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Final Report

ORGANOMETALLIC MATERIALS FOR SPACECRAFT USE

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I INTRODUCTION

Almost all polymeric materials possess low thermal conductivity and high electrical resistivity. While this combination of properties is acceptable for most uses, it is not satisfactory in certain specialized applications. One important area of the latter is where the polymer is used as a potting compound for electronic components. For these applications it would be extremely important to develop materials having a high electrical resistivity and a high thermal conductivity. Metal fillers have been used for this purpose but provide undesirable electrical conductivity. An alternative approach that might yield the desired material is to utilize organometallic compounds as additives to certain polymer formulations.

The primary objective of this project, undertaken by Stanford Research Institute for NASA's Goddard Space Flight Center, was to evaluate the feasibility of using organometallic compounds as additives to polymeric materials for such applications.

A second objective has been a more general understanding of thermal conductivity in polymer materials.

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II SUMMARY

A literature survey of thermal conductivity data of organometallic compounds using a year by year search in chemical abstracts from 1907 to current 1965 issues was conducted. No such data were found.

Thermal conductivities of a number of organometallic compounds were then measured. Results of these measurements showed that simple organometallic compounds have thermal conductivities typical of organic compounds, i.e., in the neighborhood of 10^{-4} cal-cm/sec-cm^2-°C.

Preliminary data were obtained on the effect of filling a typical epoxy adhesive with aluminum metal. It was found that an excessive amount of powdered metal would have to be used in order to achieve a significant increase in thermal conductivity.

Various approaches for increasing thermal conductivity without decreasing electrical resistivity were evaluated. From this evaluation the concept evolved that a polymeric structure containing heavy atoms in the backbone and having structural continuity might satisfy the objectives of this study.

An outline of a recommended experimental program is presented.

Author

III RESULTS AND DISCUSSION

The initial phase of this research project consisted of a survey of the literature with the objective of tabulating all available data on thermal conductivities of organometallic compounds. This tabulation was expected to provide data for correlating the structure of organometallic compounds with their thermal conductivity. The data would then be used as a basis for selecting and/or synthesizing materials as additives for typical potting compounds and adhesives presently used in unmanned spacecraft.

The literature review consisted of a thorough search of chemical abstracts from 1945 to current issues and a less detailed review of the 1907 to 1945 issues. In the 1945-1965 search all available cited literature which had some probability of containing the desired thermal conductivity values of organometallic compounds was consulted and scanned for additional references. Both Stanford University and Stanford Research Institute libraries were used. In addition to this work, a bibliography concerned with thermal conductivity of organic polymers compiled by D. R. Anderson and J. M. Holovka at the Sandia Corporation covering the period from 1941 through 1963 was studied.

The literature search failed to uncover any data on the thermal conductivity of organometallic compounds. It is of course possible that there may be isolated reports of such values. However, the difficult and time-consuming task of retrieving these was considered neither justified nor desirable. Instead, it appeared more appropriate to set up a thermal conductivity apparatus for measurements on representative organometallic compounds.

An adaption of the commercially available Cenco-Fitch apparatus was available at the Institute and was used during the initial phase of this program. It consists essentially of two parts: the "source" designed to hold a refluxing liquid and a "sink" or the receptacle containing a heat-insulated copper plug. The specimen is placed between the source and the sink and the differential temperature between the source and sink is then measured at regular intervals. The slope of the curve obtained by plotting time against differential e.m.f. gives a measure of thermal conductivity.

After some initial experimentation, it was decided to modify the usual experimental procedure and to start with the source and sink at the same temperature. Heat was then slowly applied to the source and the temperature change of the source and receiver plotted as a function of time on an X_1-X_2 recorder. The thermal conductivity K of the material was then calculated from the slope of a plot of T_2-T_O/T_1-T_2 <u>vs</u> Δt using the following equation

$$\frac{T_2-T_O}{T_1-T_2} = \frac{KA}{XcM}\Delta t \qquad (1)$$

where

T_O = starting temperature
T_1 = temperature of source
T_2 = temperature of sink
K = thermal conductivity
A = area of sink
c = specific heat of sink
M = mass of sink
X = thickness of specimen
Δt = elapsed time

The derivation of this equation is given in Appendix A.

A typical X_1-X_2 trace is shown in Fig. 1 and the necessary calculations are given in Table I. Figure 2 shows the plot from which the thermal conductivity is calculated.

Table I

DATA AND CALCULATIONS FOR A TYPICAL THERMAL CONDUCTIVITY MEASUREMENT

Δt	E_2	T_2	E_1	T_1	$T_1 - T_2$	$T_2 - T_0$	$\frac{T_2 - T_0}{T_1 - T_2}$
0	1.115	28.098					
5	1.150	28.95	1.430	35.69	6.74	0.85	.126
10	1.255	31.48	1.830	45.26	13.78	3.47	.252
15	1.430	35.69	2.210	54.07	18.38	7.68	.421
20	1.645	40.83	2.555	62.00	21.17	12.82	.605
25	1.875	46.26	2.870	69.14	22.88	18.25	.799
30	2.110	51.74	2.145	75.29	23.55	23.73	1.008
35	2.335	56.98	3.380	80.51	23.53	28.97	1.230
40	2.545	61.77	2.595	85.24	23.47	33.76	1.439
45	2.740	66.20	3.770	89.07	22.87	38.19	1.670
50	2.910	70.04	3.945	92.85	22.81	42.05	1.842
55	3.075	73.73	4.100	96.81	23.08	45.72	1.984

The advantage of this method is that measurement is begun with all components at room temperature which allows sufficient time to properly adjust the fit between the sample and the faces of the heat source and sink. Furthermore, this procedure allows the measurement of both high and low thermal conductivities by adjustment of the rate of heating.

In subsequent work, the initial apparatus was found to be inadequate, primarily because of poor fit between the faces of the source and sink, inadequate insulation, and poor design geometry. All of these factors contributed to irreproducibility of the measurements and to an uncertainty of the values obtained.

A new apparatus was therefore constructed where an attempt has been made to eliminate these difficulties. Figures 3, 4, 5, and 6 show the construction of this apparatus. A detailed description is given in the experimental section.

Thermal conductivities of various selected compounds and polymers measured during this study are shown in Table II. The data indicate strongly that non-associated organometallic compounds have thermal conductivities falling within the range typical of other non-associated organic compounds, i.e., close to 10^{-4} cal-cm/sec-cm^2-°C. This result is not unexpected since high thermal conductivity must result from an efficient means of transmitting a disturbance from one site in the material to another one far removed. Furthermore, in solid materials having small discrete molecules, a thermal disturbance must be transmitted from molecule to molecule through the peripheries of filled electron shells. Since the forces between such molecules are the very weak van der Waals attractions, any one particular molecule will be relatively insensitive to thermal disturbance of its neighbors and thermal conductivity of the bulk material will be low. This will be the case whether the material is wholly organic, wholly inorganic, or organometallic.

Table II

THERMAL CONDUCTIVITIES OF VARIOUS SELECTED COMPOUNDS

Compounds	Thermal Conductivity (cal-cm/sec-cm^2-°C)
Sodium chloride	1.7×10^{-2}
Sodium formate	1.0×10^{-3}
Sodium acetate	5.7×10^{-4}
Sodium sulfate	6.8×10^{-4}
Sodium lauryl sulfate	4.5×10^{-4}
Mercury acetate	2.2×10^{-4}
Mercury acetylacetonate	4.0×10^{-4}
Mercury diphenyl	3.4×10^{-4}
Copper formate	9.6×10^{-4}
Copper acetylacetonate	2.0×10^{-4}
Copper-8-quinolinolate	3.3×10^{-4}
Potassium biphthalate	3.5×10^{-4}
Teflon	6.0×10^{-4}
Mylar	1.2×10^{-4}
Polystyrene	3.7×10^{-4}
Epon 828	3.4×10^{-4}

The physical incorporation of powdered or bulk metal into such high insulators would, for the same reason, be expected to contribute little towards significantly increasing the thermal conductivity. Thus, even though the thermal conductivity of each individual piece of metal is high, each piece is, in effect, insulated from all other pieces and there is no structural continuity. Data shown in Table III obtained by filling Epon 828 with various amounts of powdered aluminum corroborate this concept. Similar data were also obtained by Hirsch and Koved[1].

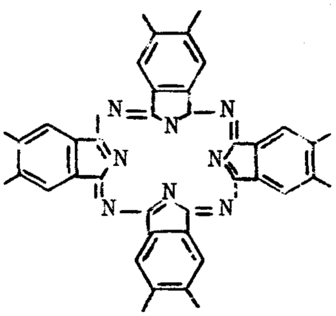
Table III

THERMAL CONDUCTIVITY OF EPON 828 FILLED WITH VARIOUS AMOUNTS OF POWDERED ALUMINUM

Epon 828-Al (1:1)	5.7×10^{-4}
Epon 828-Al (1:2.5)	1.9×10^{-3}
Epon 828-Al (1:3.2)	2.3×10^{-3}

The high thermal conductivity of metals arises very largely from motions of valence electrons which are not bound to any particular atom or small group of atoms, but instead are delocalized over a very large number. However, delocalization of this sort leads also to a high electrical conductivity which, for the present purpose, is undesirable.

Were this not the case, an obvious suggestion would be to utilize polymer systems which have long systems of conjugated double bonds. Two examples where thermal conductivity values are available are pyrolyzed pyromellitonitrile-methanol and pyromellitonitrile-hydrogen sulfide systems. Proposed structures for these systems are as follows[2]:



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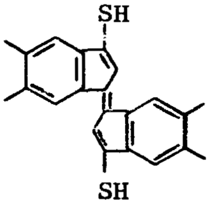


II

The reported[3] thermal conductivities are 1.2 to 7.5×10^{-2} for I and 7.1×10^{-3} for II. However, since these materials are noncrystalline, infusible, and insoluble, a direct structure proof is impossible, and relatively little importance should be attached to these values beyond their showing that an increase in thermal conductivity is very likely due to a delocalized π-electron system. These materials also show the expected decrease in electrical resistivity; depending on the method of preparation, values between 6.9×10^{-1} and 2.8×10^{-3} ohm-cm have been obtained for I and 8.0 x 10^{-3} ohms-cm has been observed for II.[2] The physical properties of these materials would of course make them totally unsuitable for any practical application.

In view of these data it is obvious that thermal conductivity cannot be increased by means of delocalized valence or π-electrons without an attendant rise in electrical conductivity. It might, however, be possible to increase only thermal conductivity by increasing the degree of structural continuity without delocalizing valence or π-electrons. For example, a single crystal of sodium chloride, in which each ion is strongly bound electrostatically to somewhat less than six nearest neighbors of opposite charge (exactly six in a perfect crystal), exhibits a thermal conductivity approximately 100 times as great as that of a variety of salts examined as compressed powders (see Table II).

In a similar manner, the thermal conductivity of a polymer should improve by increasing the degree of structural continuity. In this manner, a large number of atoms at or near the source of the thermal disturbance become linked by a continuous sequence of covalent bonds to atoms at the edge of the material.

Structural continuity in a polymer can be achieved in two different ways. One is by crosslinking the polymer, where essentially the whole polymer mass becomes one molecule. The other is by achieving a high degree of crystallinity in the polymer; the crystallites then provide structural continuity in much the same way as in a sodium chloride crystal although, of course, to a much lesser degree.

Although thermal conductivity data for a considerable number of polymers have been reported, surprisingly little has been said about the relationship of thermal conductivity and various molecular parameters such as molecular weight, crystallinity, degree of orientation, crosslinking, etc.

Data by Hansen and Ho[4] have shown an increase in the thermal conductivity of polyethylene with increasing molecular weight. Thus, the thermal conductivity for a 10,000 molecular weight polymer was 4 x 10^{-4} while that for a 160,000 molecular weight polymer was found to be 6 x 10^{-4}.

However, no further increase at higher molecular weights was found. These same workers also found an increase in thermal conductivity with increasing crystallinity.

Additional preliminary data on the effect of crystallinity on thermal conductivity have also been obtained during this study. A comparison of amorphous and crystalline polyethylene yielded values of 3.6×10^{-4} and 5.3×10^{-4}, respectively, showing that crystalline polymers do, indeed, show a slight improvement in thermal conductivity.

It appears likely that after a high degree of structural continuity has been achieved by either crosslinking the material or improving its crystallinity or both, further increases in thermal conductivity could be realized by incorporating metal atoms into the polymer structure. This improvement would result only from the large concentration of electrons at the metal atoms (i.e., from their high atomic number) and should not be confused with the thermal conductivities of metals in the elemental state which results from the freedom of their valence electrons. Similar improvements should likewise result from incorporation of such heavy nonmetals as arsenic, selenium, and tellurium.

It is very likely that such heavy atoms must be incorporated into the backbone of the continuous chains rather than the short side-chain. If this is not done, any advantage resulting from the metal atom will be nullified by the discontinuity at the end of the side-chain. This concept is corroborated by data presented in Table IV, which gives our measurements of thermal conductivity of poly(acrylic acid) and some of its salts.

Table IV

THERMAL CONDUCTIVITY OF POLY(ACRYLIC ACID) AND SOME OF ITS SALTS

Salt	Thermal Conductivity (cal-cm/sec-cm^2-°C)
H	4.0×10^{-4}
Na	1.8×10^{-4}
Cu	3.0×10^{-4}
Hg	1.2×10^{-4}

Polymers containing metal atoms in the backbone have been described in the literature[5], but are not very easily prepared and characterized. Thus, despite the desirability of measuring their thermal conductivity values, they could not be included in this brief study.

IV EXPERIMENTAL

Apparatus

The apparatus constructed during this study consists of a well-insulated heat source (Figs. 3 and 4) and a heat sink (Fig. 5). An over-all view of the apparatus is shown in Fig. 6.

The heat source is a copper block 2 inches in diameter and 1 inch thick containing a protrusion, 0.5 inch thick and 1 inch in diameter on top. The sample to be measured contacts this protrusion. An exploded view is shown in Fig. 3 and a top view in Fig. 4. The mass of this block is 940 grams. Insulation is provided by marinite rings. The block is heated by means of a 200 watt heater which fits into a cavity machined into the copper block. A thermocouple fits into a well located near the upper surface of this block.

The heat sink (Fig. 5) is an insulated 40.2-gram copper block, 3/4 inch in diameter and 5/8 inch thick containing a thermocouple near its lower surface. The block with its marinite insulation is bonded to a Lucite block fastened to a rod which can slide within a vacuum-tight seal. The whole unit is very carefully aligned so that the precision-machined surfaces of the source and sink meet with no gaps.

Both the source and heat units are placed within a Pyrex pipe, 6 inches wide and 12 inches tall. The ends of the Pyrex pipe contain a groove for a rubber O-ring which with the Plexiglass end-pieces provides a vacuum-tight seal.

The temperature of the source is controlled by means of an auto-transformer, although provisions for automatic temperature programming were also made by placing an additional thermocouple close to the heater.

Thermocouple outputs were recorded on a Leeds and Northrup 69955 Speedomax G X_1-X_2 Recorder. Both functions were equipped with continuously adjustable azar units.

Procedure

Approximately 1 to 2 grams of the material were compressed in a die using a hydraulic press at a pressure of up to 20 tons. The usual sample size was 1-1/2 inches in diameter by 0.1 to 0.5 inch.

The pellet was then placed on the source and the sink brought in contact with the sample. A 1.5 Kg lead weight placed on the sink shaft assured good contact.

The apparatus was then evacuated to approximately 2 mm/Hg and current supplied to the heater to produce a temperature rise of approximately 2° C/minute.

V RECOMMENDATION FOR FUTURE STUDY

In order to be useful for their intended application, the polymers must fulfill the following requirements:

(1) They must be thermally conductive, but retain high electrical resistivity.

(2) They must have physical properties which make them suitable for potting and adhesive applications.

While these requirements are obviously difficult to meet, they are not, at the present time, considered to be impossible. Based on the findings of the initial study, we suggest that an approach embracing the synthesis of polymers containing heavy atoms in the backbone and in which a high degree of structural continuity is provided represents a feasible approach.

Since many organometallic polymers contain a large percentage of organic moieties, the choice of suitable structural features might yield materials having useful physical properties.

It is, therefore, suggested that significant progress in the present problem could be realized by one year's further work. This period of investigation would be provisionally divided into three phases.

Phase I - Apparatus and Technique of Measurement

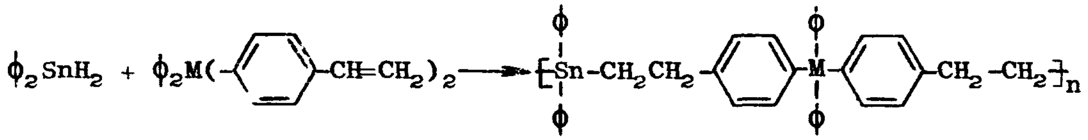
Since it is very likely that the early attempts to improve the thermal conductivity of polymers will involve relatively small changes, it is imperative that the measurement of thermal conductivity be highly reproducible, and that, in particular, there be no ambiguity concerning the direction of change when a preparative modification is introduced.

The present apparatus and techniques were satisfactory for the initial research effort where approximate values were acceptable. However, if thermal conductivity measurements are to be an important guideline to a sizable research effort, the technique and apparatus used for such measurements must be refined. It is estimated that this phase might require up to three months effort.

Phase II - Preparation of Organometallic Polymers

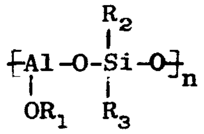
Although no polymers in this class appear to be commercially available, a number of synthetic methods are available in the literature and could presumably be duplicated.

The following type-polymer would be an extremely interesting candidate for initial evaluation.



where M = Ge, Sn, Pb.

Another interesting candidate would be the aluminosiloxanes



$$\left[\underset{OR_1}{\underset{|}{Al}}-O-\overset{R_2}{\overset{|}{\underset{R_3}{\underset{|}{Si}}}}-O\right]_n$$

Phase III

After Phase I has been completed and adequately characterized materials from Phase II become available, a study of the thermal conductivity of these novel materials would be initiated. Concurrently with thermal conductivity studies, evaluations of physical properties would also be carried out.

Based on these findings, modifications in both starting materials and synthetic conditions would be carried out in attempts to achieve the desired combination of properties. In particular, the concept of the importance of structural continuity would be tested by preparing materials with the maximum degree of crosslinking consistent with obtaining nonbrittle materials. Also, catalysts and reaction conditions would be chosen so that stereoregularity of the resulting polymer would be maximized wherever possible in attempts to induce crystallization.

ACKNOWLEDGEMENT

Significant contributions to this research effort were made by Mr. F. J. Martinelli who designed the thermal conductivity apparatus and evolved the method of data treatment.

Some of the concepts evolved resulted from discussions with Drs. E. S. Gould, P. J. Flory, A. G. Brown, and L. A. Dickinson.

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5. M. C. Henry and W. E Davidson, Ann. New York Acad. Sci., 125, 172 (1965)

APPENDIX A

Derivation of Equation Used in Thermal Conductivity Measurement

Thermal conductivity is defined as the coefficient K in the following equation

$$\vec{q} = - K \vec{\nabla} T \qquad (1)$$

where $\vec{q}$ is the flow of heat through a homogeneous solid and $\vec{\nabla} T$ is the temperature gradient.

In the present case, Eq. (1) reduces to

$$\vec{q} = - K \frac{dT}{dz} \vec{k} \qquad (2)$$

from which the flux of q over the upper surfaces s of the sample is

$$\int\int \vec{q} \cdot \vec{n} \, ds = - K s \frac{dT}{dz} = q \qquad (3)$$

where $\vec{n}$ is the unit normal to the surface and s is its area.

Since Eq. (3) represents the quantity of heat leaving the surface per unit time, then

$$q = K A \frac{dT}{dz} \Delta t \qquad (4)$$

represents the quantity of heat entering the sink, where A is the area of the sink and Δt is the elapsed time.

The quantity of heat entering the sink can also be determined from the following equation:

$$q = cM \Delta T \qquad (5)$$

where M is the mass of the sink, c is its specific heat, and ΔT is the change in temperature during the elapsed time Δt .

Equating (4) and (5)

$$cM \, \Delta T = K \, A \frac{dT}{dz} \, \Delta t \tag{6}$$

Rearranging and integrating

$$cM \, \Delta T \int_{o}^{x} dz = K \, A \, \Delta t \int_{T_2}^{T_1} dT \tag{7}$$

where x is the thickness of the sample

$$cM \, \Delta T \, x = K \, A \, \Delta t \, (T_1 - T_2) \tag{8}$$

thus

$$K = \frac{cMx}{A\Delta t} \left[\frac{\Delta T}{T_1 - T_2} \right] \tag{9}$$

Letting $\Delta T = T_2 - T_o$

where

T_1 = temperature of source
T_2 = temperature of sink
T_o = initial temperature of sink

We find

$$\frac{T_2 - T_o}{T_1 - T_2} = \frac{KA}{XcM} \, \Delta t \tag{10}$$

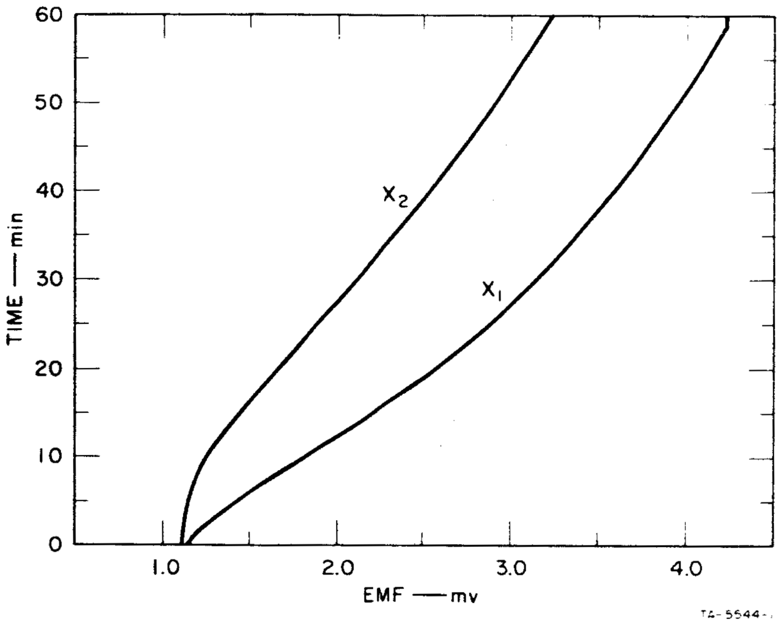

FIG. 1 RECORDER X_1 - X_2 TRACE FOR A TYPICAL THERMAL CONDUCTIVITY MEASUREMENT

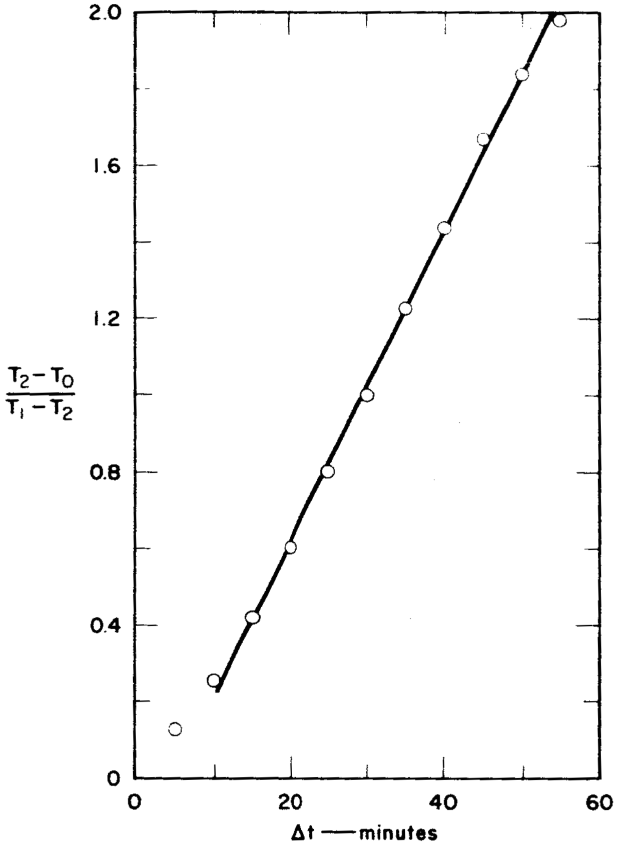

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FIG. 2 PLOT OF $(T_2 - T_0)/(T_1 - T_2)$ vs. Δt

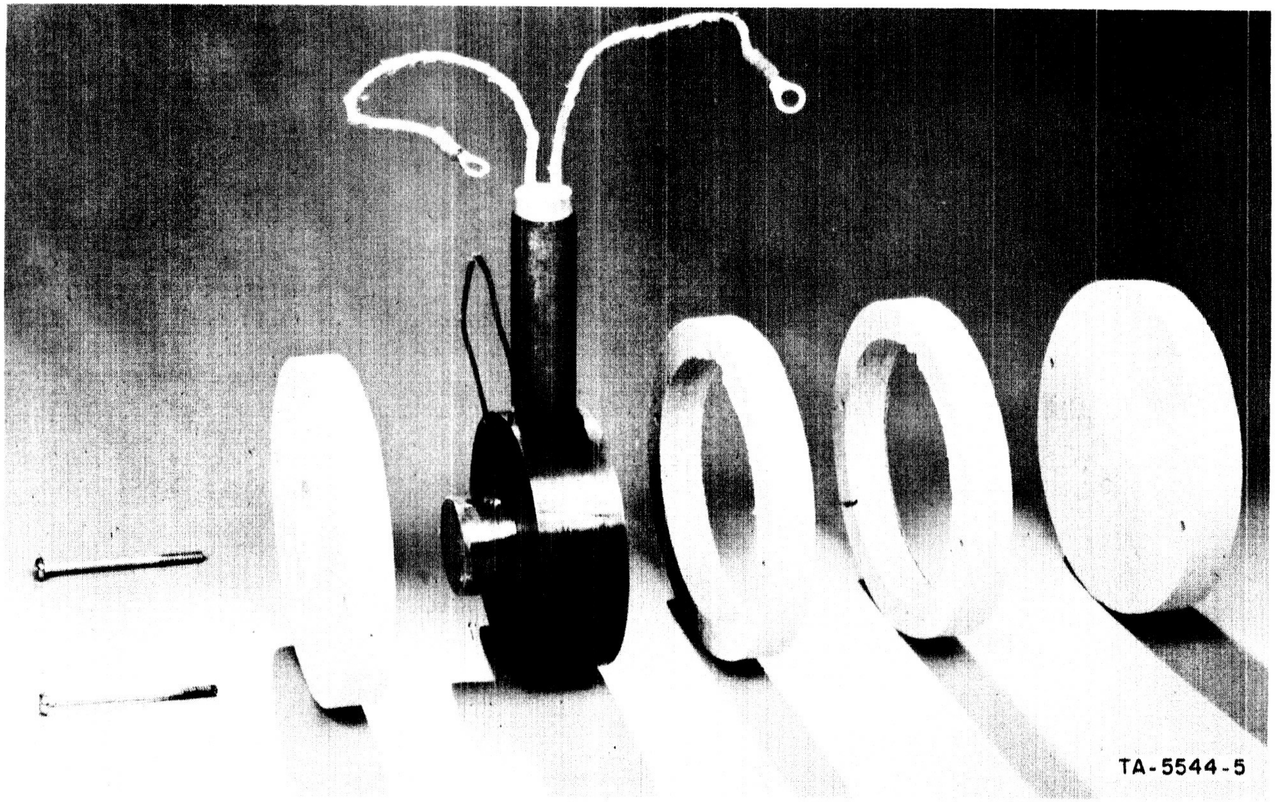

FIG. 3 EXPLODED VIEW OF HEAT SOURCE

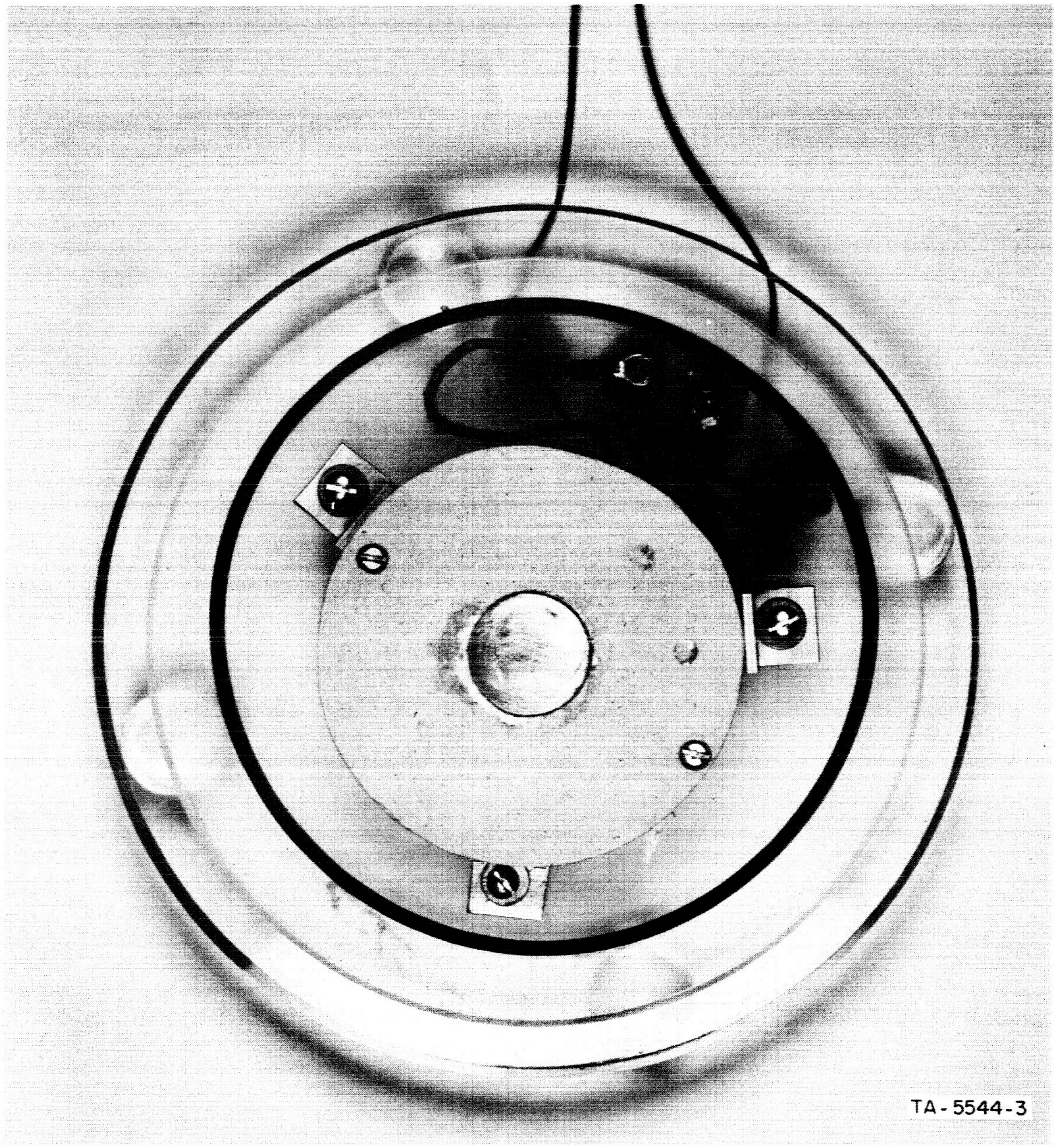

FIG. 4 TOP VIEW OF HEAT SOURCE

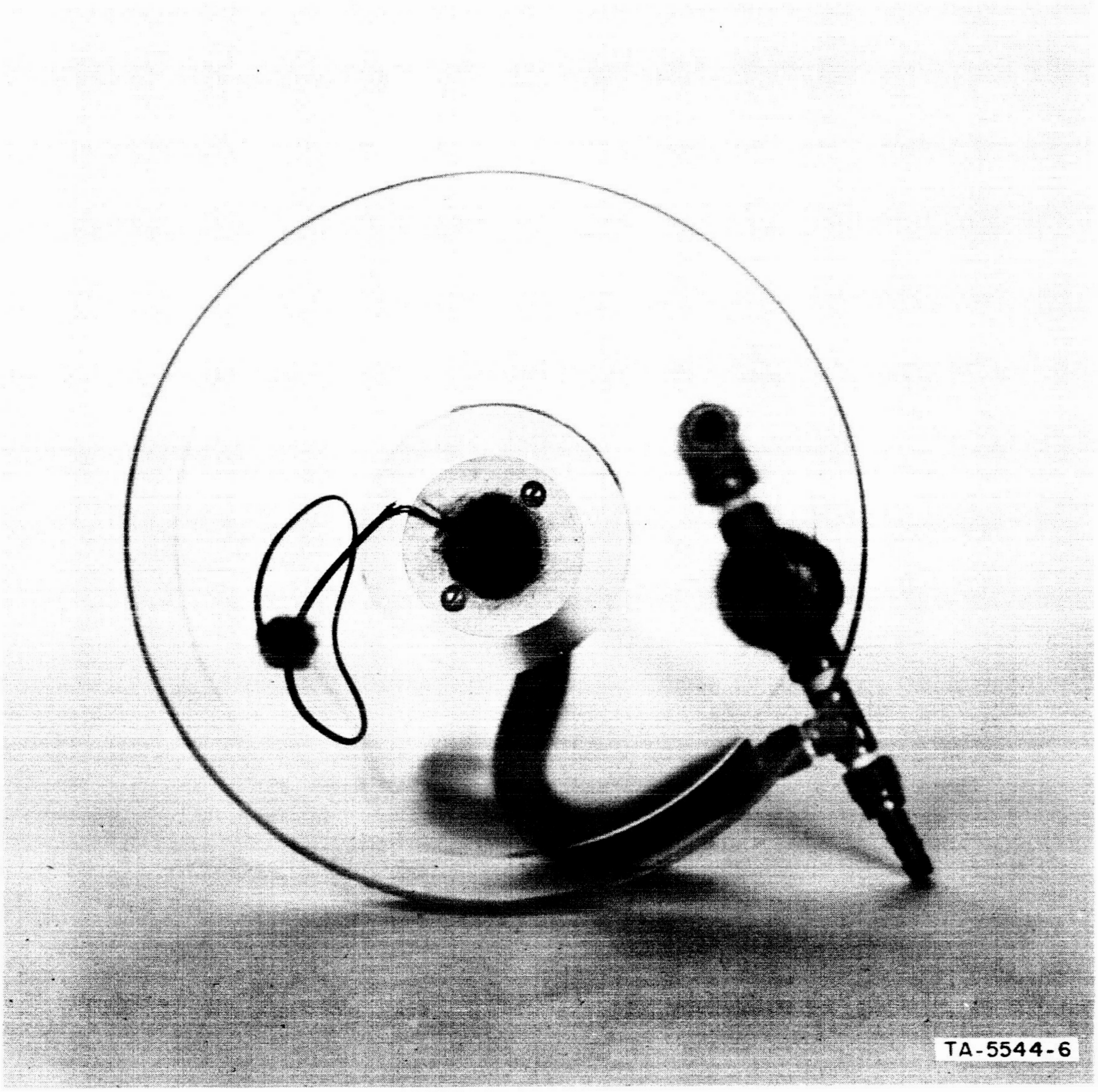

FIG. 5 BOTTOM VIEW OF HEAT SINK

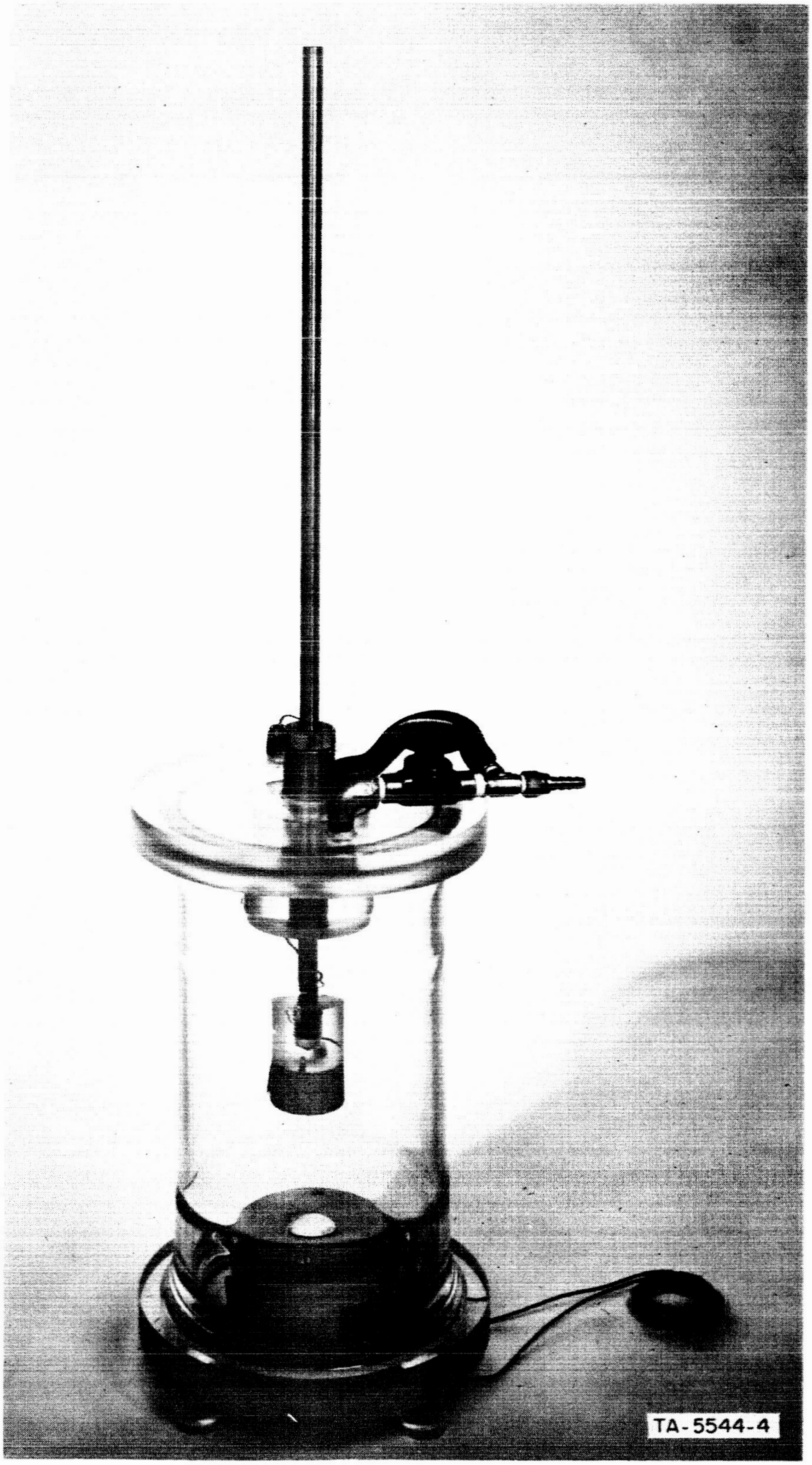

FIG. 6 OVER-ALL VIEW OF THERMAL CONDUCTIVITY APPARATUS

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