



CRYOGENIC CAPACITOR INVESTIGATION

Final Report

By

K.N. Mathes and S.H. Minnich

MAY 1967

Prepared for

ASTRIONICS LABORATORY
GEORGE C. MARSHALL SPACE FLIGHT CENTER
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
HUNTSVILLE, ALABAMA

CONTRACT NAS 8-20617

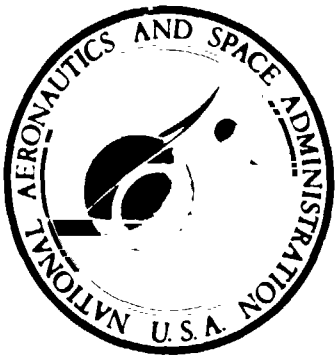
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FOREWORD

The cryogenic capacitor materials investigation described in this report was accomplished under Contract NAS8-20617, Cryogenic Capacitor Investigation. The work was sponsored by the Manufacturing Engineering Laboratory at the George C. Marshall Space Flight Center, Huntsville, Alabama. The program was under the technical direction of Mr. Robert Schwinghamer of NASA/MSFC.

The work was conducted at the General Electric Company's Research and Development Center, Schenectady, New York. Mr. S. H. Minnich was the project engineer and Mr. K. N. Mathes was the chief technical contributor.

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Final Report
CRYOGENIC CAPACITOR INVESTIGATION

NASA Contract NAS8-20617

17 May 1967

INTRODUCTION

Contract NAS 8-20617 was executed on 16 June 1966 to terminate originally on 16 December 1966 but was extended on 16 January 1967 to 17 May 1967. A condensed work statement for the program is given below:

Conduct experimental investigations to determine dielectric properties of promising materials for cryogenic capacitors to be used in energy storage and pulse applications.

Phase I - obtain dielectric data on promising materials including screening tests, tests in liquid nitrogen and techniques for winding or stacking small test capacitors.

Three classes of materials are to be investigated as appropriate:

1. Inorganic bonded ferroelectric materials
2. Anodic coatings on metal foils
3. Polar low temperature liquids

Phase II - Three analytical tasks on the cryogenic capacitor are specified.

1. Interpret data to provide an estimate of the energy storage densities which can be achieved in a cryogenic capacitor.
2. Estimate the feasibility of fabrication methods.
3. Analyze the performance potential of the overall refrigeration and capacitor system.

Technical progress has been described in 9 monthly letter reports. Data from these reports as well as additional sources have been used in this final report. However, only those data have been included which are essential to the overall summary. These data have not necessarily been included in the chronological order in which they were obtained. The experimental techniques and results are described under Phase I and the analytical work in Phase II.

SUMMARY AND CONCLUSIONS

Permittivity and Dielectric Loss

A considerable understanding of the properties of dielectrics at cryogenic temperatures has been developed in this program which provides a reasonable basis for judging their potential usefulness as cryogenic dielectrics in capacitors. Values of permittivity from 20 to as high as 38 have been achieved in ferroelectric powder films impregnated with liquid nitrogen. The permittivity (ϵ') can be increased still further by impregnation with polar liquids such as 1-nitropropane and a number of special silicone fluids. The greatest advantage from such impregnation is achieved when a temperature is selected for which ϵ' is maximum and the dissipation factor ($\tan \delta$) is minimum. In this respect, the silicone liquids are superior. It should be recognized that temperature control may pose difficulties in practical capacitors but the refrigeration costs at the lower temperatures (-105°C for example) will be less than for liquid nitrogen at -196°C . (In this program liquid nitrogen temperature has been assumed for refrigeration calculations).

In general an increase in ϵ' is achieved with an associated undesirable increase in $\tan \delta$ as shown in the tabulation below selected from typical results obtained in this program.

<u>Temp. $^{\circ}\text{C}$</u>	<u>Ferroelectric</u>	<u>Liquid</u>	<u>ϵ'</u>	<u>$\tan \delta$</u>
-196	TiO_2	Nitrogen	18	.0002
-196	SrTiO_3	Nitrogen	28.5	.004
-196	SrTiO_3	XF-1150	34	.0012
-88		+ Isopentane	46	.0025
-35	BeTiO_3	XF-1150	64	.05
-62	SrTiO_3	XF-1125	80	.105

It is apparent that many variables are involved which are not yet understood in a systematic fashion. Many more ferroelectric materials could be considered. It is very likely that, with more study, combinations can be found for which high values of ϵ' can be obtained with lower values of $\tan \delta$ than those which are shown in the tabulation above. Nevertheless, so far as ϵ' and $\tan \delta$ are concerned, the values already attained with ferroelectric powder film could make a significant contribution to capacitor design.

The polar, high permittivity liquids are of interest as impregnants for ferroelectric powder film but have not been as interesting so far as impregnants for ferroelectric powder film. They have not been as interesting so far as impregnants for porous sheet dielectrics such as paper. However, this approach might benefit from greater study particularly in the direction of low density and perhaps synthetic fiber sheet.

The use of anodic coatings at cryogenic temperatures has received only very limited study but to date high values of permittivity have not been achieved. This approach does not appear to be promising.

Voltage Breakdown

The values of voltage breakdown achieved so far in this program have been disappointing. Part of the problem involves the use of single film dielectrics which has been made necessary by mechanical limitations to be described in the next section. In conventional capacitors, multiple layer insulation is used to avoid the registry of the faults found in single layers. Only in capacitors with evaporated metal electrodes can single dielectric films normally be used. The thin metal is sputtered away from areas of failure by the application of voltage with a high resistance in series to limit the current. Evaporated metal electrodes could be used in the cryogenic design but might constitute a limitation in discharge applications.

The impregnation of ferroelectric powder films with liquid nitrogen or with high permittivity liquids appears to involve problems not yet understood. (It has taken 40 years to develop the impregnation techniques used with conventional liquid filled capacitors and even they are not yet perfect). Pressure appears to be useful in achieving improved liquid penetration. Vacuum impregnation may be useful but it may be necessary to impregnate cold so as to avoid the loss of moisture, which appears to be beneficial.

The production of uniform, void and defect-free films may be the most critical factor in the attainment of increased electric strength. Many factors are undoubtedly involved including impurity content but the rheology of the mixture to be coated is probably most important. Many variables appear to affect the

nature of the film including:

- Powder size and nature
- Binder characteristics
- Dispersant and dispersing agents
- Anti-foam agents
- Humectants, flexibilizers. etc.
- Drying characteristics

It is obvious that an optimum combination could hardly have been obtained in this limited program but sufficient success has been achieved so as to produce useful films which can probably be used at DC stresses as high as 1500 volts/mil and perhaps higher. To achieve the necessary continuity of electric strength for large values of capacitance, it will probably be necessary to apply a continuous voltage withstand test to the dielectric film. The higher the voltage, the greater will be the rejection rate in manufacture.

All of the work in this program has been based upon direct voltage test. For a capacitor which must provide an undamped oscillation discharge, some voltage derating is necessary with conventional discharge capacitors and this probably would be true also for a cryogenic capacitor. The amount of derating needed for a cryogenic dielectric in an oscillating discharge application is not known.

Mechanical Characteristics of Dielectric Materials

In order to achieve high values of permittivity in ferroelectric powder films, it is necessary to use very large ratios of powder to binder. Such large ratios also lead to somewhat porous films which can be impregnated with liquid. However, with such a small percentage of binder, it is difficult to obtain good mechanical strengths. In consequence, the aluminum foil has been used to provide the needed mechanical strength and to act as a "carrier" for the insulating film which is coated on it. Obviously, problems develop when a .00025 in aluminum foil is required to "carry" a heavy .002 in. insulating film. It seems unlikely that such a film can be wound with conventional capacitor winding equipment, at least at usual winding speeds.

When the dielectric film is cast directly on the aluminum foil, no dielectric will "protect" the edge of the film unless the insulating film can project beyond the edges (be wider than the foil). So far it has been impossible to make the insulating film wider than the foil.

Without question, a more practical capacitor design could be achieved if satisfactory unsupported, ferroelectric powder films could be made. So far only a parallel glass thread supported free film has been made which approaches this goal. This unsupported film was rough and the value of permittivity (about 15) was too low to be practical for the intended application. However, effort directed to the development of self-supporting film may be the most important step which may need to be taken in the development of a cryogenic capacitor dielectric. The use of two layers of unsupported film will solve many problems. However, the thickness of each layer should probably not exceed about .002" in order that the voltage per "section" will not be too great.

It is possible that the attempts to use water soluble binders may have been in the wrong direction. Possibly, tough thermoplastic resinous binders, consolidated with heat and pressure, might constitute a better approach. If this very different approach is taken, it will be necessary to prevent thin films of clear resin from forming on the surface of the film.

The Overall Material Problem

From the foregoing it is apparent that the electrical objectives for a cryogenic capacitor dielectric have been achieved although improvement is to be desired in electric strength. The mechanical characteristics needed for a practical cryogenic capacitor have not been achieved but approaches to the solution of the problem have been suggested. The mechanical problems should be solved and a suitable unsupported dielectric film should be developed before construction of prototype cryogenic capacitors is attempted. As an alternative, new methods of winding or assembling capacitors might be developed.

In about one year a number of very new and potentially useful concepts for capacitor dielectrics have been developed with relatively little applied time. Conventional capacitors have been under extensive development for over 50 years with very intensive effort in³ great many different areas. It is always difficult for new ideas to compete with long established ones.

Cryogenic Capacitor Design

In the second section of this report are presented estimates of size, weight and losses for cryogenic capacitor systems, using as a basis the dielectric parameters developed during the course of this investigation. These data may be used to form a tentative evaluation of the potential payoff of successful development. In general, the data indicate that relatively compact capacitor systems are possible. This is especially true if the cases where the more optimistic estimates of dielectric capability are used. Refrigeration loads and/or nitrogen consumption are quite reasonable, as well as systems volumes and weights, compared to more conventional approaches.

The peripheral components required to construct a cryogenic capacitor system are well developed and essentially state-of-the-art. The principle unknown is the complexity of the development task to perfect the dielectric system itself. In view of the potential payoff, it appears that continued research in the field of cryogenic dielectrics for energy storage application would be justified.

MEASUREMENT TECHNIQUES

Tests in Liquid Nitrogen

Most of the electrical measurements were made with flat or rolled test specimens immersed in boiling liquid nitrogen at atmospheric pressure. No effort was made to remove the air in the specimen since it was recognized that the air would condense to liquid (the small amounts of liquid oxygen, argon, etc. were not considered to be important). The liquid nitrogen was contained in a small dewar or more usually in a polystyrene foam container. The electrical leads to the test specimen were supported so that frost formation above the liquid level did not influence the measurements.

During the last part of the program it was believed that simple immersion in liquid nitrogen might not be adequate to obtain complete impregnation. Moreover, advantages might be obtained if measurements were made in non-boiling liquid nitrogen under some pressure. For this purpose a small pressure cell was built as shown in Photo 1 and in outline form in Figure 1. In order to achieve pressures of 1000 psi safely with the least expense, the cell was made as small as possible. Unfortunately, it was difficult to obtain a high electric strength with the small electrical bushing. Moreover, the bushing was difficult to seal. While a fair number of tests were made under pressure, a redesign of the pressure cell is needed.

The test specimen was placed within the test cell and the top sealed. The cell was then evacuated with a mechanical pump, flushed with nitrogen, evacuated again and filled with nitrogen under the desired pressure. The cell was then immersed in boiling liquid nitrogen to within about an inch of the top seal so that the gaseous nitrogen under pressure inside the cell would condense. Liquid nitrogen was added until temperature equilibrium was achieved. The pressure applied to the cell was cycled to achieve better impregnation. The pressure was limited to about 250 psi to minimize the leakage problem around the bushing. Voltage breakdown tests in the pressure cell were cumbersome because the evacuation and pressure cycling had to be repeated before each test could be made.

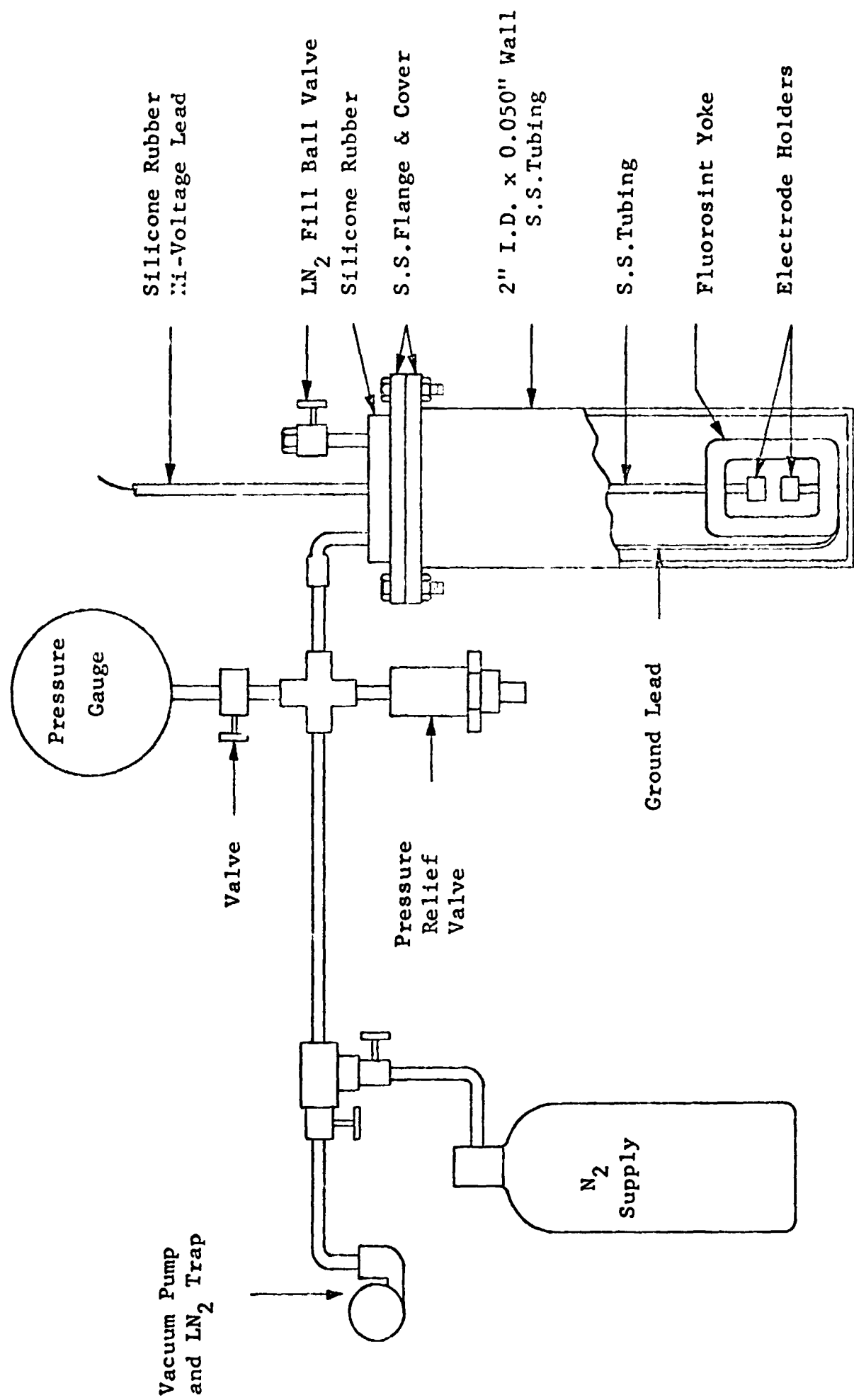


Figure 1. Pressure Cell

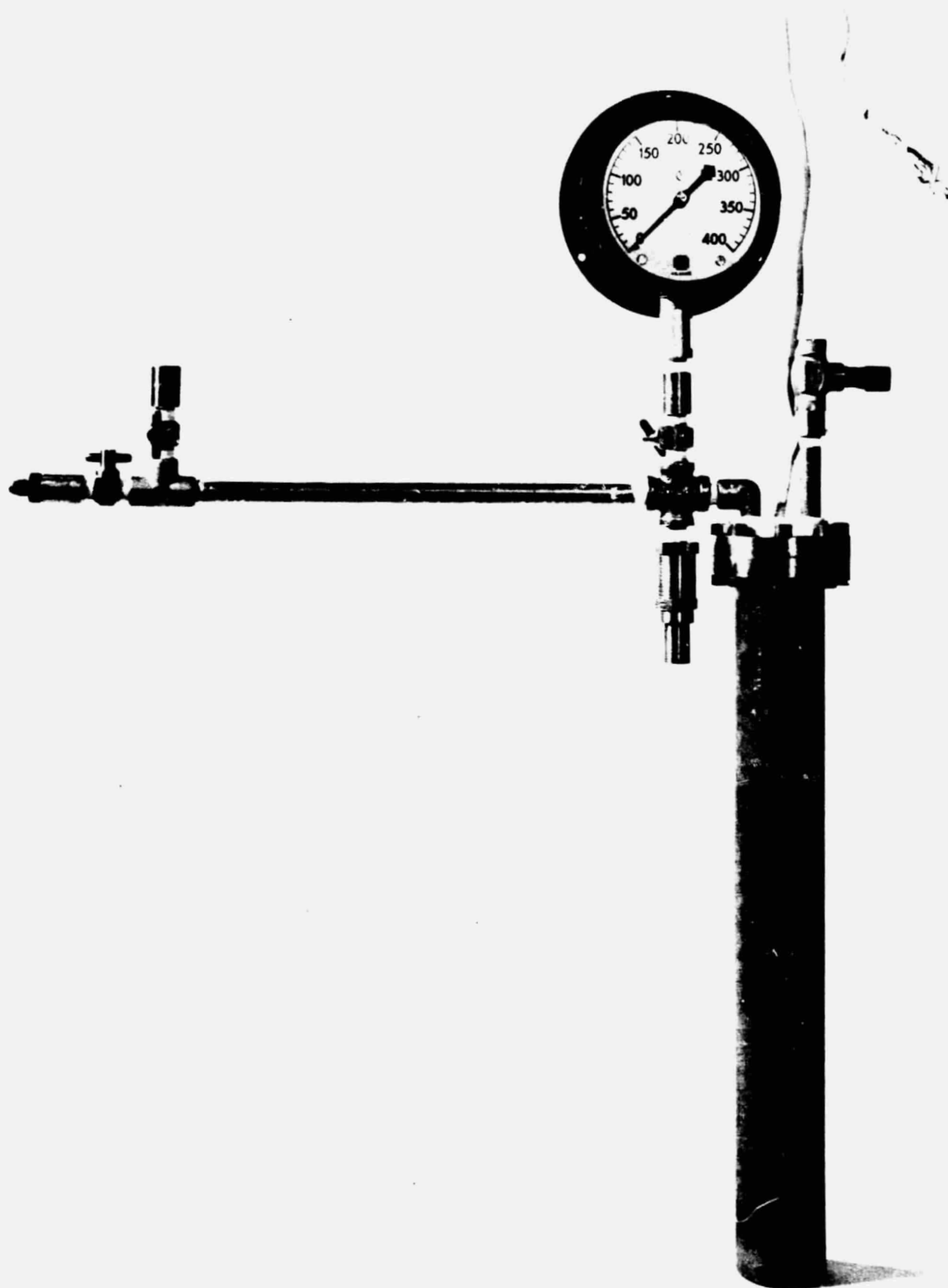


Photo 1. Pressure Cell for Voltage Breakdown Tests

Tests with Polar Liquids

For the tests with polar liquids it was necessary to vary the test temperature while dielectric loss measurements were made. In order to cover a wide range of temperatures in a relatively short time, the test specimen* was first cooled by immersion in liquid nitrogen. The nitrogen was removed and the test specimen with its heat sink was quickly surrounded with glass fiber thermal insulation so that warming would occur slowly. A thermocouple junction was positioned so as to measure the specimen temperature as closely as possible. It was recognized that some error in temperature measurement was unavoidable but the results were considered adequate for the intended purpose - to determine the trend of the values as well as the magnitude of the absorption peaks (maxima in dissipation factor and capacitance). A few measurements were made within a temperature controlled cabinet in which temperature stability was achieved at each measurement temperature. These results checked those with varying temperature quite well. It would have been completely impractical to have made measurements at many temperatures if stability had to be achieved at each temperature.

Test Specimens and Electrodes

Most of the measurements in the program were made on films which were coated directly on aluminum foil. (The development of self-supporting dielectric film is discussed in a later section of the report). The films of bonded ferroelectric powders were coated with a doctor blade on .00025 to .002 inch aluminum foil usually, about 2 inches wide. The aluminum foil was adhered with a thin layer of petrolatum to a very flat and smooth glass plate. The coating equipment is shown in Photo 2. The thickness of the coating could be varied from about .0015 to .003 inch thick. Aluminum foil thinner than .002 inch was coated but it was difficult to remove it from the glass plate and it tended to tear when handled.

In most cases the coated foil was allowed to air dry until the coating became firm and was then placed in an oven usually at 85°C to complete the removal of the dispersing agent (usually water). The film was then allowed to "stabilize"

*The test specimen was partially surrounded by a block of metal with considerable heat capacity to supply a "heat sink". For tests on the liquids themselves, the heavy nickel test cell provides the heat sink.

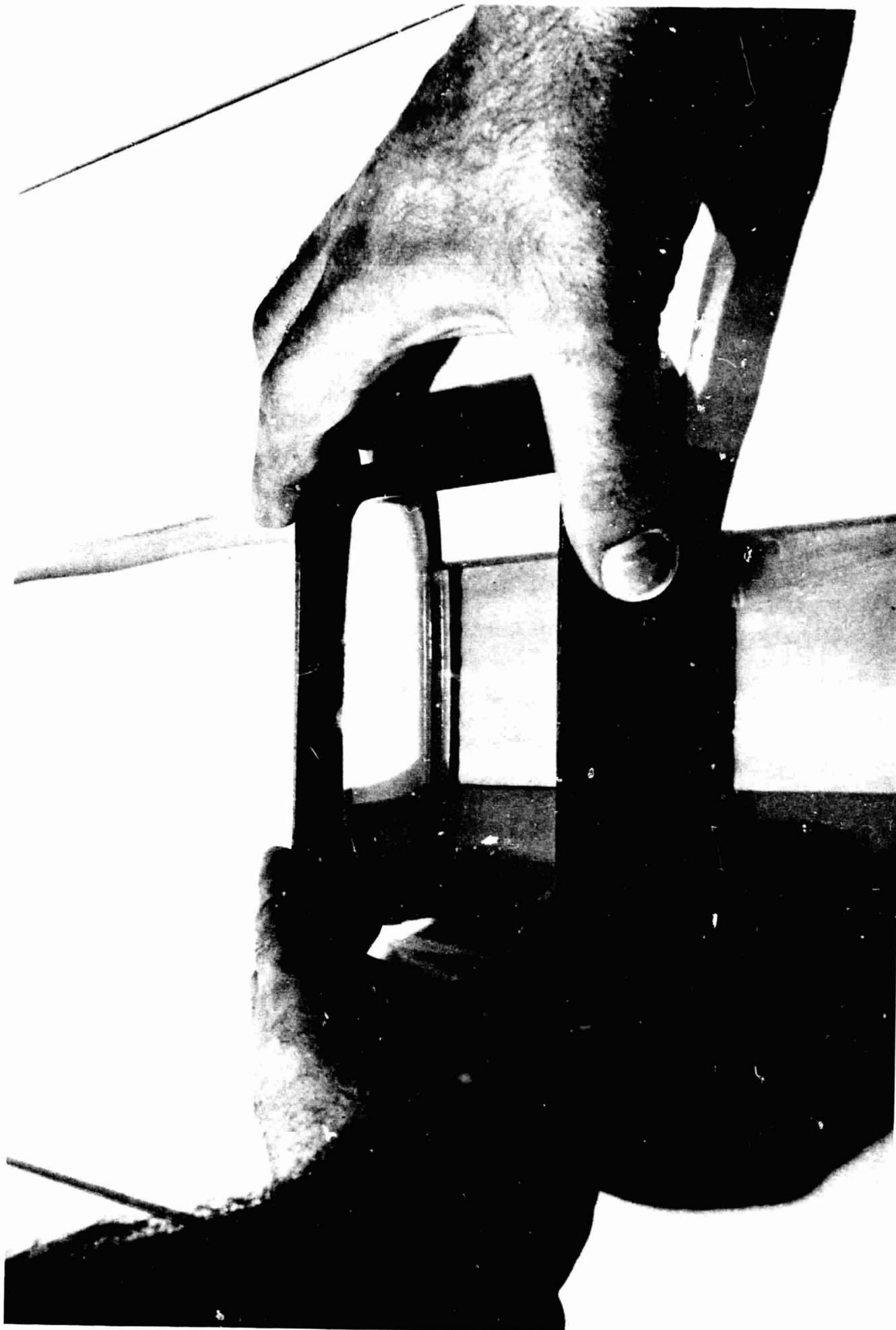


Photo 2. Coating Aluminum Foil with Bonded Ferroelectric Powder

in the room at 23°C and 50% RH. In some cases the dried film was reconditioned in a "desiccator" over water to increase the water content.

For screening tests a .0005 inch aluminum foil was pressed firmly against the insulating coating on the heavier foil. The applied foil was usually at least $\frac{1}{2}$ " narrower than the heavy foil to provide a margin and thereby to prevent flashover. Test specimens several inches long were usually used so that the capacitance would be adequate for the dielectric loss measurements. The end of the thinner foil was raised to provide a tab for electrical connection. A typical test specimen is shown in Photo 3. The foil test specimen was used for both dielectric loss and breakdown measurements. In order to study the distribution of the breakdown values, a $\frac{1}{2}$ inch diameter brass electrode was sometimes used instead of the thin foil electrode. In this way it was possible to make several breakdown measurements in a small section of insulated foil by simply moving the electrode around on the surface of the film. The brass electrode as well as the insulated film was immersed in liquid nitrogen during the voltage breakdown tests.

Problems were encountered in making rolled capacitors. In the first place it was difficult to roll the .002 inch aluminum foil on itself and it was, of course, recognized that such a thick foil could never be used in a practical capacitor. Moreover, many of the bonded ferroelectric powder films were too fragile or brittle to be flexed appreciably. The latter problem was overcome to a considerable extent with the development of the protein colloid binder to be described later. Despite considerable effort to do so, a foil with insulation projecting beyond the edges was not made successfully. In consequence it was necessary to interpose a narrower uninsulated foil between wider insulated foils with the insulated sides facing each other. Unfortunately this method of winding will permit the use of only one layer of insulation. It was possible to coat heavy aluminum foil on both sides but this approach was less practical than coating thinner foil on one side. With considerable effort it was possible to make a number of rolled capacitors. The inability to control tension in hand winding contributed in large measure to the tearing encountered. With machine winding it seems likely that thinner foils could be handled but the long lengths of insulated film needed were beyond the scope of the present program.



Photo 3. Coated Foil, Free Film, and Rolled Capacitor Test Specimens

In the wound capacitors, tabs insulated with duPont Mylar film were used successfully for connections to the inner foil. The Mylar proved to be satisfactory in liquid nitrogen.

A few stacked capacitors were made. The lack of edge coverage on the foil constitutes a serious problem also with the stacked configuration. Such a configuration could be used with the "free" films which were too stiff to be wound.

For the measurement of dielectric loss in polar liquids, a small solid nickel, Berberich cell holding about 70cc of liquid with an air capacitance of about 30 pfd was used. In some cases the coated foil specimens were immersed in the polar liquids. In a few cases, the ferroelectric powder coatings were vacuum impregnated with the polar liquids and the counter electrode subsequently applied.

Electrical Measurements

The measurements of capacitance and dissipation factor were made in accordance with ASTM method D150. Some measurements were made with a high voltage GE Schering bridge at 60 Hz. Most of the measurements were made at 1000 Hz (1 kHz). For measurements at a single temperature a #1620A General Radio bridge was used. For measurements in which the temperature was changing fairly rapidly the automatic balancing General Radio #1680A bridge assembly was used so that temperature measurements could be simultaneously reported with the electrical measurements.

The permittivity (dielectric constant) was calculated from the geometry of the foil test specimen and the measured capacitance. It is recognized that the accuracy of such calculations depends to a very large extent upon the adequacy of the thickness measurements. Moreover, even a very small space between a high permittivity material and the electrode (lack of adhesion) will very greatly decrease the measured value of capacitance. However, in a practical capacitor such factors also are involved so that in this program the reported values of permittivity are those calculated from average measured dimensions. Unfortunately, it was not possible to measure the dimensions of the test specimen while immersed in liquid nitrogen so that in this sense some small error will have been introduced. It was possible to detect major loss of adhesion between foil and insulating film upon immersion in liquid nitrogen by observing changes in measured

capacitance. Errors arising in this fashion will lead to values of permittivity smaller than the correct values.

The "air" capacitance of the Berberich liquid cell was measured as a function of temperature. The very small change in capacitance with temperature was found to be less than the error involved in assembling the cell and was disregarded.

Voltage breakdown measurements were made usually with steadily increasing direct voltage but also in some cases at 60 Hz. The short-time test or ASTM method D-149 was followed so far as it is applicable. Generally, breakdown was obtained within one minute. In some cases voltages below the short-time breakdown voltage were applied for appreciable periods of time. No systematic study of voltage endurance was made.

EXPERIMENTAL PROGRAM - PHASE I

Objectives

It has been the overall objective of this program to develop a combination of materials which will achieve a maximum capacitive energy storage density. The storage energy is given by the equation:

$$\text{Energy (joules)} = \frac{1}{2}CV^2$$

C = capacitance in farads

V = voltage in volts

Thus both a high permittivity and high electric strength are needed in the dielectric. As a secondary objective it is desired to obtain a minimum charge "leakage" (high resistivity) and a low dielectric loss on discharge. The dielectric loss affects voltage breakdown but the quantitative effect cannot be described. In a cryogenic capacitor the dielectric loss is particularly important since repeated discharges may produce sufficient dielectric heating to affect the design of the refrigeration system (see Phase II). The dielectric loss is given by the following equation:

$$\text{Watts (loss)} = 2\pi f \cdot k \cdot E^2 \cdot C \cdot \tan \delta$$

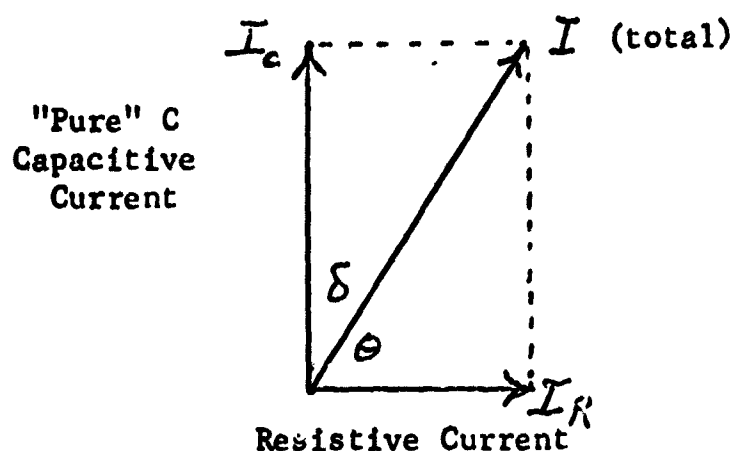
f = frequency of discharge

k = factor determined by discharge wave shape

c = capacitance in farads

$\tan \delta$ = dissipation factor

δ = "defect" angle (see diagram below)



Corona discharges influence the life of a capacitor under repeated discharges but this subject was considered to be beyond the scope of the program.

The work on three classes of materials to achieve the objective listed above will be described below under separate headings.

Films of Bonded Ferroelectric Powders

In work done before the start of this contract it had been found that ferroelectric powders could be combined with a binder to make a thin film with a high permittivity (dielectric constant). Many binders with poor electrical properties at conventional temperatures could be used at cryogenic temperatures since the dielectric loss decreased markedly at the low temperatures. Inorganic binders such as sodium silicate in water solution were thought to be especially suitable since they would not carbonize during electric breakdown.

The goal of this program involved the selection of ferroelectric materials and binder to give the optimum combination of high electric strength, high permittivity and low dielectric loss. It was assumed that liquid nitrogen would be used to impregnate the film. Polar liquids have also been used as impregnants as described later in this report.

In this program three ferroelectric powders have been studied:

<u>Ferroelectric Powder</u>	<u>Description</u>
Titanium Dioxide	Ticon T
Barium Titanate	Ticon B
Strontium Titanate	Ticon S

All of these materials were purchased from the National Lead Co., New York.

A great many combinations of these powders with a considerable variety of bonding materials have been investigated. The possible permutations are so great that a systematic approach alone would have been too limited. An intuitive approach was used as well in which the extremes of the possible variables were considered. It is recognized that such an approach permits a broad study but unfortunately the combination of materials which give the optimum properties may be missed.

The binders listed below were used singly or in combination in various percentages. They were mixed with water using either a high speed blender* or a ball mill. In general, a dispersing agent such as Triton X-100, an anti-foaming agent and a humectant such as glycerine or ethylene oxide were used in varying amounts as needed.

<u>Binder</u>	<u>Source and Remarks</u>
Sodium Silicate	Philadelphia Quartz Co. - various ratios of Na_2O & SiO_2
Polyvinyl Alcohol	#P X 1295, Matheson, Coleman and Hill, E. Rutherford, New Jersey
Protein Colloid	Swift's #2226, Chicago, Illinois
Starch Paste	Carter's Desk Glue
Polyvinyl Methyl Ether	Gantrex M-155, General Aniline & Film Corp.
Dimethyl Hydantoin-Formaldehyde Resin	Dantoin #684, Glyco Chemicals, Inc.
Gum Tragacanth	Stein Hall & Co., New York City
Carboxy Methyl Cellulose	Dow Chemical, Midland, Michigan

*In the last stages of the program it was felt that the steel blades of the blender might have eroded and produced metal particles which contributed to the poor values of electric breakdown obtained.

It is not necessary to report in detail here all of the formulations considered. In many cases the materials could not be coated so as to make a continuous thin film. Some materials produced powdery, rough or discontinuous films as they dried. Others lost adhesion to the underlying aluminum. It was finally possible to "zero in" on several formulations which gave the best mechanical properties. The protein colloid and polyvinyl alcohol gave the best results. The nature of the powdered ferroelectric powder as well as the binder proved to be important. The TiO_2 appeared to aid in dispersing the titanates. The fine powder size may be the important contributing factor. An effort was made to obtain different particle sizes of the titanate powders without immediate success. The effort was not pressed because successful films with values of permittivity as high as 29 were obtained. When the protein colloid was used as a binder, adequate dispersions were obtained with strontium titanate and without any TiO_2 .

When dissipation factor measurements were made on the ferroelectric powder films in liquid nitrogen, it was found that the incorporation of barium titanate and sodium silicate increased the dielectric loss. Efforts were made to react the sodium silicate with dilute HCl and wash out the resulting salt from the silicic acid remaining. Such films were brittle when dried and the electrical properties were not significantly improved. The relative success of the protein colloid reduced the effort with the other binders.

Following the preliminary work described above, a series of 11 compositions were made. These are described in the following section along with the pertinent electrical data obtained with some of them.

Dielectric Properties of Ferroelectric Powder Films

In order to study the permittivity (ϵ') and dissipation factor ($\tan \delta$) of just the ferroelectric powders at low temperatures, the powder was mixed with distilled water and coated on aluminum foil without using any binder. It was necessary to use relatively thick coatings (about .025 in.) in order to overcome the fragile nature of the unbonded coating. Measurements were made in liquid nitrogen at -196°C and continued as the temperature was permitted to increase slowly. Typical results are given in Table I.

From Table I it is apparent that barium titanate powder has a relatively high dissipation factor compared to titania (TiO_2) and the strontium titanate. The

Table I

DISSIPATION FACTOR AND PERMITTIVITY
OF FERROELECTRIC POWDER FILMS (WITHOUT BINDER) OVER
A RANGE OF TEMPERATURE FROM -196° TO ABOUT 0°C

<u>Material (no binder)</u>	<u>At -196°C</u>	<u>Measurements at 1 KC</u>		
		<u>Tan δ</u> <u>Min.</u>	<u>At -196°C</u>	<u>ϵ'</u> <u>At Min. tan δ</u>
100% TiO_2	.0002	*	18	*
100% Barium Titanate	.0035	.0025	23	23.5
100% Strontium Titanate	.0006	.0004	11	10
80% TiO_2 + 20% Strontium Titanate	< .0003	*	20.5	*
85% Strontium Titanate + 15% Barium Titanate	.0012	*	21	*
90% Barium Titanate + 10% Strontium Titanate	.0026	.0017	20	18
55% TiO_2 + 35% SrTiO_3 + 10% BaTiO_3	.0005	.0003	17.5	15.5

*Minimum value of tan δ was obtained in liquid nitrogen at -196°C

Notes: Permittivity (ϵ') of TiO_2 and Strontium Titanate is maximum at -196°C and decreases as the temperature increases.

Permittivity of Barium Titanate is minimum at -196°C and increases as the temperature increases.

values of permittivity are difficult to compare. The values are lower than those for the bonded materials to be described later as shown in Table II. The rheology of the mixture and resulting density of the film apparently are important in determining the value of the permittivity.

From Table II it becomes apparent that the electrical characteristics are influenced to some extent by the nature of the binder. Up to this point, the nature of the binder had been dictated very largely by attempts to improve the physical properties of the films. It is certain that the optimum electrical properties have not been achieved yet. In Table III, the permittivity (ϵ') for three films is compared to the measured density of the films with reasonably good correlation. The reason for the difference in density is not obvious. It is probably attributable to the rheology of the mixture. The factors controlling the rheology are not understood. The addition of very small amounts of the water soluble resins - polyvinyl alcohol (PVA) and polyvinylmethyl ether (PME) - appear to have reduced the density of the film but they resulted in improvement of mechanical properties. Film #10 contained three times as much glycerine as Film #9 and #11 so that the glycerine does not seem to be a controlling factor. However, some glycerine is needed to provide flexibility in the dried film. The protein colloid has an ammoniacal odor. It is probably that conducting ions in the binder contribute to the dielectric loss in liquid nitrogen (-196°C) and are primarily responsible for the relatively high dielectric loss at room temperature.

Voltage Breakdown in Ferroelectric Powder Films

One of the most important reasons for the development of cryogenic capacitor dielectrics involves the possibility of obtaining a high electric strength with liquid nitrogen impregnation of porous ferroelectric films. In earlier work values of 2000 volts per mil were achieved. As the film technology was developed to produce films with better mechanical properties, it was discovered that the voltage breakdown of the films would occur as low as 200 volts per mil and was seldom better than 500 volts per mil. It seemed certain that these low values of breakdown voltage were due to the presence of conducting impurities in the films.

A considerable effort has been expended to determine the reasons for the low values of breakdown voltage. "Clean" room techniques subsequently were used for

Table II

DISSIPATION FACTOR AND PERMITTIVITY (AVG. VALUES)
FOR
FERROELECTRIC POWDER FILMS WITH DIFFERENT BINDERS

<u>Film*</u>	<u>Tan δ</u>	<u>ϵ'</u>
#3 - 19% TiO_2 , 81% SrTiO_3	.0024	25.5
#6 - 20% TiO_2 , 80% SrTiO_3	.0025	25
#7 - 100% BaTiO_3	.006	31
#8 - 100% BaTiO_3	.007	28
#9 - 100% SrTiO_3	.004	28.5 (37)**
#10- 100% SrTiO_3	.004	23.5
#11- 100% SrTiO_3	.004	24.5

*The composition of the binders is given in Appendix A.

**Value for freshly cast film.

NOTE: Films #9, #10 and #11 had been allowed to come to equilibrium at 23°C and 50% RH. The condition of the other films may be somewhat variable.

Table III

COMPARISON OF DENSITY AND PERMITTIVITY (AVG. VALUES)
FOR
FERROELECTRIC POWDER FILMS

<u>Film</u>	<u>% - Binder*</u>	<u>ϵ'</u>	<u>ϵ'</u>	<u>density(D)</u>	<u>ϵ'/D</u>	<u>$\tan \delta$</u>	
		<u>23°C</u>	<u>-196°C</u>		<u>-196°C</u>	<u>23°C</u>	<u>-196°C</u>
#9	5 Protein Colloid	28.5(?)	28.5	2.8	1.0	0.055	.004
#10	10 Protein + PVA	33	23.5	2.1	1.1	0.09	.004
#11	5 Protein + PME	31	24.5	2.1	1.2	0.10	.004

*100% SrTiO_3 was used as the filler. The complete composition of the binders is given in Appendix A - the % of binder is approximate by weight.

NOTE: Films were allowed to come to equilibrium at 23°C and 50% RH.
 Values at 23°C were variable.

coating the foil with the ferroelectric powder films to avoid contamination with conducting particles so far as possible. It is recognized that the ferroelectric powders themselves may not be completely free from such impurities but a few attempts to use purer grade (CP) titanate did not give better results. It was felt also that ball milling the compositions rather than using a high speed blender might reduce the conducting particles in the mix. All of these techniques were combined and a considerably higher electric strength was achieved.

Test results with a $\frac{1}{2}$ inch electrode (rather than foil) placed on top of the coated foil are given in Table IV. The small electrode was used to determine the extent of the variability. As expected the values of voltage breakdown were very variable. Despite the variability, some comparisons between materials and test conditions can be made.

To aid the comparison, the test results have been plotted on arithmetic probability paper as Figures 2 and 3. It should be recognized that true statistical distribution cannot be expected but the results can be visually and quantitatively analyzed.

In Figure 2 for tests at room temperature it is apparent that the thicker Film #9A has the greatest variability in breakdown stress values but the maximum value is next to the greatest value for all the films combined. If conducting particles were involved, the thicker film would be expected to be superior. It is more likely that the thicker film is less homogenous. There is little to choose between the values of Films #9, #10 and #11.

In Figure 3 the test results in liquid nitrogen for Film #9A have not been plotted because of their great variability but all the values were below any of those for the other three films. From Figure 3 it is apparent that the conditioning of Films #9 and #10 at 100% RH before immersion in liquid nitrogen contributes slight if any improvement in electric strength. However, the moisture conditioning of Film #11 has apparently markedly increased its electric strength unless some other and unknown factor is involved. Foil electrodes were applied to the conditioned Film #11. At 1500 volts per mil for over one hour there was no evidence of failure.

Table IV
DC ELECTRIC STRENGTH - VOLTS/MIL
HI-K CERAMIC COATINGS ON ALUMINUM FOIL
 (½" Electrode on Single Sheet)

<u>Coating Type</u>	<u>Coating Thickness Mils</u>	<u>As rec'd. - Tested at 23°C - 50% RH</u>	<u>As rec'd. Tested in Liq. N₂</u>	<u>72 hrs. at 100% RH Tested in Liq. N₂</u>
9	1.4	261	1420	1650
		265	1610	1650
		265	1680	1790
		287	1780	
		293		
9A	3.0	153	800	835
		200	910	1270
		271	1130	
		328		
10	1.25	233	1280	1360
		240	1680	1360
		240		1490
		264		
		273		
11	1.4	243	1200	2000
		247	1540	2280
		307	1670	2860
		315		
		343		

Table V
DC ELECTRIC STRENGTH - VOLTS/MIL
HI-K CERAMIC COATINGS ON ALUMINUM FOIL
 (½" Electrode on Single Sheet)

<u>Coating Type</u>	<u>Coating Thickness Mils</u>	<u>As rec'd. - Tested in Liquid N₂</u>	<u>Soaked in Isopentane Tested in Liquid N₂</u>	<u>Soaked in XF-1105 Tested in Liq. N₂</u>
10	1.25	1280	1920	1290
		1680	2860	2380
				3360
				>4000

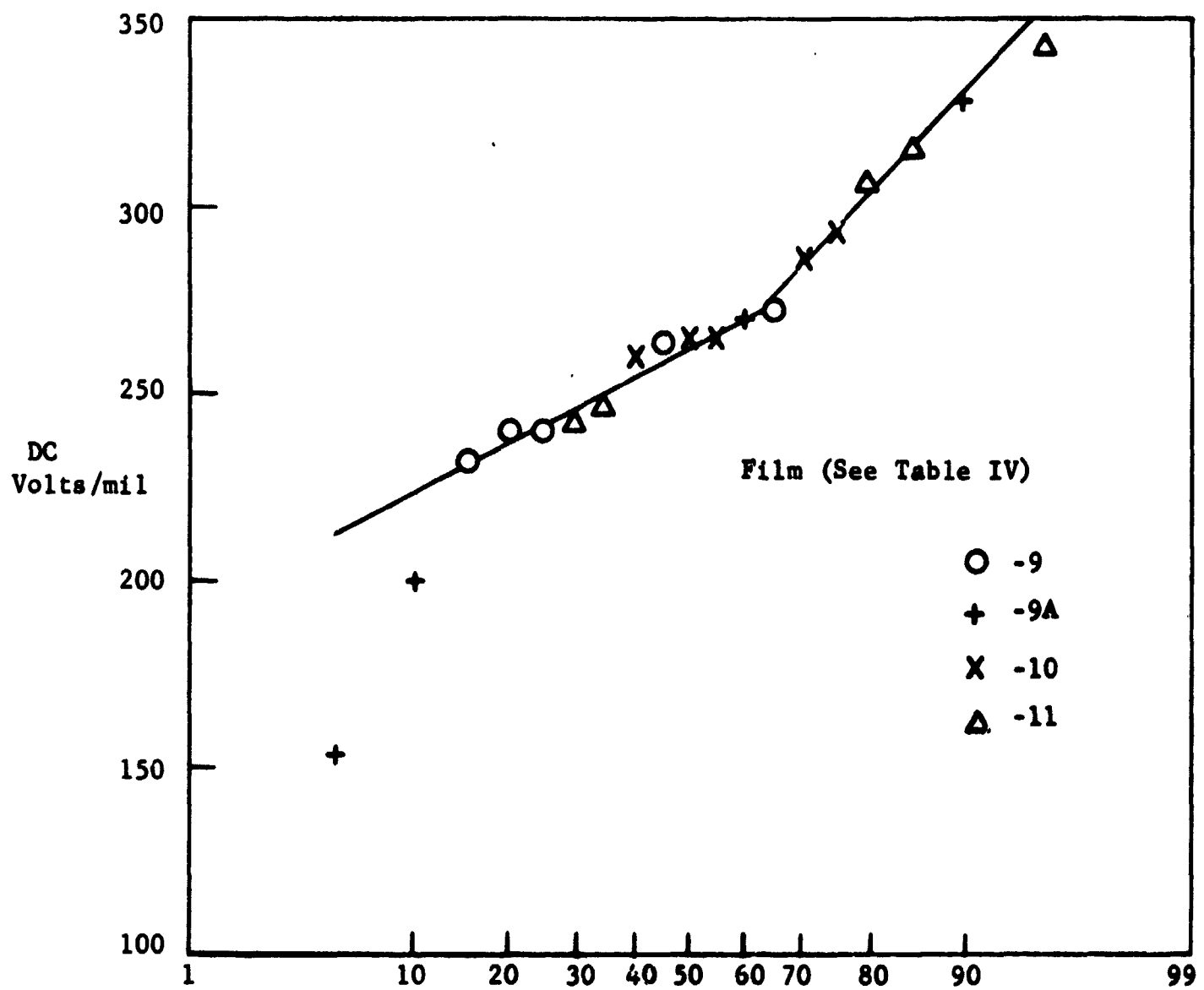


Figure 2. Distribution of Voltage Breakdown Values, Test at 23°C
50% RH

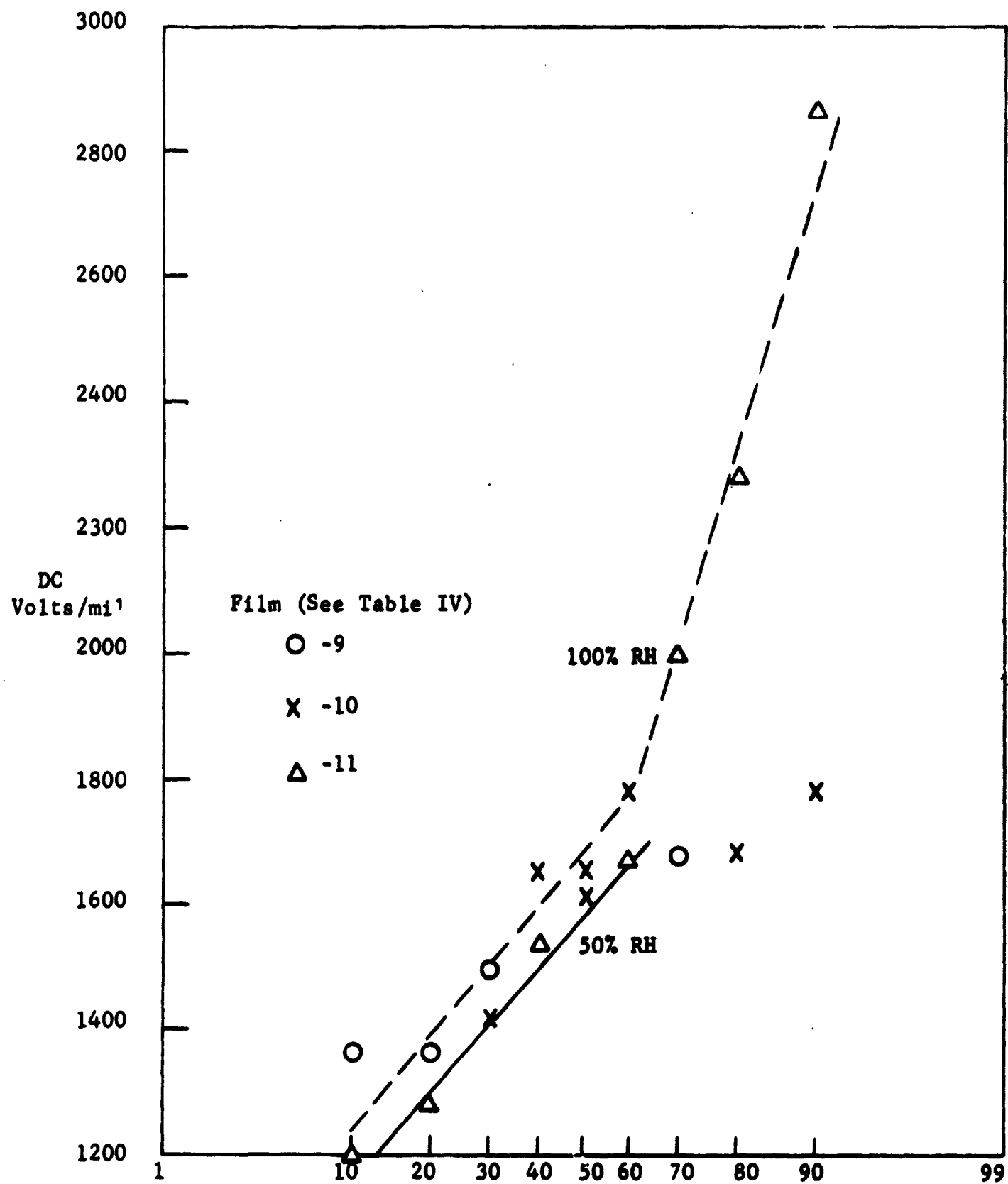


Figure 3. Distribution of Voltage Breakdown Values. Tests in Liquid Nitrogen at -196°C

While it was recognized that impregnation with liquid nitrogen should have advantages, a few measurements were made with specimens of Film #10 which had been immersed in liquid isopentane and in silicone oil #XF-1105 before test in liquid nitrogen. Both of these liquids freeze at very low temperatures to a glass rather than a crystalline form. The limited results, shown in Table V, indicate that such liquid impregnation may result in improvement. Better impregnation of the films with the liquid may be needed to achieve a reliable improvement in electric strength. Vacuum impregnation is very difficult with isopentane because of its high vapor pressure. It is possible to vacuum impregnate with silicone oil but these tests were not completed before the close of contract work.

The foregoing indicates that the impregnation of the films with liquid nitrogen may be inadequate. If this is the case, then tiny voids within the film could be filled with gas perhaps at low pressure. A very curious set of test results is reported in Table VI. Here, successive breakdowns were made on the same spot without moving the brass electrode. A 10-megohm resistor in series prevented excessive current flow and gross disruption of the test specimen. For seven breakdowns in a row, the value of breakdown voltage kept increasing. It is possible, of course, that the electrodes were being "conditioned" or that areas of higher conductivity within the film were "improved". It seems more likely that the thermal "shock" at failure increased the impregnation of the film with liquid nitrogen. The presence of voids and a deficiency in impregnation with liquid nitrogen possibly is indicated also by the results shown in Table VII. (It should be recognized that the self-supported film is much thicker than those previously described). The increase in dissipation factor ($\tan \delta$) occurs at voltage stresses so low that a corona mechanism in voids is probably not involved although the effect is difficult to explain by any other mechanism.

The results just described led to the development of a test cell so that voltage breakdown measurements could be made in non-boiling liquid nitrogen under pressure. As described earlier many problems were encountered with the test cell and in use it proved to be so cumbersome that the number of test results is very limited. The available results are given in Table VIII. A number of measurements were made at 60 Hz because it was believed that the AC measurements might be more

Table VI

DC ELECTRIC STRENGTH - VOLTS/MIL
HI-K CERAMIC COATINGS ON ALUMINUM FOIL

($\frac{1}{2}$ " electrode - successive breakdowns on same spot - 10 megohms in series)

<u>Coating Type</u>	<u>Coating Thickness Mils</u>	<u>Failure No.</u>							
		<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>
10	1.25	2010	2200	2270	2340	2530	2580	2650	2110

Table VII

60 HZ DISSIPATION FACTOR TAN δ VS. VOLTAGE STRESS - IN LIQUID N₂

.024 inch Ceramic Impregnated Glass Tape
 Aluminum Foil Electrodes

<u>Volts/Mil</u>	<u>Tan δ</u>	<u>Approx.*</u>
12	.00156	13.0
24	.00212	13.0
48	.00318	13.3
72	.00639	13.6
96	.00952	13.8
120	.01335	14.1

*Change with voltage is significant

Table VIII
VOLTAGE BREAKDOWN MEASUREMENTS
MADE IN PRESSURE CELL

<u>Film</u>	<u>Pressure</u>	<u>60 Hz. - Peak volts/mil</u>			<u>D.C. - Volts/mil</u>		
		<u>Avg.</u>	<u>Max.</u>	<u>Min.</u>	<u>Avg.</u>	<u>Max.</u>	<u>Min.</u>
#11	100-120 psi	1480	1620	1400	2723	2880	2570
#11	0 (gage)	650	695	595	1503	1670	1200
#11	0 after being at 120 psi	1200	1220	1170			
#11*	120 psi	1590**					
	0 (gage)	1310**				>4000***	2380***

*Soaked in XF-1105

**Single value

***From previous results

Table IX
PERMITTIVITY (ϵ') AND DISSIPATION FACTOR ($\tan \delta$)
.0023 inch "Free" Ceramic Film
(Lead Foil Electrodes)

<u>Temp.</u> <u>°C</u>	<u>State</u>	<u>120 Hz</u>		<u>400 Hz</u>		<u>1 kHz</u>	
		<u>ϵ'</u>	<u>$\tan \delta$</u>	<u>ϵ'</u>	<u>$\tan \delta$</u>	<u>ϵ'</u>	<u>$\tan \delta$</u>
23	As rec'd.	16.3	0.354	14.6	0.248	13.2	0.184
-92	Cooled from above					7.6	0.0007
23	Warmed from above (Condensed H ₂ O)	6309	0.342	4817	0.427	3623	0.573
-189	Cooled from above					9.16	0.0009

sensitive to the presence of voids in the film. The test results indicate that pressure does have a considerable effect on the voltage breakdown of ferroelectric powder Film #11. The voltage breakdown of liquid nitrogen also depends upon pressure. However, such a pressure effect cannot explain the relatively high values after the film was first exposed to 120 psi pressure and then returned to room pressure. It is not known if the nitrogen was boiling in the latter case. At any rate pressure impregnation seems to have accomplished a considerable improvement in electric strength for Film #11. However, the same degree of improvement has not been obtained for the silicone oil impregnated film as would be expected if it is lack of impregnation or boiling of nitrogen which is responsible for the poor performance of the liquid nitrogen by itself.

Free Films from Ferroelectric Powders

If more than single film dielectrics are to be achieved in the cryogenic capacitor, it will be necessary to produce self-supporting (free) films of the dielectric spacer. Throughout this program it has been the objective to keep a very high percentage of the ferroelectric powder filler in the films and so far as possible maintain a degree of porosity so that the film could be impregnated with liquid. To obtain good films on aluminum foil it was apparently desirable to attain a fair degree of adhesion between the coating compound and the aluminum. However, such adhesion is disadvantageous in the production of free films. Efforts were made to coat films on polytetrafluoroethylene and on silicone oil coated surfaces without much success. On such surfaces the coatings tended to coat non-uniformly or to "ball up".

It was possible to coat the ferroelectric powder coatings #9, 10 and 11 on smooth plastic films such as polycarbonate (GE Lexan). The coatings could be removed from such films in small sections by slight flexing in liquid nitrogen but all the free films produced in this manner were so fragile that they could not be evaluated electrically. It was possible to dissolve the plastic film away but in so doing the plastic impregnated the ceramic film. Results for the #11 composition coated on polycarbonate film with the film removed by solvent (methylene chloride) are given in Table IX. The measurements at room temperature were made at several frequencies to show that absorbed water was in fact responsible for the high dielectric loss and permittivity observed after the cooled film had picked up

considerable water upon returning to room temperature. At low temperatures the permittivity is very low compared to the values for films cast on aluminum foil. It is quite likely that a very thin film of unfilled resin at one surface of the free film may be responsible for these low values and such an effect seems unavoidable with such a process.

A very limited amount of work was done with ferroelectric powder films which were cast over a group of parallel glass threads somewhat spaced from one another. A film about .0055 inch thick resulted which had considerable strength in the direction of the threads. The thickness of the films was so uneven that the permittivity was estimated only rather roughly as perhaps about 15. This low value and the thickness of the film discouraged additional work.

High Permittivity Liquids

A considerable amount of effort was directed to the development of high permittivity liquids which hopefully might have relatively low dielectric loss. It was suggested that such liquids could be used to impregnate the high permittivity ceramic films or to impregnate a very porous (low density) paper. From the dielectric point of view the ceramic film offered the greatest promise but paper would permit a more feasible mechanical construction much like that in a conventional oil filled capacitor.

The investigation was concentrated on polar liquids which had high permittivity and low melting temperatures. The permittivity of a number of these materials had been measured previously as a function of temperature but only rarely had $\tan \delta$ been measured also. It was recognized that the permittivity would be highest at temperatures near the freezing point. Dissipation factor and capacitance were measured as a function of temperature for:

- Nitroethane
- 1-Nitropropane
- 2-Nitropropane
- 1-Nitropropane plus added isopentane
- Acetonitrile
- Propionitrile

Results are plotted in Figures 4-19. With nitroethane and nitropropane some measurements were made with a 500 volt DC bias applied as the temperature was decreased.

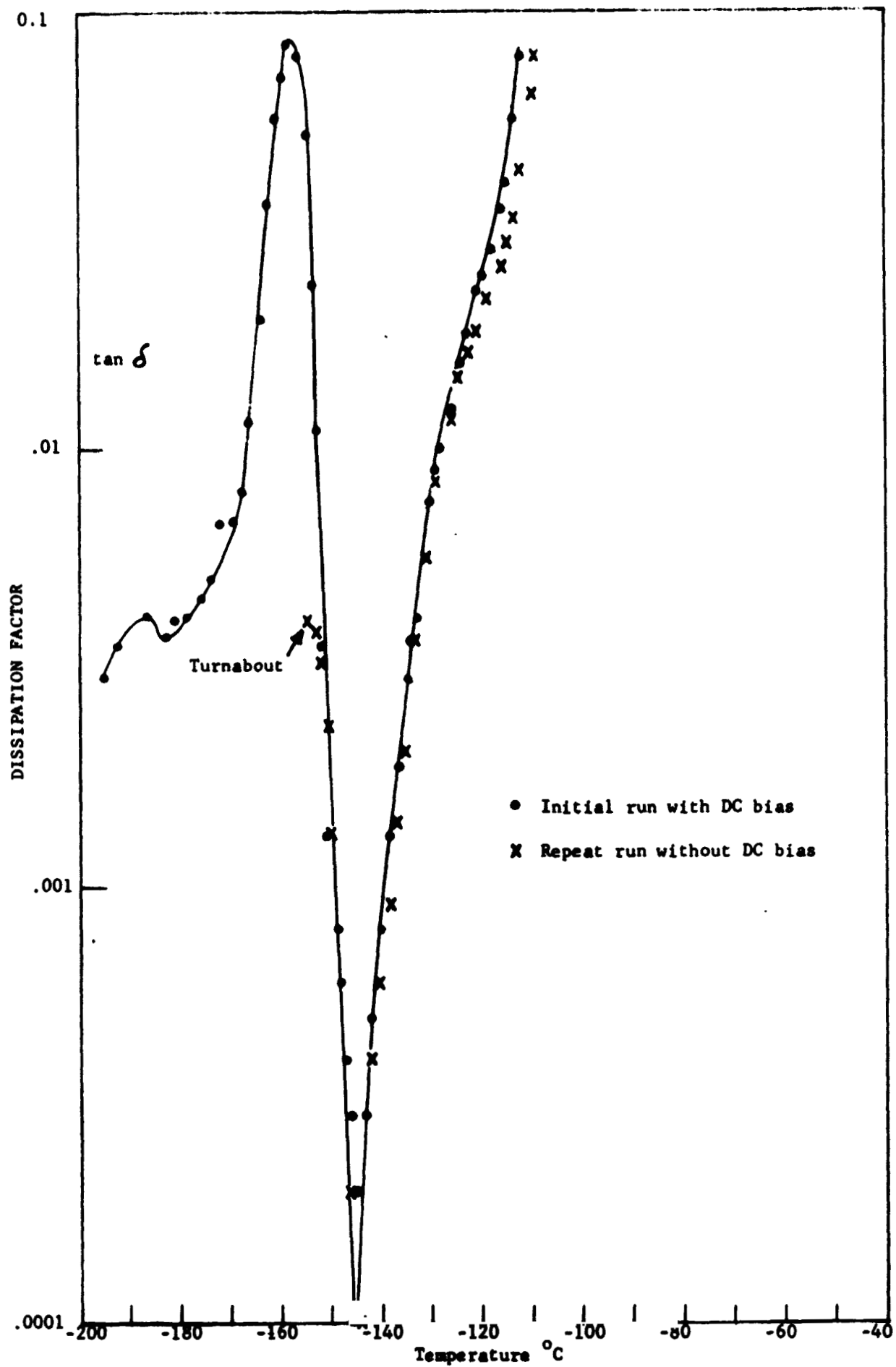


Figure 4. Dissipation Factor at 1 kHz vs Temperature - Nitroethane

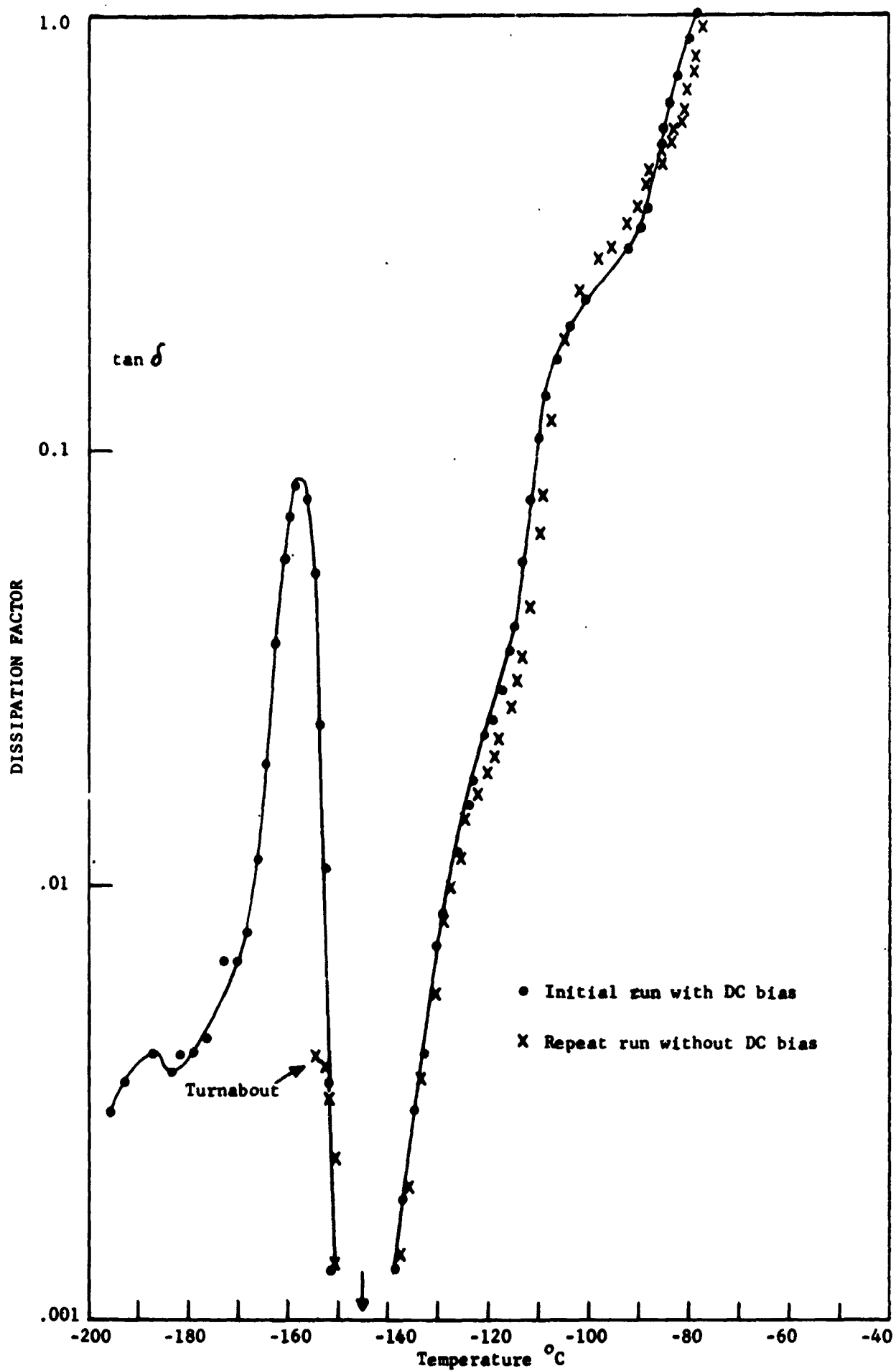


Figure 5. Dissipation Factor at 1 kHz vs Temperature - Nitroethane
(Extension of Figure 1 with Different Vertical Scale)

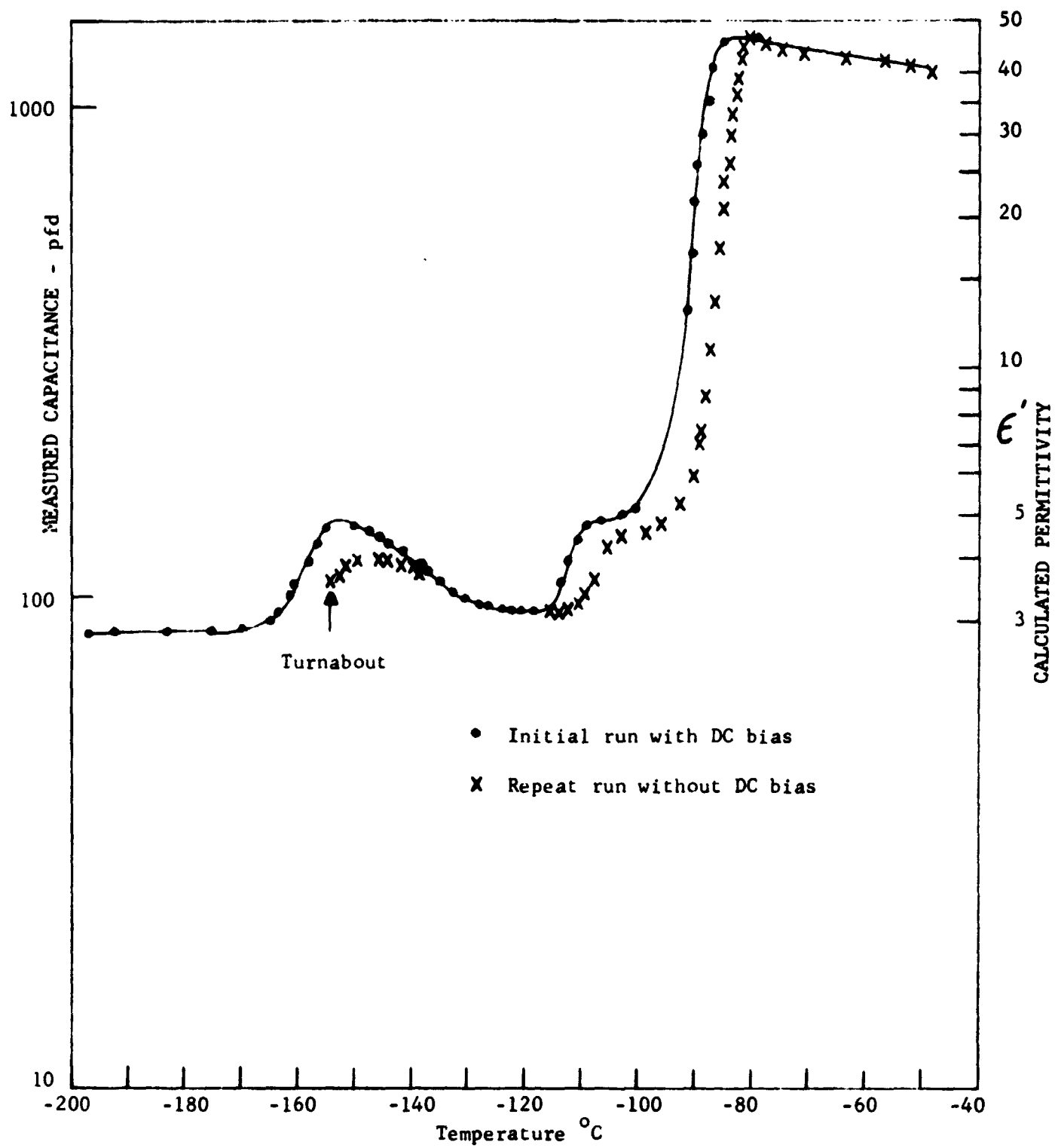


Figure 6. Permittivity at 1 kHz vs Temperature - Nitroethane

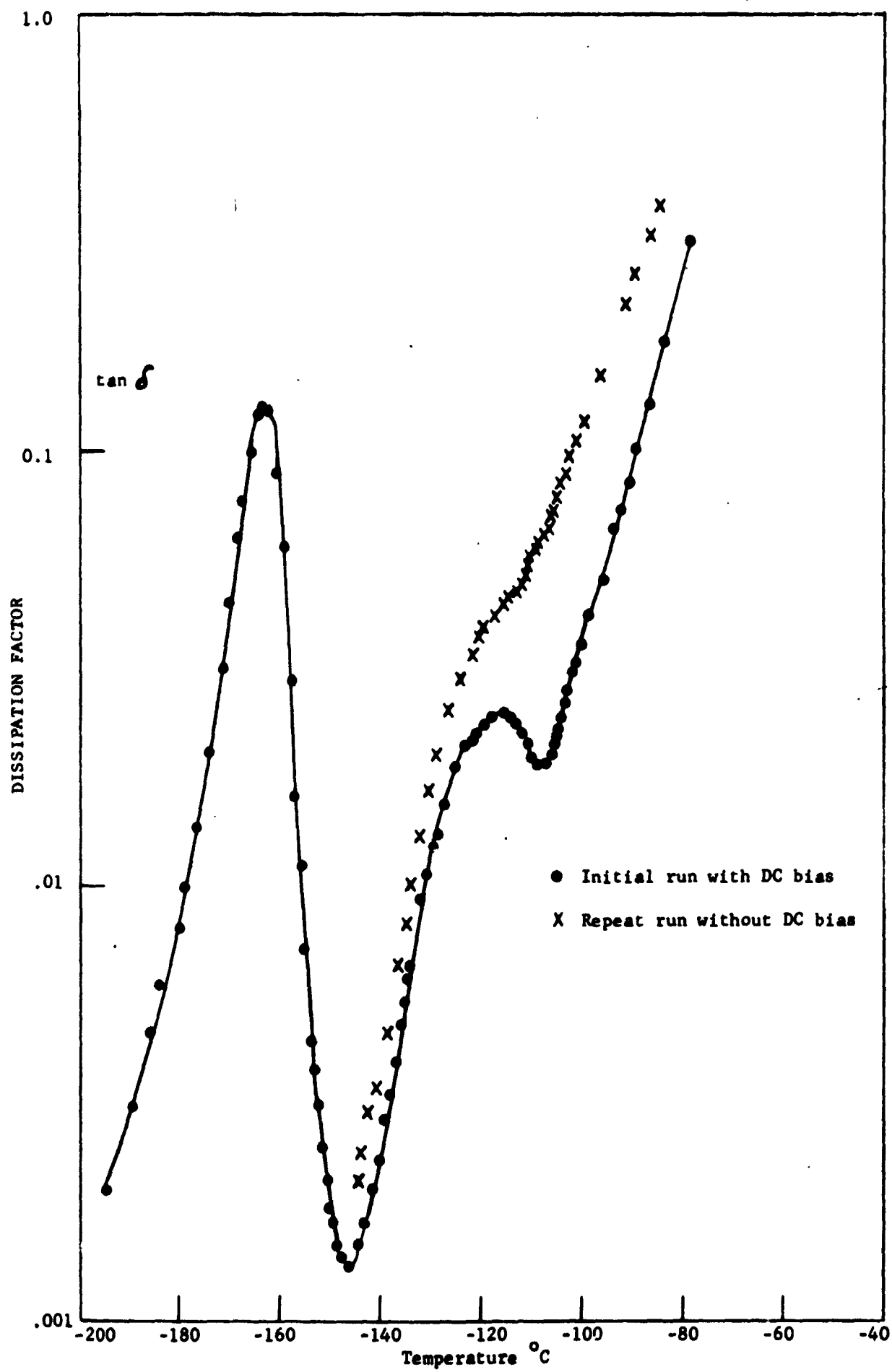


Figure 7. Dissipation Factor at 1 kHz vs Temperature - 1-Nitropropane

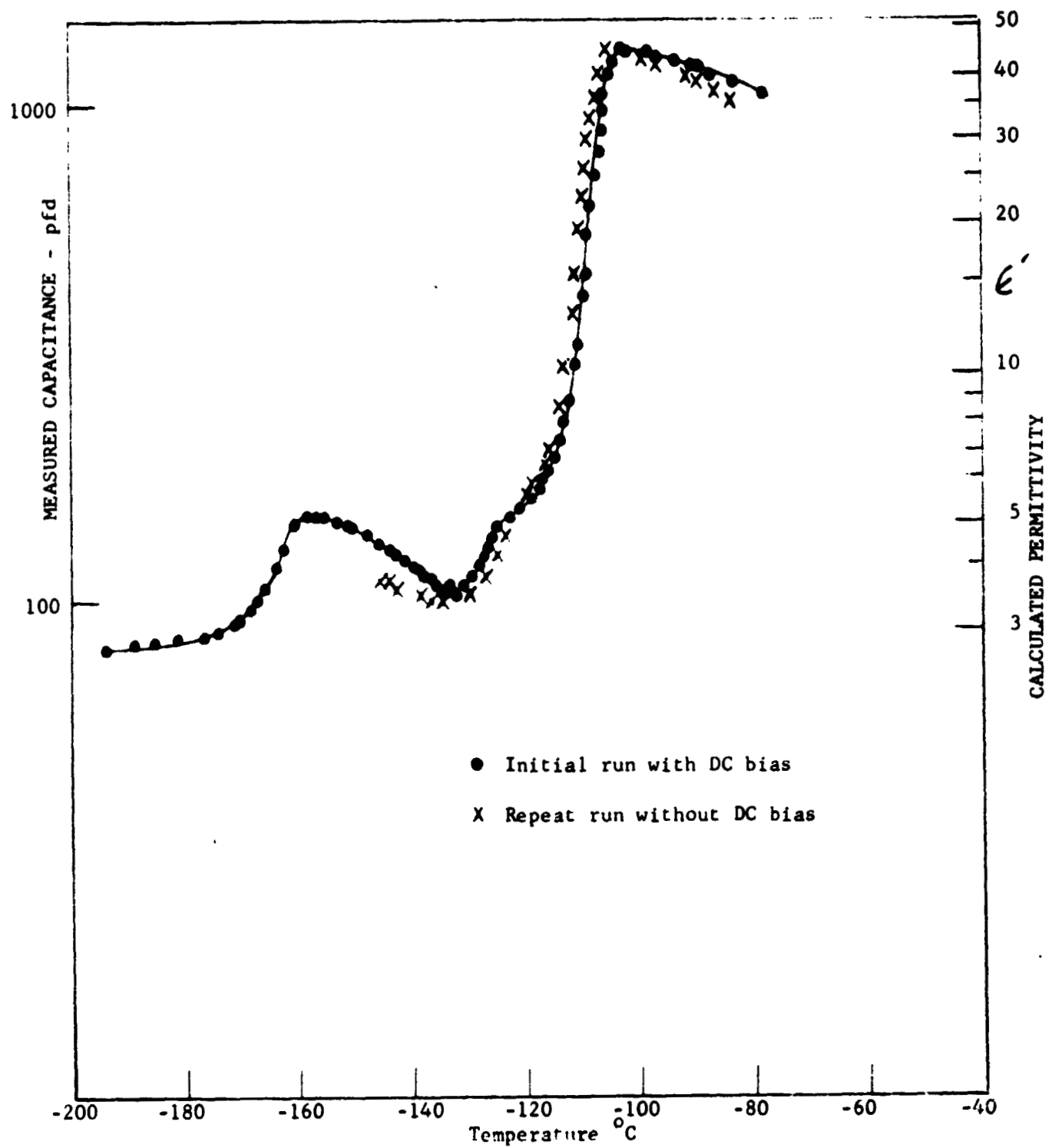


Figure 8. Permittivity at 1 kHz vs Temperature - 1-Nitropropane

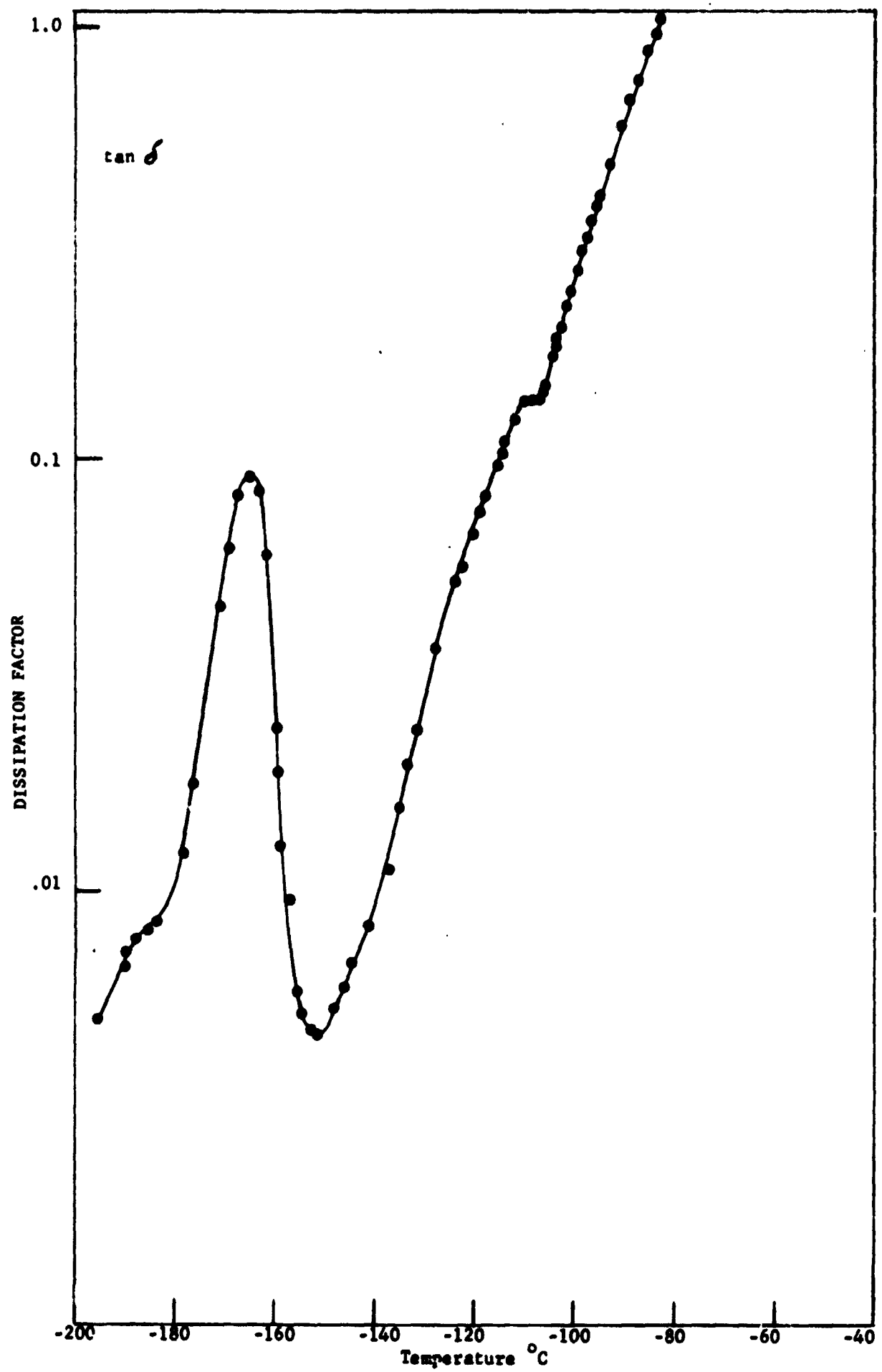


Figure 9. Dissipation Factor at 1 kHz vs Temperature - 1-Nitropropane.
(Frozen Without DC Bias)

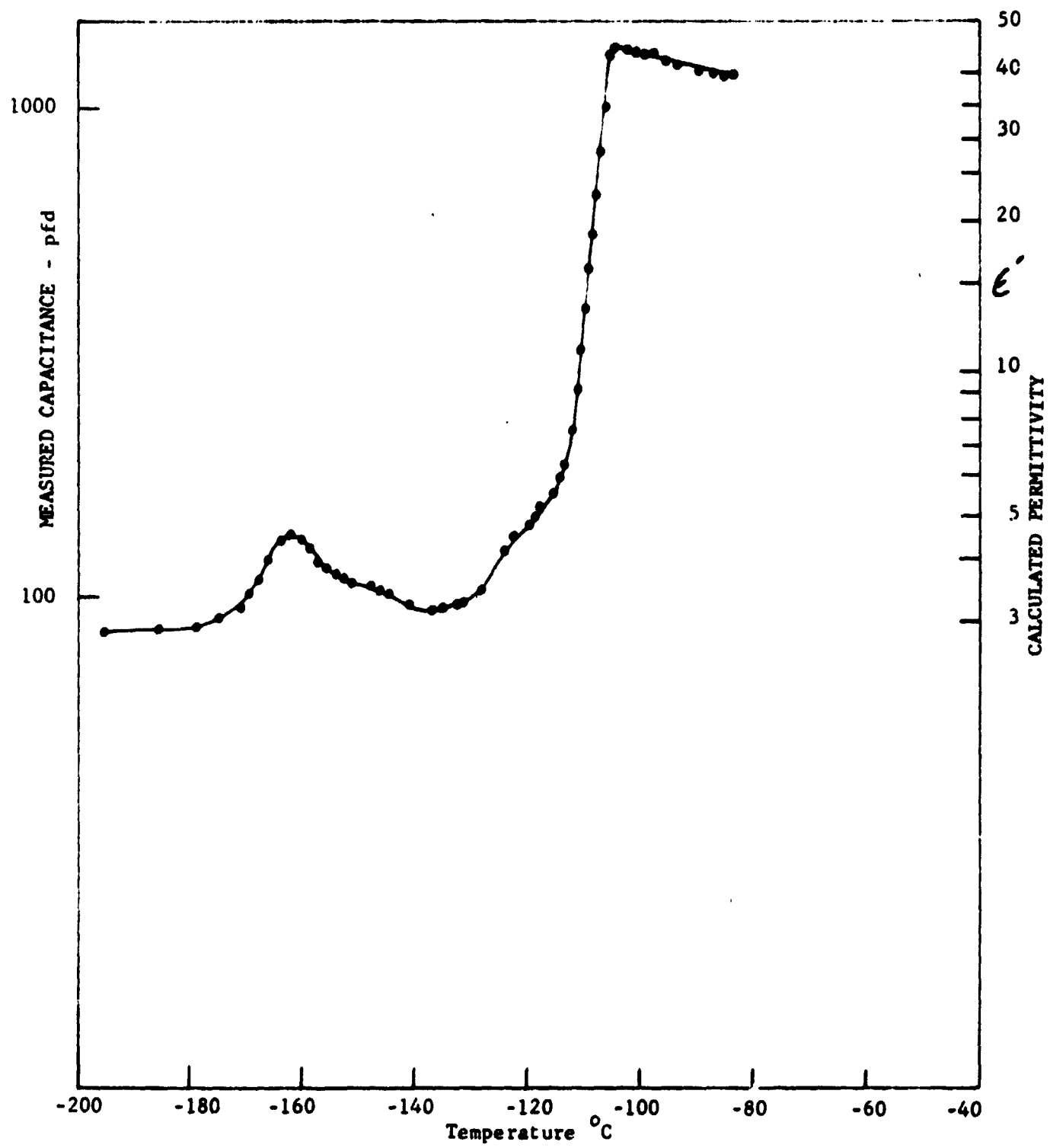


Figure 10. Permittivity at 1 kHz vs Temperature - 1-Nitropropane. (Frozen Without DC Bias)

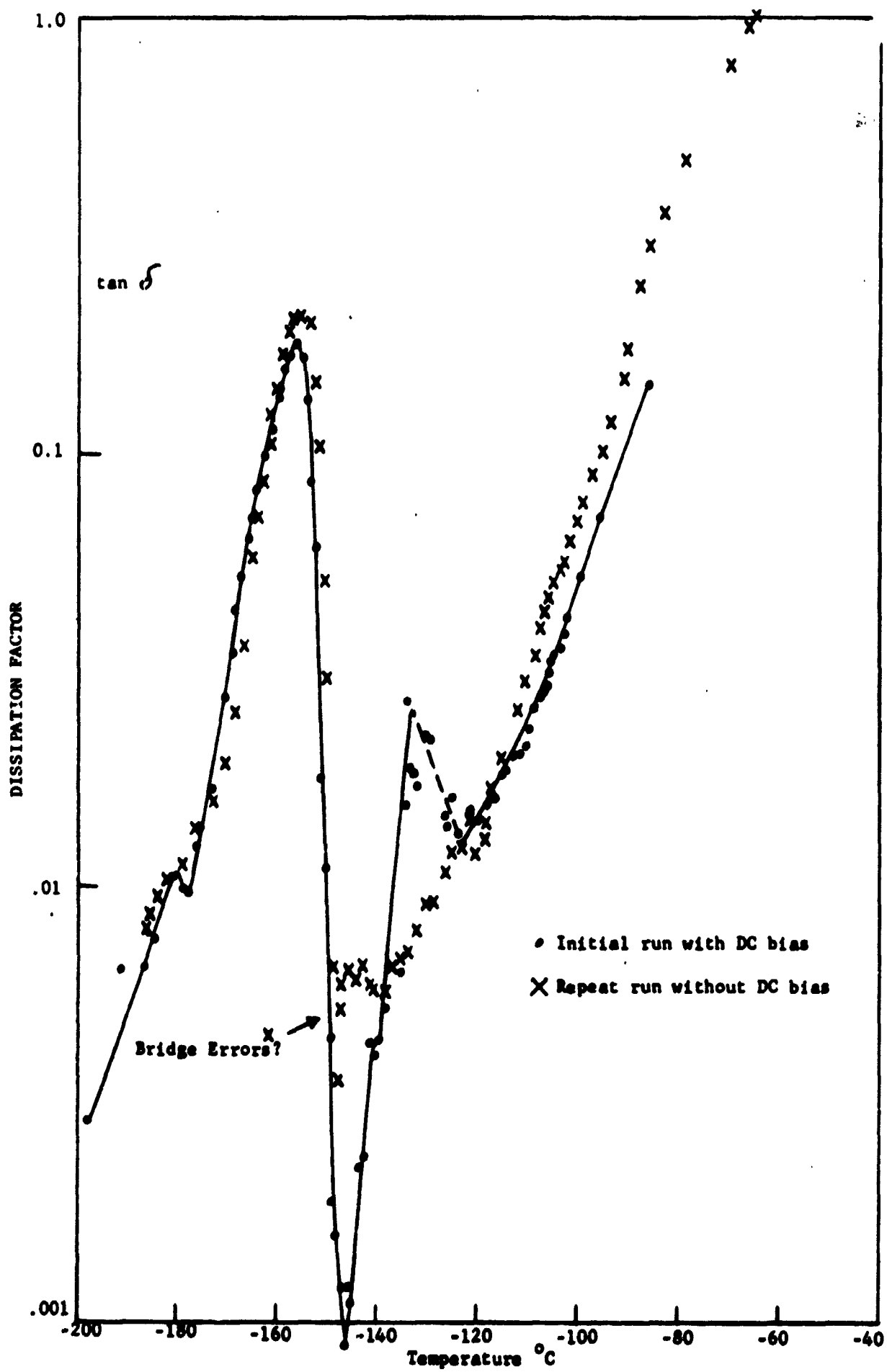


Figure 11. Dissipation Factor at 1 kHz vs Temperature - 1-Nitropropane with Isopentane

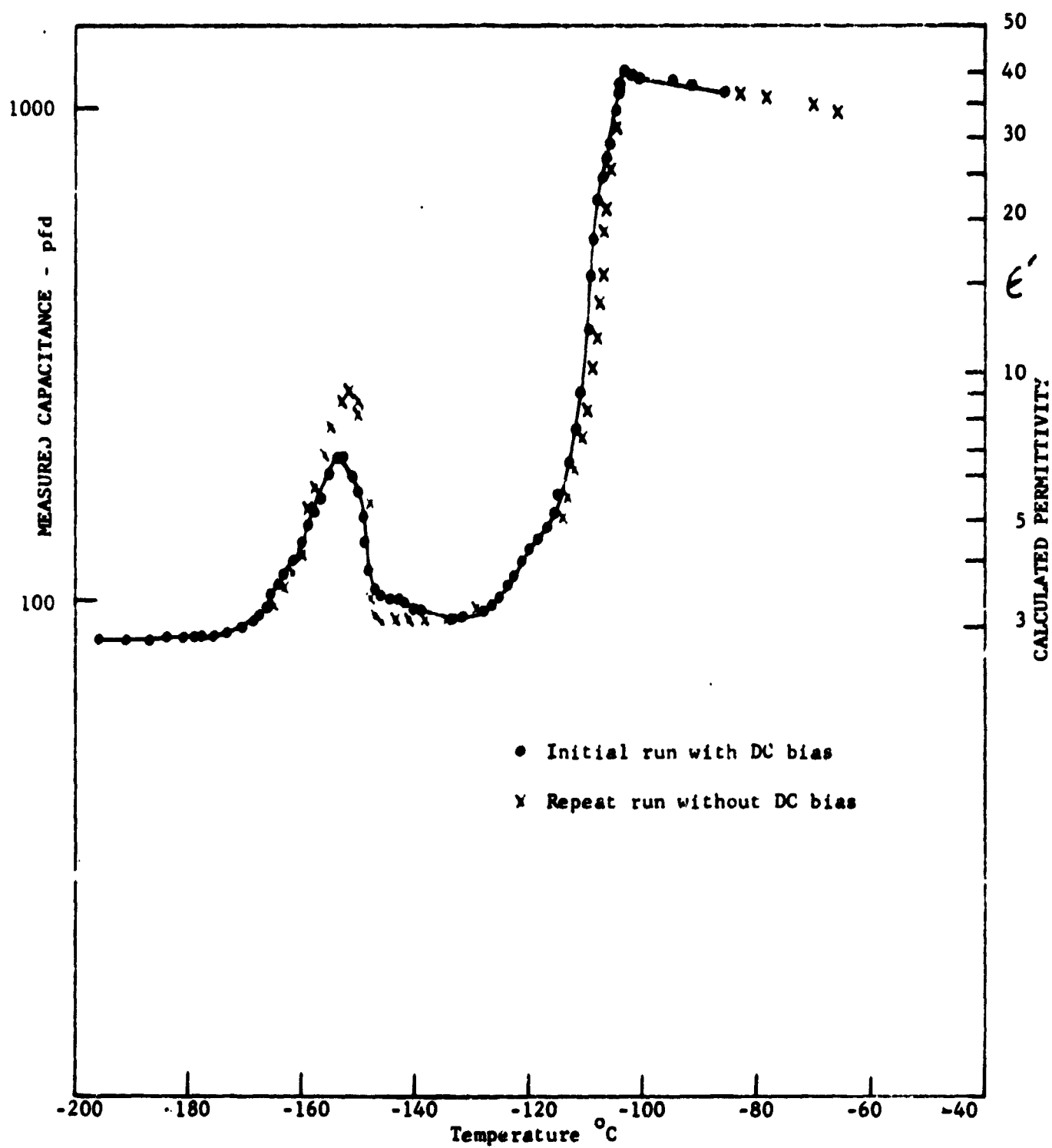


Figure 12. Permittivity at 1 kHz vs Temperature - 1-Nitropropane with Isopentane

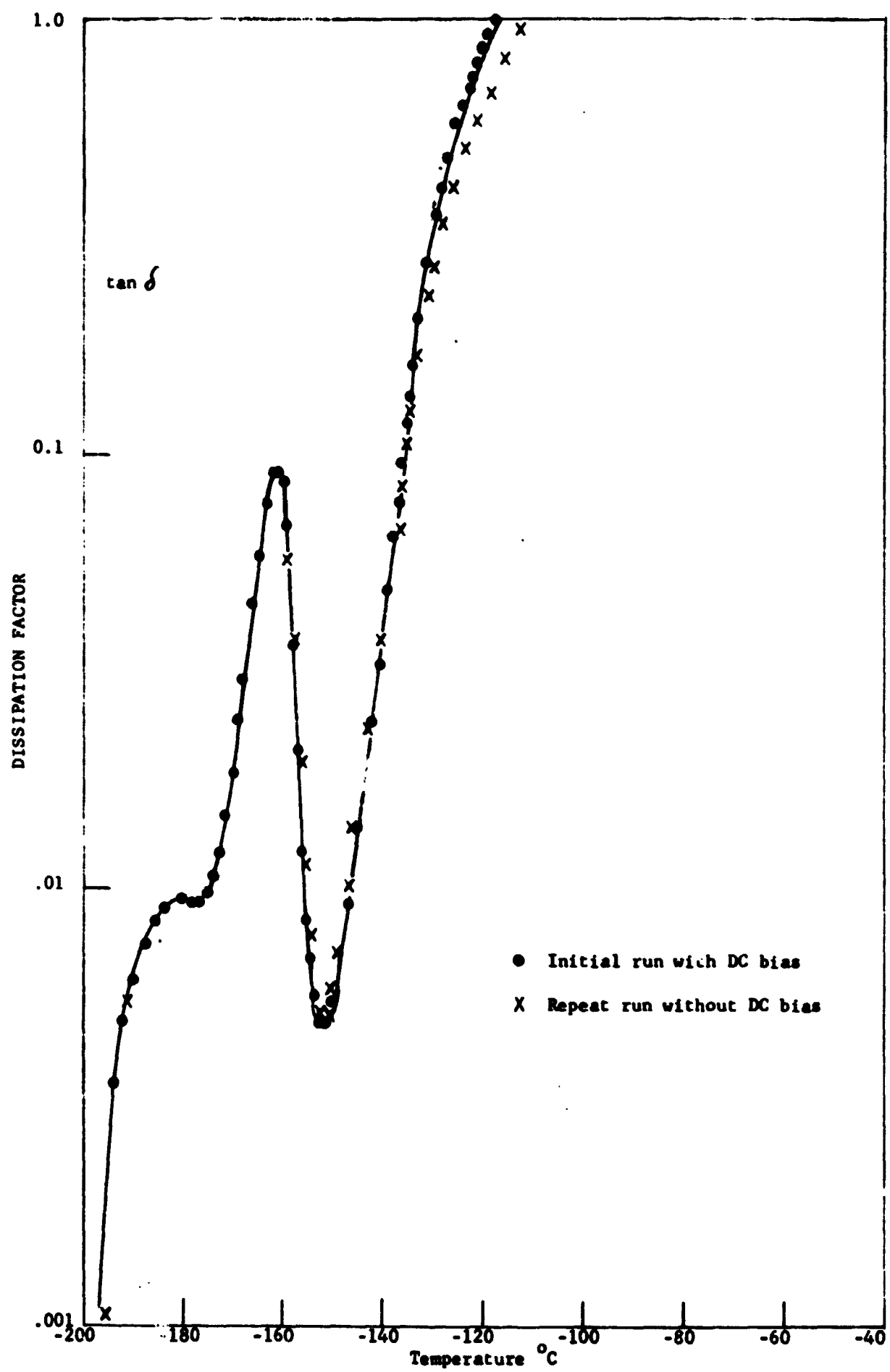


Figure 13. Dissipation Factor at 1 kHz vs Temperature - 2-Nitropropane

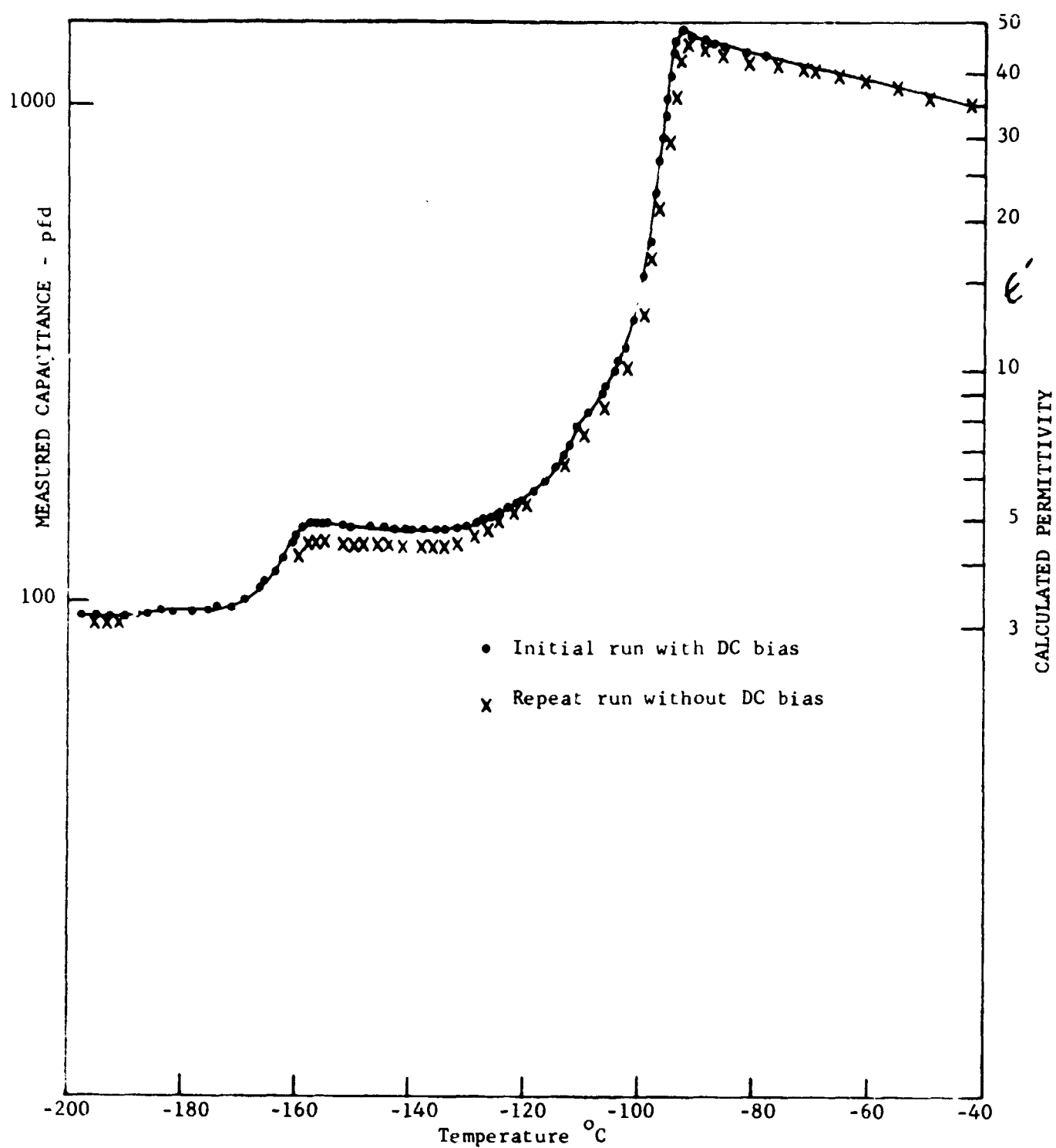


Figure 14. Permittivity at 1 kHz vs Temperature - 2-Nitropropane

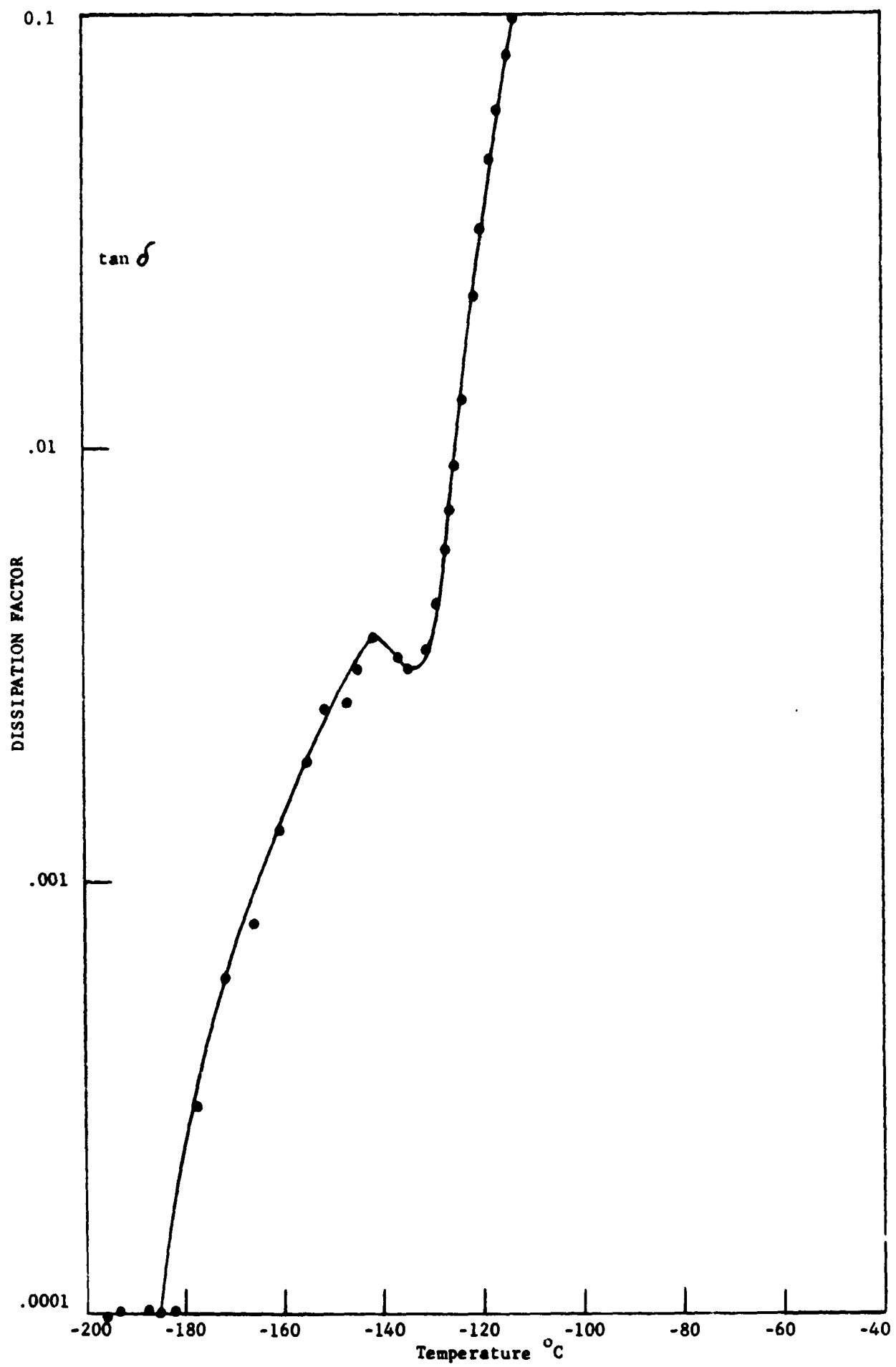


Figure 15. Dissipation Factor at 1 kHz vs Temperature - Acetonitrile.
(Frozen Without DC Bias)

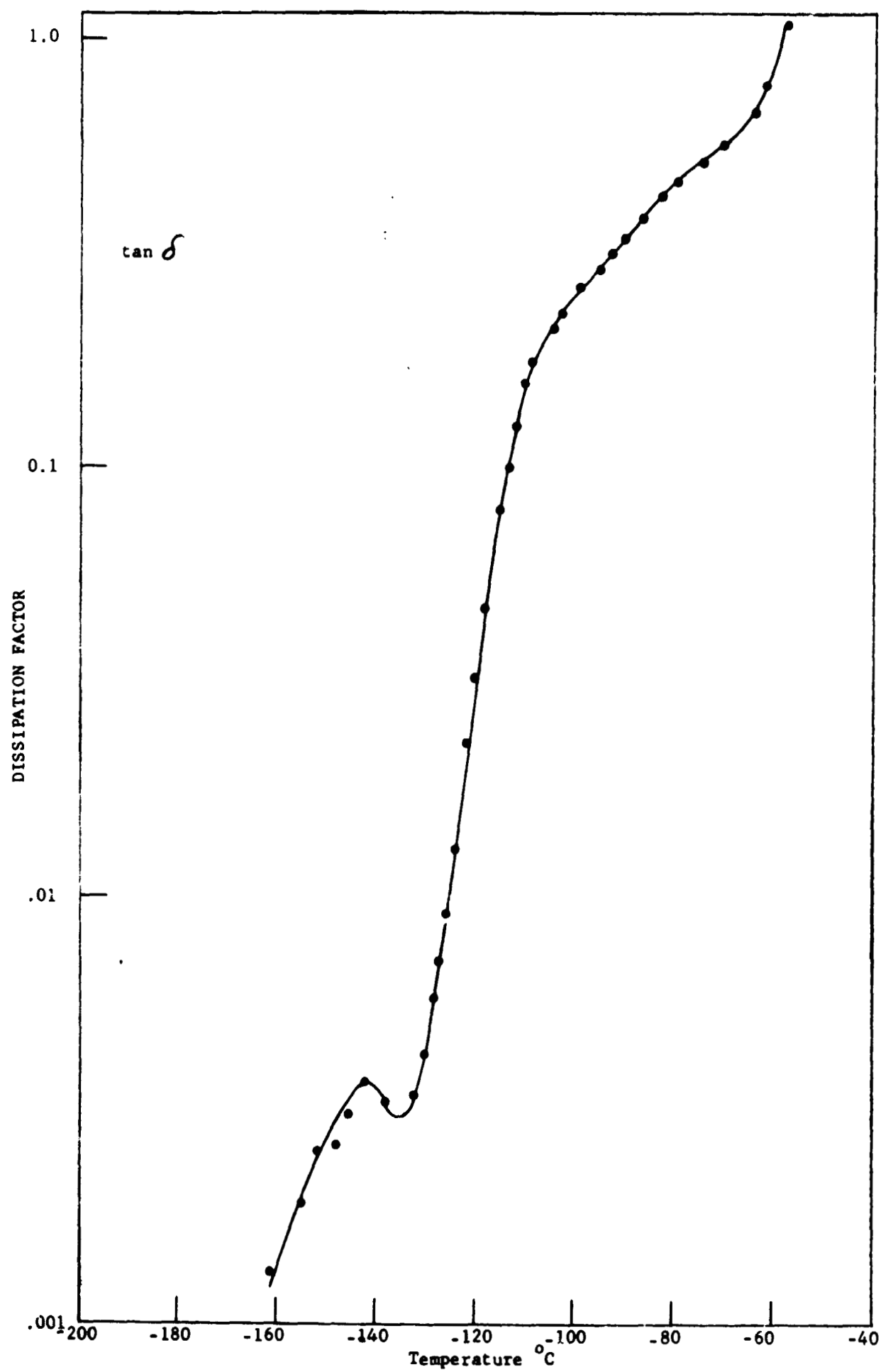


Figure 16. Dissipation Factor at 1 kHz vs Temperature - Acetonitrile.
(Extension of Figure 12 with Different Vertical Scale).
(Frozen Without DC Bias)

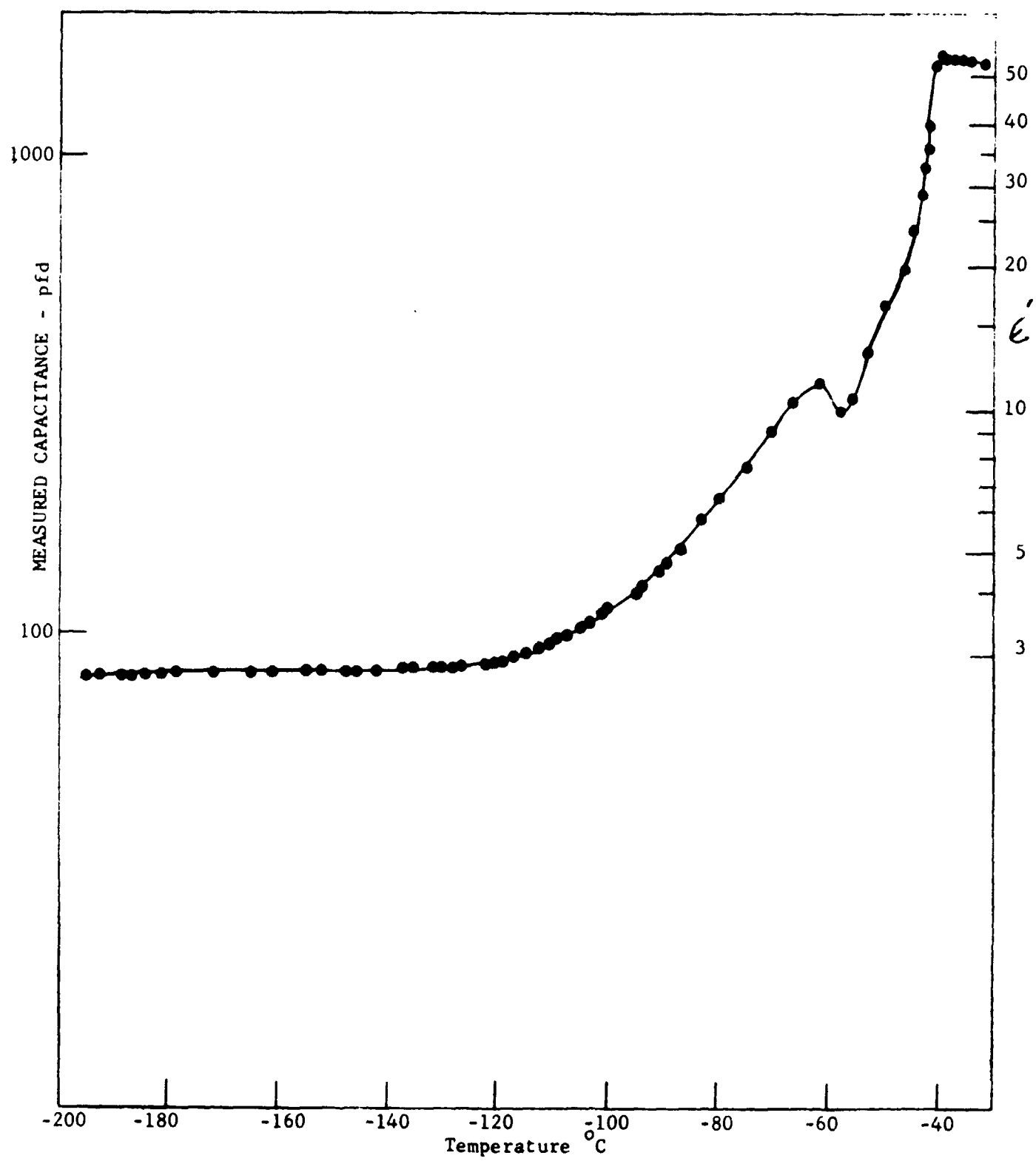


Figure 17. Permittivity at 1 kHz vs Temperature - Acetonitrile. (Frozen Without DC Bias)

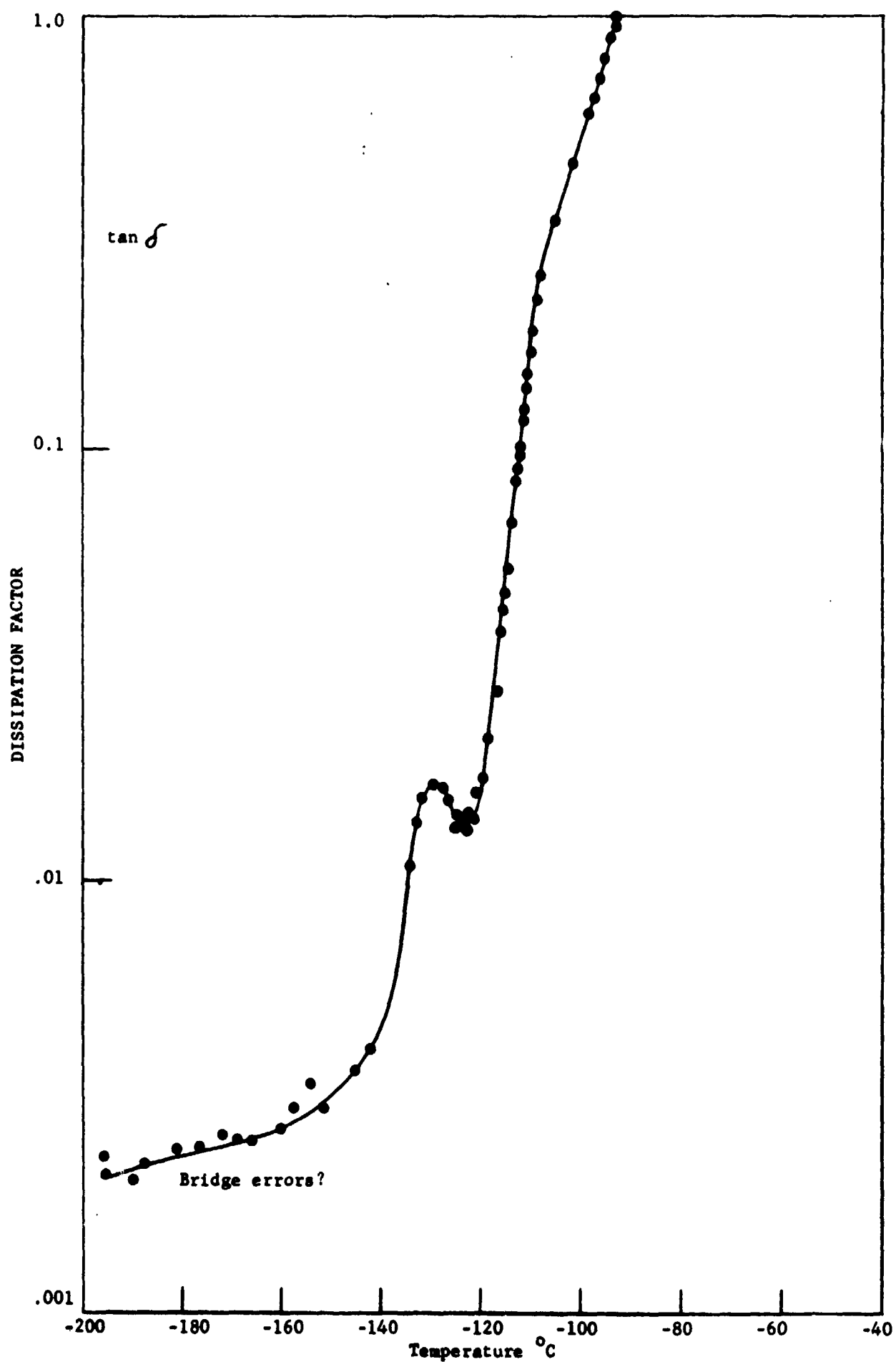


Figure 18. Dissipation Factor at 1 kHz vs Temperature - Propionitrile

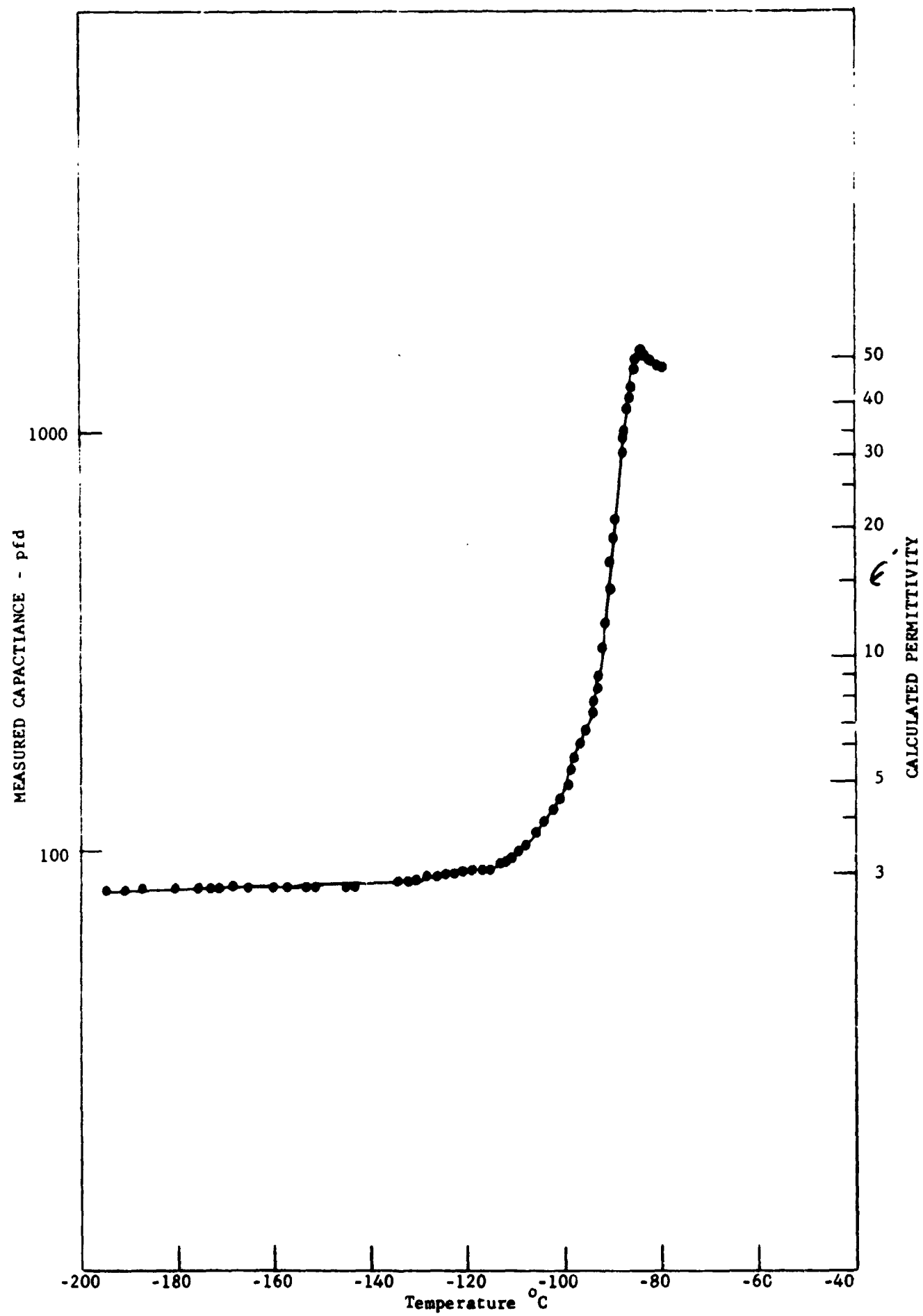


Figure 19. Permittivity at 1 kHz vs Temperature - Propionitrile

The voltage was removed during the measurement*. Generally, when permittivity is high for these liquids, the dissipation factor ($\tan \delta$) is also high. The best results were achieved with 1-nitropropane frozen with a DC bias. The appearance of a dissipation factor minimum of .019 (see Figure 7) at about -105°C (the approximate freezing temperature) with an associated permittivity of about 45 is encouraging. Unfortunately, without the bias, the loss was increased by a factor of 3 or more. The mixture of 1-nitropropane and isopentane was used in an attempt to lower the freezing temperature of the nitropropane. Down to quite low temperatures isopentane and nitropropane are miscible in all proportions. However, at just below the freezing temperature of the nitropropane, the isopentane separates out and the results reported are probably those for 1-nitropropane. A number of measurements were made with alcohols also. For butyl alcohol a maximum value of $\epsilon' = 11$ with $\tan \delta = .106$ was obtained. The lower alcohols have higher permittivity but also much higher losses.

It is recognized that purity and dryness may be very important as demonstrated by Prof. la Coste at the University of Toulouse in France. Attempts were made to dry and purify 1-nitropropane by distilling it over P_2O_5 . Test results over the full temperature range failed to show any decrease in dissipation factor as compared to the undried material. Perhaps the drying was unsuccessful or the liquid picked up moisture as it was transferred to the measuring cell which also had been carefully dried.

During the study of the dielectric liquids, L. J. Hogue suggested that some very newly developed silicone liquids with which he was working might have interesting properties at low temperatures. A series of three of these liquids were measured as a function of temperature with results given in Figures 20 and 21. While the maximum permittivity of the silicones is less than that for 1-nitropropane, the dissipation factor is very low at the minimum associated with the capacitance peak as summarized below:

*However, the voltage may have reappeared with the material acting as an electret. This voltage may have been responsible for the subsequent failure of the automatic bridge.

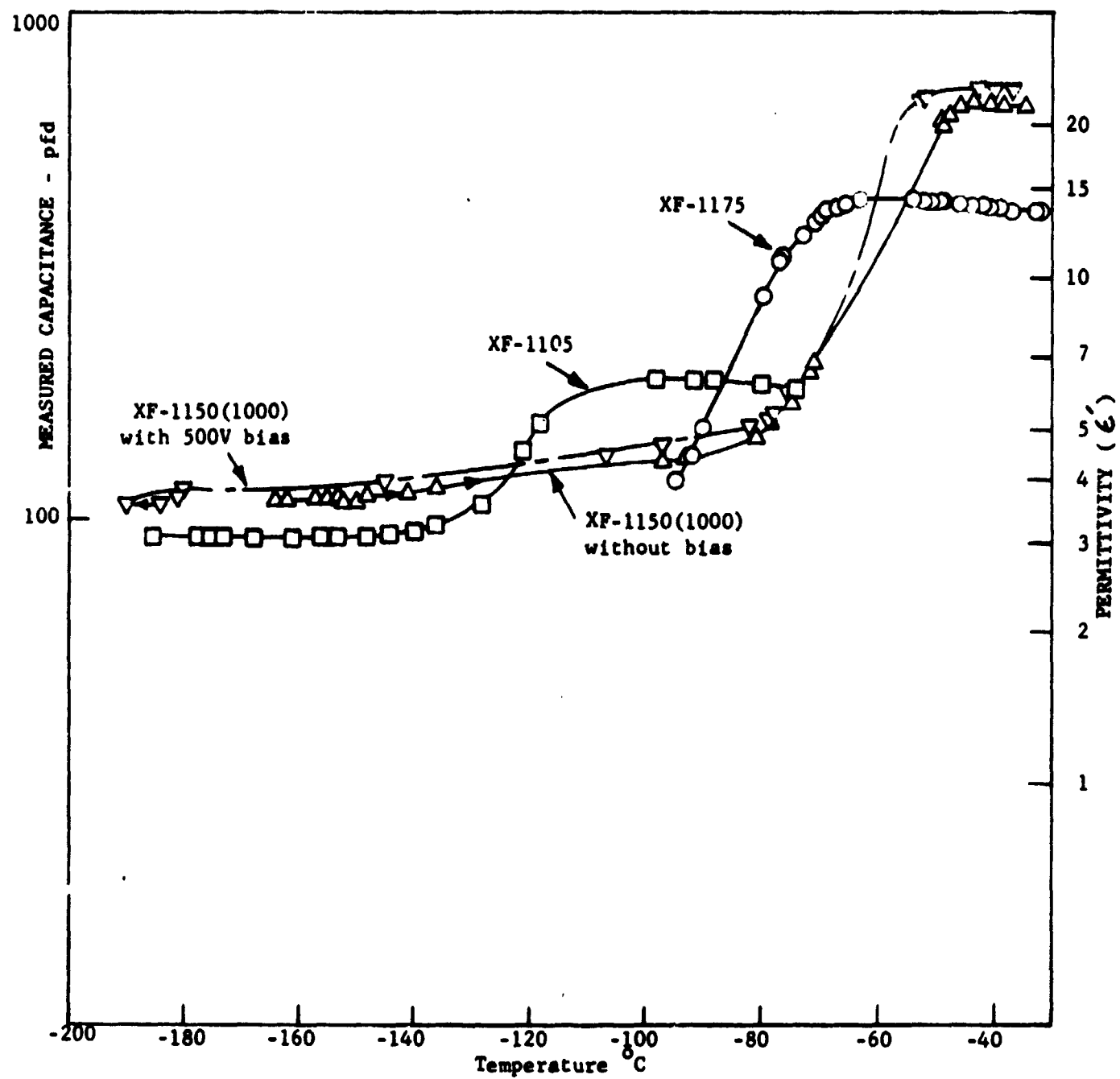


Figure 20. Permittivity, ϵ' vs Temperature Hi-K Silicone Liquids

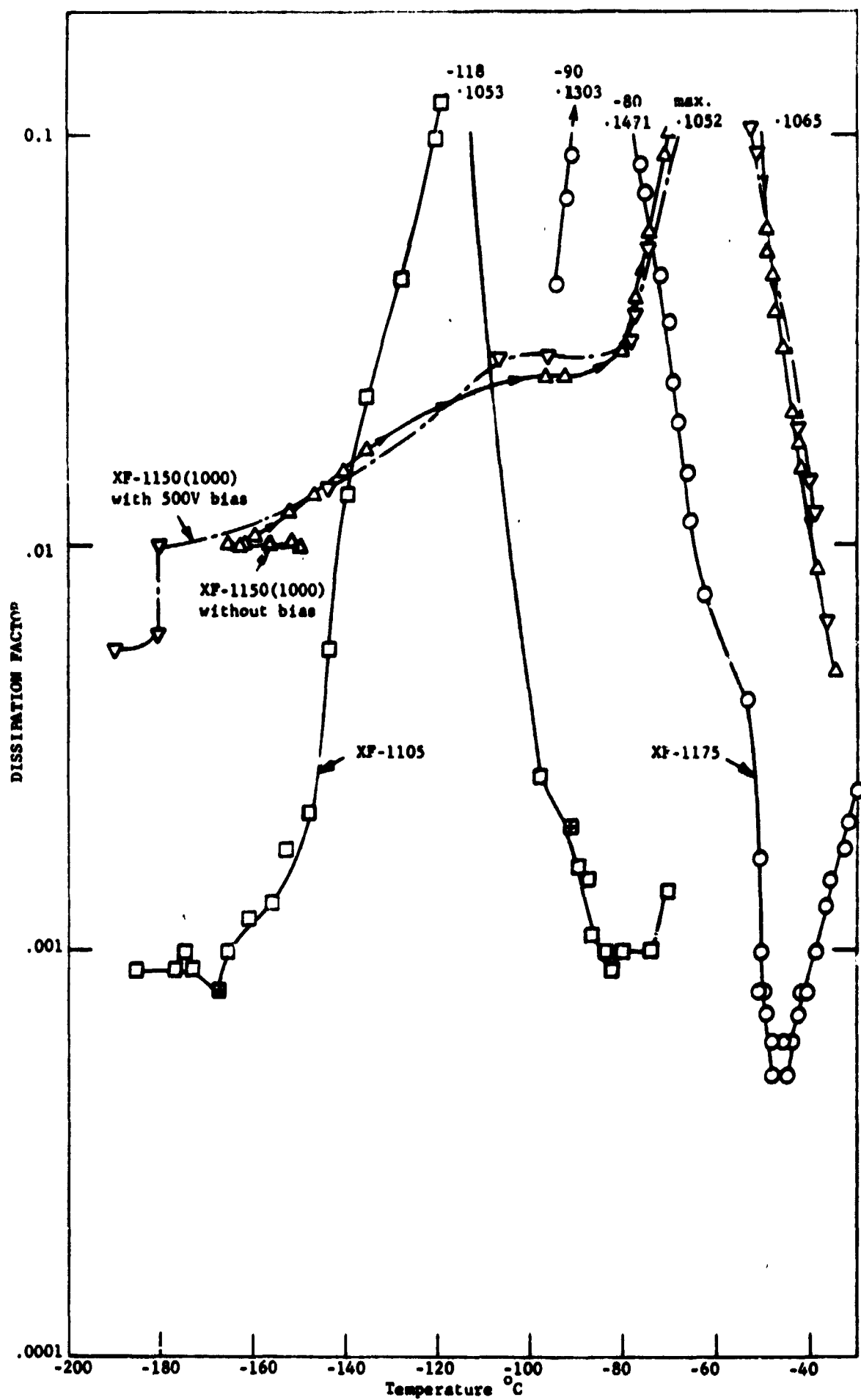


Figure 21. Dissipation Factor, $\tan \delta$ vs Temperature Hi-K Silicone Liquids

<u>Silicone No.</u>	<u>Temp. °C</u>	<u>Permittivity</u>	<u>Dissipation Factor</u>
XF 1150	above -35	21.5	less than .005
XF 1175	-47	14	.0005
XF 1105	-83	6	.0009

Unfortunately, the silicone liquid with the highest ϵ' also freezes at the highest temperature. Isopentane is miscible with the silicone liquids throughout the temperature range even as they freeze. Unfortunately a combination of silicone and isopentane was not measured in the liquid cell. However, measurements have been made of such a mixture as an impregnant for a small capacitor.

Wound Capacitors

Generally, it is possible to "stack" capacitors even with brittle insulating film. As described in Table X, two small capacitors were made in this way using #6 film. However, it was ultimately possible to roll even #6 film. Permittivity for the capacitor dielectrics was calculated from the measured capacitance and the dimensions of the rolled area. Consequently, the permittivity depended to some extent on the mechanical "tightness" to which the insulated foil could be wrapped around the support (usually a Teflon or phenolic-paper rod or tube). As skill developed, the mechanical construction was improved. However, all of the values for ϵ' in Table X are really estimates for rough comparison. The relative values for the same capacitor at different temperatures can be compared more closely.

The influence of 1-nitropropane and the silicone liquids on the $\tan \delta$ and ϵ' of the powdered ferroelectric coatings (#6, #7 and #9) and on three types of paper is shown in Table X. From the curves for the liquids by themselves (Figures 9, 10, 20 & 21) it is apparent that maxima should occur in $\tan \delta$ and ϵ' for impregnated capacitors. From Table X it is obvious that they do. The curves of $\tan \delta$ and ϵ' versus temperature can become quite complicated as illustrated in Figure 22 for capacitor B (Table X) with nitropropane + isopentane as the impregnant. It should be remembered that isopentane separates as the nitropropane freezes. The isopentane remains as a liquid surrounding the crystals of frozen nitropropane. The liquid phase appears to increase the electric strength. As with the nitropropane liquid by itself, high values of ϵ' are achieved only with associated high values of $\tan \delta$.

Table X
DISSIPATION FACTOR AND PERMITTIVITY
Small Capacitor Specimens

<u>Capacitor</u>	<u>Coating</u>	<u>Liquid</u>	<u>Temp. °C</u>	<u>Tan δ</u>	<u>ϵ'</u>
A	#6*	Nitrogen	-196	.0019	20.1
B	#6*	1-nitropropane + isopentane 3:1	-196	.0020	25.9
			-140	.0035	30.0
			-105	.30	60.0
C	#6	XF-1150 Silicone	-196	.002	29
			- 35	.05	64
D	#7	XF-1125 Silicone	-196	.005	36
			- 72	.045	45
			- 62	.105	80
E	#9	XF-1105 Silicone + isopentane, 4:1	-196	.0012	34
			-115	.0104	47.5
			- 88	.0025	46
F	.001"-0.9 density cel- lulose paper	1-nitropropane + isopentane, 3:1	-196	.011	3.5
			-155	.187	6.6
			-105	1.05	9.0
G	.002" Schweitzer MX-paper	1-nitropropane	-196	.0027	3.5
			-108	.05	10.5
H	.002" Nomex paper	1-nitropropane	-196	.0022	4.0
			-156	.0082	5.5
			-104	.294	38.5
I	.002" Schweitzer MX-paper	XF-1105 Silicone + isopentane, 4:1	-103	.0093	12

*Stacked capacitor. All others are rolled.

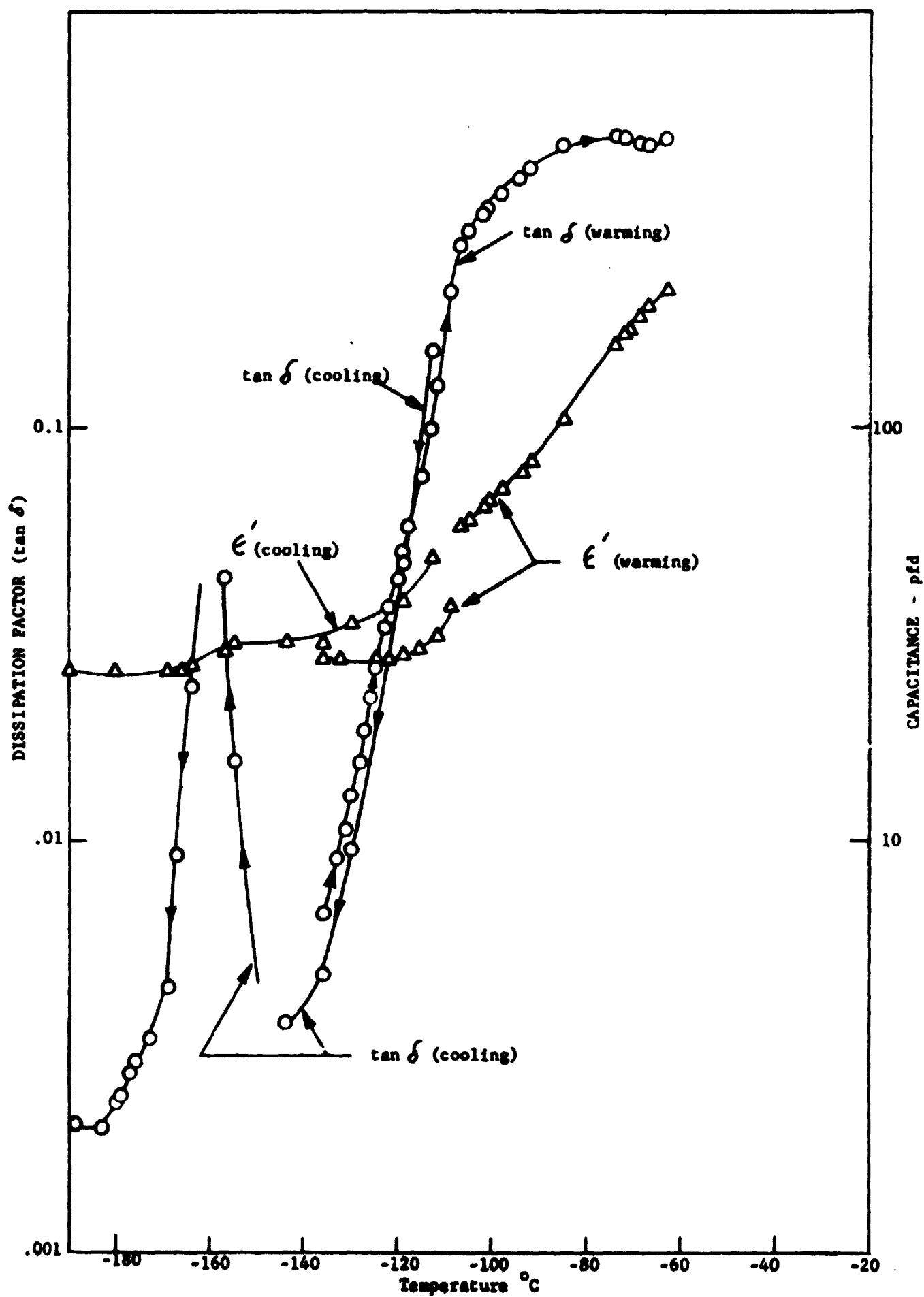


Figure 22. Permittivity, ϵ' , and Dissipation Factor, $\tan \delta$, vs Temperature Stacked Capacitor - #6 Ceramic Coating + 1-Nitropropane with Isopentane

Results for capacitor C are plotted in Figure 23 and for Capacitor D in Figure 24. By comparison with Figure 20 it is apparent that the minimum in $\tan \delta$ occurs at about the same temperature when silicone liquids are used as impregnants as for the liquids alone. The sharpness of these minima will make the control of temperature very important if a capacitor is to be designed to operate in the range of the $\tan \delta$ minimum. Of course, nitrogen alone can be used as an impregnant and its temperature is controlled primarily by boiling at atmospheric pressure.

Three paper dielectrics were impregnated with 1-nitropropane and XF-1105 silicone fluid (see Table X). Both liquids were also used in combination with isopentane. As noted earlier, the isopentane impregnates the crystals of frozen nitropropane. With the silicone fluids, the addition of isopentane depresses the freezing point so that the combination appears to freeze to a glassy rather than a crystalline solid.

From the results in Table X it is apparent that a sufficiently high permittivity to be interesting is not achieved when the liquids are used as impregnants for paper except for nitropropane with duPont Nomex (an aromatic polyamide film paper). In this case a value of $\epsilon' = 38.5$ was achieved but the associated value of $\tan \delta$ is high.

Measurements were made in some cases as a function of frequency but for capacitors only at -196°C in liquid nitrogen. Rather typical results are shown in Table XI. While the changes are small, the effect of the dipole nature of the dielectric is obvious. Similar and larger changes have been measured for nitropropane and the silicone liquids near their freezing temperatures.

Attempts were made to measure the resistivity of the capacitors at 500 volts DC. Unfortunately, capacitors A, B, and C failed. This failure has been attributed to imperfections in the film (see earlier results) but faulty construction may have been involved also. With the remainder of the capacitors, the leakage resistance at low temperatures was too high to measure (above 10^{15} ohms) or in some cases was erratic and variable.

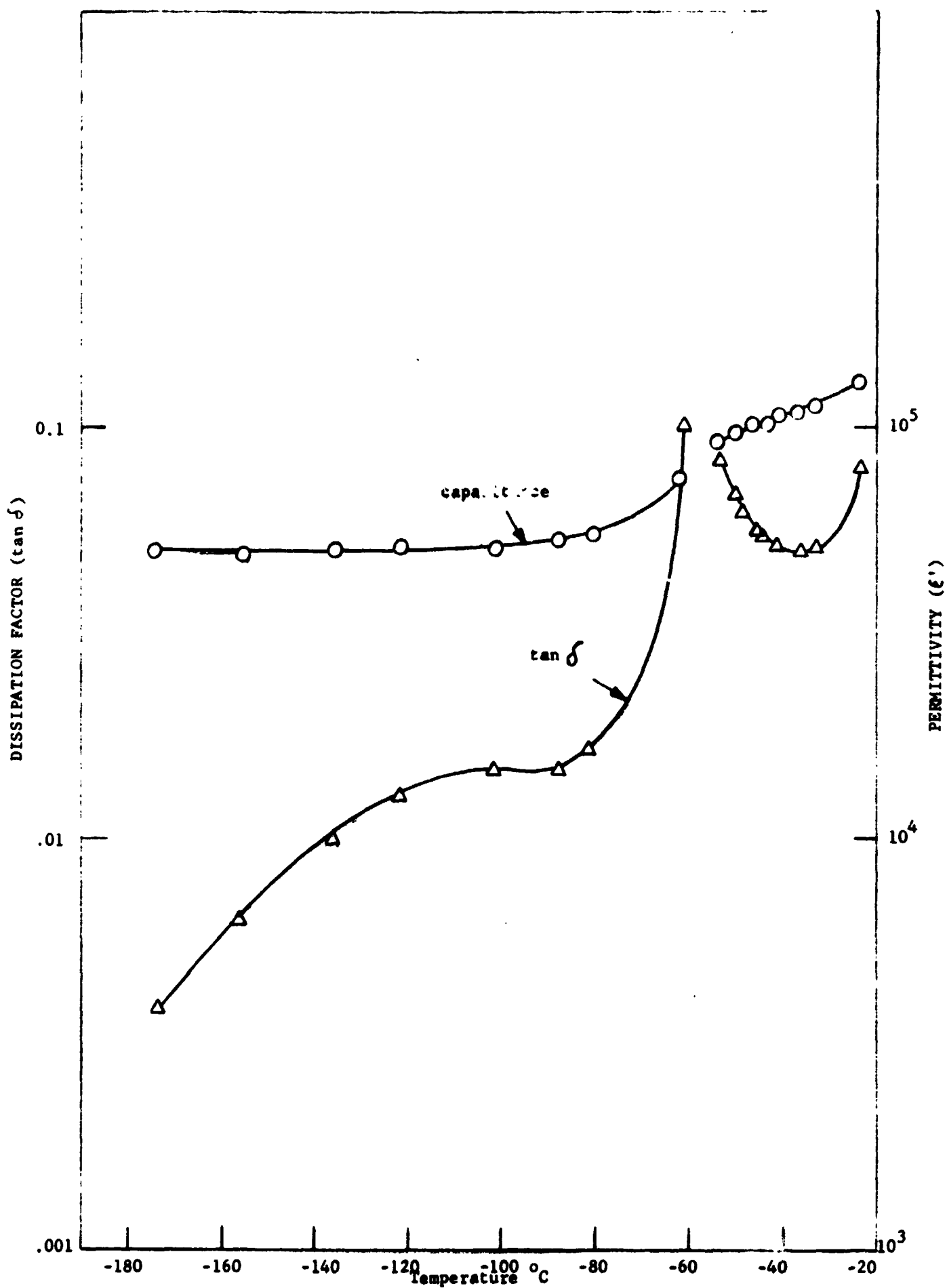
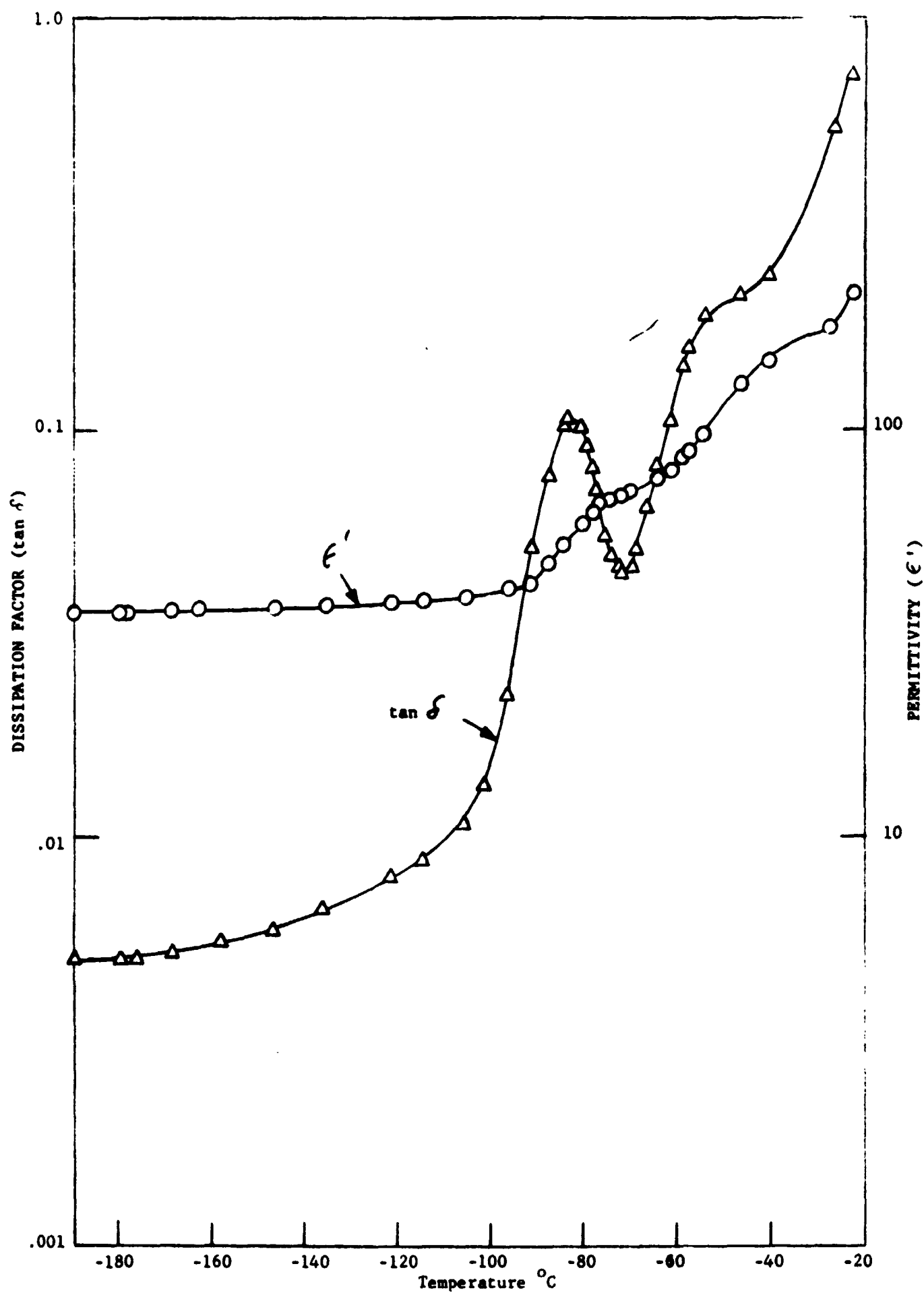


Figure 23. Capacitance, ϵ' and Dissipation Factor, $\tan \delta$, vs Temperature Wound Capacitor with #6 Ceramic Coating + Silicone



• Figure 24. Permittivity, ϵ' , and Dissipation Factor, $\tan \delta$, vs Temperature Stacked Capacitor - #7 Ceramic Coating + 1105 Silicone

Table XI

AC CHARACTERISTICS VS. FREQUENCY

Stacked Capacitor A - .0025 in. #6 Coating on .00025" foil
In Liquid Nitrogen at -196°C

<u>Frequency</u> <u>Hz</u>	<u>Capacitance</u> <u>pF</u>	<u>ϵ'</u>	<u>$\tan \delta$</u>
100	4766	20.2	.00135
500	4757.8	20.2	.00168
1,000	4753.5	20.1	.00189
2,000	4748.8	20.1	.00194
5,000	4742.9	20.1	.00170
10,000	4739.7	20.1	.00152

A voltage stress of about 1500 volts per mil was held on capacitor #E for over an hour without failure but it failed at about 1800 volts per mil when the voltage was increased. The inability to obtain good voltage performance led to the studies described earlier. Voltage breakdown tests were not attempted with capacitors F, G and H since their values of ϵ' were too low to be of interest in this program.

Anodic Coatings

In the various types of electrolytic capacitors, the intrinsically high electric strength and the large surface of oxide film on base metals such as aluminum are utilized. To achieve electrical contact with the large surface area it is necessary to use a liquid or "solid" electrolyte against the surface of the oxide. The electrolyte introduces relatively high dielectric loss and contributes to limitations in overall electric strength. Nevertheless, the energy storage density in electrolytic capacitors is very high.

A concept was advanced that it might be possible to achieve a higher electric strength in oxide films at low temperatures since the influence of moisture would be "frozen" out. To attain a good contact to the anodic film, the use of high permittivity liquids was proposed. Since the permittivity of the oxide film is low, most of the voltage should appear across the oxide film.

To obtain a wide variety of anodic coatings would have exceeded the capability of this program. Instead, one type of anodized foil, used in conventional electrolytic capacitors, was obtained and washed in distilled water. Both 1-nitropropane and XF-1150 silicone were used as impregnants. The permittivity attained at -105°C was estimated at about 10 or less and the values of $\tan \delta$ were high. It was obvious that more time was needed for more intensive study than was justified by the relatively uninteresting results obtained. The program on anodic films, therefore, was discontinued.

PHASE B - CRYOGENIC CAPACITOR PERFORMANCE ESTIMATES

In this section we have estimated the expected performance of cryogenic capacitors based on the values of dielectric constant and voltage stress obtained in the experimental program. By performance, we mean essentially energy density, size and weight of the package including refrigeration. The refrigeration capacity is governed by the total system losses, which include dielectric losses in the capacitor itself, lead losses, and conduction losses through the cryogenic vessel.

Capacitor Parameters

Although the results of the experimental program are somewhat tenuous in terms of firm predictions of what can actually be achieved in capacitor systems, we have chosen three levels of parameters, in terms of relative confidence of achievement. The parameters pertinent to these levels are listed in Table XII below, where three confidence ratings are chosen as probable, possible and optimistic. In Table XII we also list the dielectric constant, voltage stress achievable, and the resulting theoretical energy density; i.e., $\frac{1}{2} \epsilon E^2$

TABLE XII

<u>Case</u>	<u>Confidence Level</u>	<u>Voltage Stress V/mil</u>	<u>Dielectric Constant</u>	<u>Loss Tangent</u>	<u>Theoretical Energy Density Joules/cu in</u>
1	Probable	1500	40	0.004	21
2	Possible	2500	40	0.001	60
3	Optimistic	2500	80	0.001	120

Whether or not these levels can be achieved remains for more experimental work. Therefore, this section essentially defines the payoff which might result if these properties could be achieved. Estimates of vessel size - heat loads, etc. have been made for cases 1 and 2 (only) above, and are summarized below.

Performance Results

The theoretical energy densities above, of course, must be de-rated since the volume referred to is strictly the volume of dielectric itself. Electrode

material, supports, leads, and other factors will decrease the actual energy density to be achieved. Therefore, we have de-rated the theoretical energy densities by a factor of 2 to allow for the density of a practical capacitor system. In addition to that volume, we have added extra volume for the dewar system, as discussed later. The method of calculating loss in the capacitor is discussed in a later section. This loss, of course, is related to the duty cycle and we have calculated the total losses as a function of duty cycle for a number of assumed energy levels ranging from 20 to 200 kilojoules. The results are shown in tabular form in Tables XIII and XIV. Tables XIII and XIV give the capacitor volume, the dewar dimensions, and a breakdown of the losses for various assumptions. In this table, the dewar dimensions have been calculated assuming a right circular cylinder of height approximately 4 times the diameter. Thirty percent of the dewar height is taken up by the neck. As can be seen from Tables XIII and XIV, the energy deposited in the leads by resistive heating is an important load. In this case, the leads were calculated in such a way that the steady state background heat loss to the dewar was kept at a reasonably low value, since presumably, the duty cycle would be random, and it is best to minimize this loss while accepting a somewhat higher loss during discharge. This trade-off could be changed in many ways, depending on the particular application and duty cycle. Fig. 25 shows estimated refrigerator sizes, weights and costs for various heat loads. These data were taken from manufacturers specifications.

TABLE XIII - CAPACITOR DATA
Case 1 - Probably Achievable

Stored Energy kJ	Capacitor Volume cu. in.	Dewar Dimensions Diameter/ Height Inches	Dewar Loss watts	Lead Conduction Loss watts	Dielectric Loss joules	Lead Resistive Loss-joules	Total Loss watts for Duty cycle shots/min.				
							2	1	.5	.1	.05
20	2000	14/35	6	2	320	175	25	16	12	9	8
50	5000	19/48	9	3	800	315	49	30	21	14	13
100	10,000	23/60	13	4	1600	470	86	52	35	21	19
200	20,000	29/75	17	5	3200	750	152	89	55	29	25

TABLE XIV - CAPACITOR DATA
Case 2 - Possibly Achievable

Total Losses at Duty Cycle Discharges/min					Watts				
2	1	.5	.1	.05	2	1	.5	.1	.05
					175	15	10	8	7
20	680	11/24	4	2	80				6
50	1700	14/33	6	3	315	26	17	13	11
100	3400	17/42	8	4	470	41	27	20	16
200	6800	21/53	11	5	750	69	43	30	24
					800				20

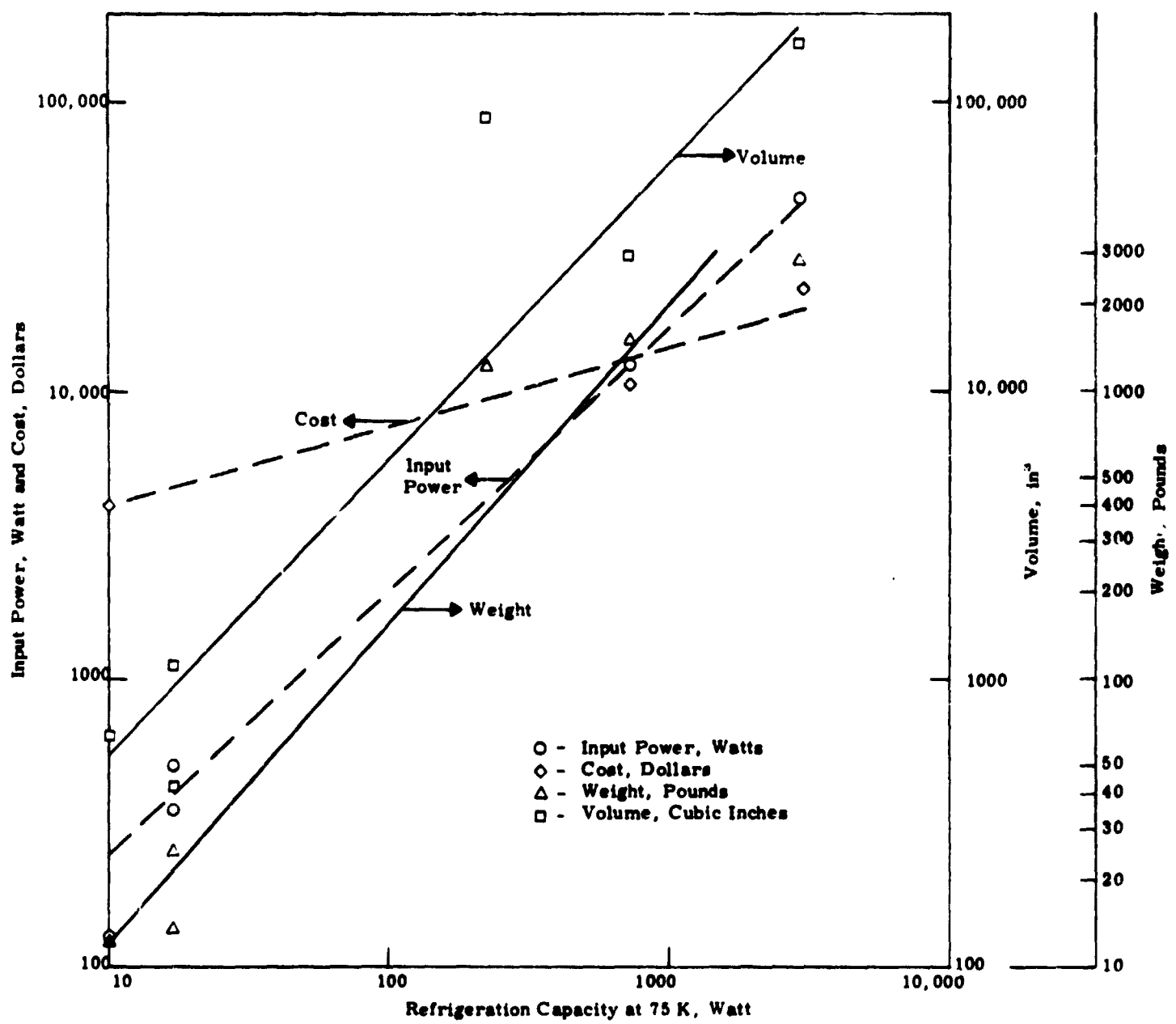


Figure 25. Performance Parameters for Commercial Nitrogen Refrigerators

For the smaller heat loads and for terrestrial applications, it is clear that the use of bulk nitrogen as a refrigerant would be most efficient and convenient. However, mechanical refrigerators are available and could be coupled to the system if desirable. While a complete range of values is not plotted, it is of interest to examine two extremes in the matter of capacitor weight, refrigerator weight and nitrogen volume requirements, should the latter be used as a batch coolant. In order to pick two extreme cases, we have taken the smallest capacitor and the largest capacitor in each tabulation. The weight of the capacitor is calculated by using an overall density figure of 0.067 per cu. in. (1.6 grams per cc), which results from the use of a density of 2.5 for the capacitor material itself, and a density of 0.8 for the nitrogen which fills the space between the capacitor units. Table XV below shows the results of this analysis.

TABLE XV

Refrigeration Data Based on One Discharge/min-average

<u>Energy</u> <u>kJ</u>	<u>Total</u> <u>Dewar</u> <u>Volume</u> <u>cu. in.</u>	<u>Refrigerator</u> <u>Volume</u> <u>cu. in.</u>	<u>Capacitor</u> <u>Weight</u> <u>pounds</u>	<u>Refrigerator</u> <u>Weight</u> <u>pounds</u>	<u>Nitrogen</u> <u>Consumption</u> <u>Liters/hr</u> <u>*</u>
			<u>Case 1</u>		
20	5600	900	120	20	0.36
200	48,000	5000	1200	130	2.0
			<u>Case 2</u>		
20	2100	550	40	12	0.23
200	18,000	2500	1200	60	1.0

* Specific gravity of LN₂ is 0.8

Dewar Configuration

The capacitors and liquid nitrogen bath will be contained in an insulated vessel or dewar. It was assumed that the capacitor bank would be in the form of a rectangular solid, with the long dimension in the vertical direction, and with a square horizontal cross-section. The vertical dimension was assumed to be three times the side of the square cross-section. The dewar was assumed circular in cross-section, and was just large enough in diameter to contain the capacitor bank. The walls of the dewar extended above the top of the capacitor bank by one-third the vertical dimension of the capacitor bank. This extension was to permit filling of the dewar with liquid nitrogen above the capacitor level and to reduce heat load due to conduction down the neck walls.

The following sources of heat leak into the system were considered:

- (1) Conduction down the electrical conductors
- (2) Conduction and radiation through the dewar insulation
- (3) Conduction down the dewar neck
- (4) Radiation through the dewar neck

Dewar insulation will likely consist of either vacuum with no radiation shielding, or vacuum with "multi-layer" radiation shielding. The latter will be used if the additional expense can be justified by the need to conserve liquid nitrogen, or to reduce the size of refrigerator used. A one-inch thickness of multi-layer radiation shielding, with a thermal conductivity of 3 microwatt/cm²K, was assumed for these calculations.

Conduction was also assumed to take place through the inner wall of the dewar neck, which extends from the room temperature environment at the top, down to the liquid nitrogen level at the bottom. In order to make removal of the capacitors easy, the neck diameter was designed as large as the rest of the dewar. The small increase in heat load resulting from the large neck diameter was considered justified by the increased ease of maintenance. The neck wall was taken to be 0.030 in. thick stainless steel.

Radiation from room temperature to the liquid nitrogen level through the neck was assumed negligible, since radiation can be reduced considerably by insertion of horizontal radiation shields or baffles. If the system is not refrigerated, then the boil-off nitrogen will cool these baffles, further reducing the radiation heat load.

Losses

In order to evaluate both dielectric and lead losses, the mode of discharge must be specified. In the NASA metal forming application, a damped oscillatory discharge is used with approximately 70% reversal. The circuit is allowed to ring down completely. This is a relatively severe condition from the point of view of losses. For a discharge of this nature, the load current is given by the expression:

$$I = I_p e^{-t/\tau} \sin \omega t \quad (1)$$

$$I_p = E/\omega L$$

where

E = capacitor voltage

L = Load inductance

ω = natural frequency = $\left(\frac{1}{LC} - \frac{R^2}{4L^2} \right)^{\frac{1}{2}}$

$\omega = \frac{1}{\sqrt{LC}}$ to high accuracy for this condition

$\tau = 2L/R$ damping time constant

Using the condition of 70% reversal it is possible to show from equation (1)

$$\omega \tau = 8 \quad (2)$$

Dielectric Losses

The dielectric losses per discharge are given by:

$$U_D = \int_0^{\infty} \frac{I^2}{\omega C} \tan \delta \, dt \quad (3)$$

$U = \text{Loss}$

$C = \text{Capacitance}$

$\tan \delta = \text{Loss tangent}$

Using (1) it is possible to show that

$$\int_0^{\infty} I^2 dt = I_p^2 \frac{\tau}{4} \left[1 - \frac{1}{(\omega \tau)^2} \right] \approx I_p^2 \frac{\tau}{4} \quad (4)$$

Then the losses are

$$U_D = \frac{I_p^2}{\omega C} \frac{\tau}{4} \tan \delta \quad (5)$$

By manipulating the above equation and using $\omega \tau = 8$ it is possible to show that:

$$U_D = 4 W \tan \delta \quad (6)$$

where W is the total stored energy.

This equation has been used to calculate the dielectric losses.

Lead Losses

The lead design is a compromise between steady state conduction of heat, for which a small conductor area is desired, and resistive heating, for which a large conductor area is desired. The lead area could be optimized for a particular duty cycle. Here we will merely give some example calculations.

Thermal Conduction

In order to evaluate the thermal conduction loss, we use the equation

$$Q = \frac{A}{l} \int_{T_1}^{T_2} k dT \quad (7)$$

$Q = \text{loss, watts}$

$A = \text{Area, cm}^2$

$l = \text{Length, cm}$

$k = \text{Thermal conductivity, watts/cm-deg C}$

The thermal conductivity varies with temperature in this expression. Values of the thermal conductivity integral are tabulated in the literature; the value for copper between 77 K and room temperature is 934.

In order to have the steady state conduction loss at a level which is comparable to the dewar loss an arbitrary value of one watt per lead will be assumed.

The lead length must be approximately 75 cm for the dewar design chosen.

Using these values yields a lead area of 0.08 cm^2 .

Resistive Losses

The resistive losses in the lead are given by

$$U_R = \frac{\rho l}{A} \int_0^{\infty} I^2 dt = \frac{\rho l}{A} I_p^2 \frac{\tau}{4} \quad (8)$$

By combining the following relationships:

$$I_p^2 = \left(\frac{E}{\omega L} \right)^2 \quad W = \frac{1}{2} C E^2$$

$$\omega = 1/\sqrt{LC} \quad \omega \tau = 8$$

It is possible to show that

$$I_p^2 \tau = \frac{16 \sqrt{2} W^{3/2}}{E \sqrt{L}} \quad (9)$$

and

$$U_R = \frac{4 \sqrt{2} W^{3/2}}{E \sqrt{L}} \frac{\rho l}{A}$$

This is a useful relation since it shows how the resistive losses scale with stored energy.

Lead losses have been calculated using the following typical values.

$W = 20,000$ joules

$L = 50$ microhenries

$E = 20,000$ volts

$l = 75$ cm

$A = 0.08$ cm

$\rho = 0.8 \times 10^{-6}$ ohm cm

The resistivity taken is half that of copper at room temperature, since the end of the lead at liquid nitrogen temperature will have approximately 1/8 its room temperature resistivity.

The above values give a lead loss of

90 Joules/lead

180 Joules/discharge

Equation (9) shows that the resistive losses increase as the $3/2$ power of the stored energy. It is probable that the load inductance will also increase making the resistive losses vary nearly directly with the energy. The capacitor voltage may stay nearly constant at its maximum practical value.

For purposes of the present calculation it will be assumed that the conduction losses are kept at a constant fraction of the vessel losses by using larger area leads at higher energy levels. The fraction $W^{3/2}/\sqrt{L}$ will be assumed constant, reflecting the fact that larger loads will undoubtedly have larger inductance. Hence, the lead resistive loss will be a smaller fraction of the total at higher levels of energy storage.

APPENDIX A

Composition of Ferroelectric Powder Coatings

(NOTE: Each coating contained 4 drops of Triton X-100 and
GE Silicone Anti-foam #60)

Coating #1

15 cc	-	Carter's Glue	
33 cc	-	Glycerine	
337 gm	-	TiO ₂	Poor Adhesion to
79 gm	-	SrTiO ₃	Aluminum Foil
72 cc	-	Water	

Coating #2

31 cc	-	Carter's Glue	
33 cc	-	Glycerine	
337 gm	-	TiO ₂	Improved Adhesion
79 gm	-	SrTiO ₃	
60 cc	-	Water	

Coating #3

34 cc	-	Carter's Glue	
33 cc	-	Glycerine	
337 gm	-	SrTiO ₃	Poor Adhesion to
79 gm	-	TiO ₂	Aluminum Foil
65 cc	-	Water	

Coating #6

15 cc	-	Swift #2266 Protein Colloid	
10 cc	-	Glycerine	
320 gm	-	SrTiO ₃	
80 gm	-	TiO ₂	
100 cc	-	Water	

Coating #7

15 cc	-	Swift #2226 Protein Colloid	
10 cc	-	Glycerine	
500 gm	-	BaTiO ₃	
90 cc	-	Water	

Coating #8

Same as Coating #7 with
glycerine omitted.

Coating did not contain glycerine
and could not be coated smoothly.
Coated satisfactorily when glyc-
erine was added.

APPENDIX A (Cont'd.)

Coating #9

15 cc - Swift #2226 Protein Colloid
10 cc - Glycerine
400 gm - SrTiO_3
90 cc - Water

Coating #10

15 cc - Swift #2226 Protein Colloid
65 cc - 2.5% Polyvinyl Alcohol (PVA) in Water
33 cc - Glycerine
420 gm - SrTiO_3
75 cc - Water

Coating #11

20 cc - Swift #2226 Protein Colloid
70 cc - 3% Polyvinyl Methyl Ether (PME) in Water
10 cc - Glycerine
470 gm - SrTiO_3
90 cc - Water

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