosities.
5. Use of fine particles of filler is also to be preferred because of more uniform dispersion and a resulting more homogeneous sample slab.
6. Although techniques of filling, mixing, casting, etc., have been successfully worked out, the results have not been particularly encouraging. The greatest enhancement found was for 50% RTV-602 (k=1.) + 50% fine aluminum oxide (k=30.) to give a slab with k = 2. BTU-inch/hr-ft^2-°F.

It is expected that the use of beryllium oxide as a filler (k = 104.) would result in significant improvement over the use of aluminum oxide (k = 30.) or magnesium oxide (k = 40.). However, all beryllium compounds are toxic and death may result from very short exposures to incredibly low concentrations. Maximum allowable concentration in air is 2 micrograms per cubic meter. Goggles, gloves, respirator, constant medical supervision, etc., are necessary, and dry box operations are very desirable. It is therefore recommended that beryllium oxide not be investigated as a filler.

As a logical extension of the present work, it is recommended that a very non-viscous silicone such as RTV 602 be tested when filled to a maximum workable viscosity with the finest particle size available of magnesium oxide.

Study of the thermal conductivities of the oxides and periodic arrangement of the elements Be, Mg, and Al leads to the conclusion that an oxide of boron, specifically B_2O_3 (boric anhydride) would be a better filler than aluminum or magnesium oxides. It is therefore recommended that this be investigated. Since boric anhydride hydrolyzes to form boric acid (expected to be too electrically conductive), it should be stored and used in a dry atmosphere and periodically heated above 185°C to dehydrate any acid which is accidently formed. Dessicator storage and a normal air conditioned laboratory should be sufficient precautions.

Although several of General Electric's more favorable RTV's have k = 2.2, and Dow Corning's best 340 heat-sink compound has k = 2.8, higher valued RTV is available. One of these is Emerson & Cuming, Inc. (Canton, Massachusetts) Eccosil 4852 with k = 8.0 BTU-inch/hr-ft^2-°F. This is a high viscosity liquid with volume resistivity of 10^{14} ohm-cm. It is recommended that the Eccosil, and other such high thermal conductivity silicones, be tested with and without fillers.

It is recommended that a fundamental study be made of how the structure and composition of silicones contributes to the thermal conductivity in order to guide the synthesis of new and improved silicones.

For some silicones, a diluent is available to reduce the viscosity. Since the lower viscosity RTV's can be filled to a greater degree, it is recommended that the use of diluents, and their effect on thermal conductivity, be explored.