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A STUDY OF THERMISTOR MATERIALS FOR USE AS TEMPERATURE-SENSING ELEMENTS IN THE HIGH-VELOCITY EXHAUST GASES OF JET-TYPE ENGINES

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FOREWORD

This report was prepared jointly by representatives of the New Jersey Ceramic Research Station, Rutgers University (Contract AF 33(616)-241) and of the National Bureau of Standards (Delivery Order 33(616)53-1). Both the Delivery Order and the Contract, identified by Project No. 3073-30245, "Thermocouples and Pyrometric Devices," are administered under the direction of the Power Plant Laboratory, Wright Air Development Center, with Lt. Don G. McKee acting as project engineer.

Part I, "Development of the Thermistors," was prepared by Harriet R. Wisely of Rutgers University, with contributions to the experimental work made by F. K. Davey and J. R. Finlayson. Part II, "Performance of the Thermistors," was prepared by Paul D. Freeze and Ernest F. Fiock of the National Bureau of Standards.

ABSTRACT

The report describes the development and evaluation of thermally sensitive resistors (thermistors) of semi-conducting materials designed for possible application in the exhaust gases of turbojet engines throughout the approximate range 1000° to 2000°F. The development and preliminary evaluations of materials were conducted at Rutgers University, and more detailed studies of performance as temperature indicators were conducted at the National Bureau of Standards. Of the wide variety of materials tested at Rutgers, vitrified alkali porcelains appear to best meet the minimum requirements as to resistance, sensitivity, and stability in oxidizing and reducing atmospheres. Four of these were provided with platinum leads at Rutgers and calibrated in exhaust gases and in a furnace at NBS, where each was checked from six to nine times. The calibration data are presented as deviations from straight lines of the form $\log R = a + b/T$, within the range 1000° to 1700°F. Of the 207 observations taken over heating periods totaling about 90 hours for each thermistor, the differences from the equations exceeded 20°F at only eight points, and exceeded 10°F at only 40 points, there being no consistent trend with either time of heating or temperature.

Much additional work remains to be done in the development of units suitable for application in turbojet engines. Problems of lead attachment, of insulation for the leads, of mechanical strength, and of rapid response are formidable. Additional information on effects of changing the voltage and frequency in the measuring circuit should be obtained. To date no promising means for using thermistors in parallel has been suggested. Some of these problems are to be investigated at NBS, using both the thermistors described in Part II and others of Shenango No. 6 porcelain prepared jointly by Rutgers and the B.G. Corporation.

PUBLICATION REVIEW

The publication of this report does not constitute approval by the Air Force of the findings or the conclusions contained therein. It is published only for the exchange and stimulation of ideas.

FOR THE COMMANDER:

for E. C. Phillips
NORMAN C. APPOLD
Colonel, USAF
Chief, Power Plant Laboratory
Directorate of Laboratories

TABLE OF CONTENTS

TABLE OF CONTENTS, CONTINUED

LIST OF ILLUSTRATIONS

LIST OF TABLES

A STUDY OF THERMISTOR MATERIALS FOR USE AS TEMPERATURE SENSING-ELEMENTS IN THE HIGH-VELOCITY EXHAUST GASES OF JET-TYPE ENGINES

Part I. Development of the Thermistors

by Harriet R. Wisely

I. INTRODUCTION

Background:

The problem of discovering a ceramic material suitable for use as a temperature sensing element in the temperature range encountered in the exhaust gas stream of jet engines was begun at Rutgers University in August 1952. This problem had been previously worked on by Lear, Inc.,(1) where the production of a useful material whose electrical resistivity varied with temperature was attempted. Desirable electrical properties were obtained with a composition of beryllium and titanium oxides, but difficulties were encountered in attaching electrodes and in obtaining reproducible resistance values in oxidizing and reducing atmospheres. The Armour Research Foundation(2) later tackled the problem. There, ceramic compositions having high electrical conductivity at room temperature were developed from vanadium and tungsten compounds. These were found to be unstable at high temperatures in oxidizing atmosphere and were, therefore, unsuitable for use in jet engines.

Aims:

The principal requirements which must be met by a material in order for it to be useful as a temperature sensing element in jet engines are:

1. Some physical property of the material must change measurably with a change in its temperature. Many materials display a pronounced change in electrical resistivity with small changes in temperature. For this reason, a search for a useful thermistor (temperature sensitive resistor) material was selected as the object of the present experimental work. To obtain high sensitivity to temperature change, compositions were sought that provided a great change in resistivity within the temperature range which was of immediate interest (1000° to 2000°F).

2. The thermistor material must be physically and chemically stable throughout a wide temperature range (at least from room temperature to 2000°F) in order to give reproducible measurements within that range for extended periods of time under the varying atmospheric conditions provided by the exhaust gases of jet engines. Only relatively refractory compositions of the more stable oxides could be expected to meet this requirement. During the present investigation many oxide compositions were tested, particular attention being given to alumina and alumina-silica compositions containing alkali or alkali-earth oxides.

3. It must be possible to fabricate the thermistor material as a mechanically strong, non-absorbent, body capable of rapid response to thermal variations and able to undergo severe thermal shock without cracking. Serious consideration was given only to those compositions that could be produced as vitrified bodies (no penetration of an ink spot) since such a dense structure provided the best conditions for obtaining high mechanical strength, good thermal conductivity and characteristic electrical resistivity values.

Theory:

The electrical resistivity of metallic conducting materials characteristically increases with rising temperature. The reverse is true of ionic conducting materials, which include the majority of the crystalline oxides. Many of these have been found to follow the law of Rasch and Hinrichsen(3) which gives the relationship between electrical resistivity and temperature:

$$R = Ae^{B/T} \quad \text{or,} \quad \log R = \log A + B/\,2.303\,T$$

$$\text{differentiating:} \quad dR/dT = -BAe^{B/T} \quad \text{or,} \quad -BR/T^2$$

where: R = electrical resistivity in ohm cm; obtained from the specimen resistance in ohms multiplied by the electrode area, in cm^2, divided by the perpendicular distance between the electrodes given in centimeters.
T = °K, absolute temperature
A and B = constants characteristic of the material
e = base of natural logarithms

From this law it may be seen that, although the rate at which resistivity changes with temperature decreases rapidly with increasing temperature, a plot of log R vs. 1/T forms a straight line whose slope is determined by the constant B. The magnitude of the resistivity is largely determined by the characteristic constant A. Any abrupt change in the phase composition of the material with temperature causes a corresponding abrupt change in the constants A and B with a consequent abrupt change in resistivity. Ford and White(4) found that, as the temperature rose to within 200°C of the melting temperature of one or more of the components of a composition, the resistivity of the material departed radically from $\log R = \log A + B/ 2.303\ T$. As discussed by Stuart and Anderson(5), near and above the melting temperature of materials (and in glasses) the resistivity may best be expressed by the equation: $\log R = A + BT + CT^2$; where A, B, and C are constants characteristic of the material.

Application of Theory:

During the present investigation, compositions were sought that gave a straight line when log R vs. 1/°K was plotted. These, being reasonably free of phase changes within the temperature range 1000° to 2000°F, would be more likely to provide reproducible resistance values under conditions of fluctuating temperature. Furthermore, compositions which departed from the straight line relationship due to incipient melting of a portion of the material could not be expected to possess long term resistance stability at the higher temperatures.

Most of the ceramic compositions that were tested during this study are considered to be excellent electrical insulators at, or near, room temperature. A rapid decrease in resistivity as temperature was increased to 1000°F resulted in the resistivity values of many compositions falling within the range considered as useful. From practical considerations, involving ease of measurement and accuracy, of results, the resistance of a thermistor should not much exceed 10^6 ohms at 1000°F or fall much below 10^3 ohms at 2000°F. To assure mechanical strength, the shape factor for the thermistor, i.e., (area/thickness) probably should not much exceed a value of ten or fall much below one-tenth. Thus, the resistivity required for a material to be suitable for thermistor use in the temperature range of immediate interest, lay between 10^7 and 10^5 ohm centimeters at 1000°F and between 10^4 and 10^2 ohm centimeters at 2000°F.

Contents

II. COMPOSITIONS STUDIED

One of the principal requirements of a material, suitable for thermistor use in jet engine exhaust gases, is physical and chemical stability in the presence of strongly reducing and strongly oxidizing atmospheres, from room temperature through the highest temperature to which it would be subjected in use. For this reason, the present investigation was chiefly directed toward the study of relatively refractory compositions of the more chemically stable oxides. Alumina and alumina-silica compositions with alkali and alkali-earth oxide additions received particular attention.

These compositions were usually prepared as polycrystalline bodies. Both chemically pure materials and naturally occurring minerals were employed. The carefully blended mixtures were formed as pellets, or discs, (usually of one-half inch diameter) in a hardened steel die using forming pressures of up to 10 tons per square inch applied by a manually operated hydraulic press. The specimens so formed were fired in the neutral to oxidizing atmosphere supplied by kilns fired with city gas and compressed air. Undue contamination of test specimens was avoided by placing them for firing on relatively thick discs pressed from the same composition.

An effort was made to produce non-absorbent ceramic bodies for resistance testing. Although no quantitative tests were conducted to determine porosity (as by means of water absorption), a rough qualitative test was frequently made. This test consisted of placing a drop of ink on the specimen, allowing it to dry, then washing the sample under running water. If any evidence of the ink spot remained the ceramic body was considered to be porous. Occasionally, compositions were encountered that could not be produced as non-absorbent bodies. Some of these were tested despite this failure, but the resistivity values obtained could only be considered as indicative of the true, lower, resistivity.

Ink spot test

A number of specimens were shaped from fired bodies prepared by commercial manufacturers, or by other investigators at Rutgers. Three compositions were obtained as single crystals formed by the flame fusion process.

The oxide and batch compositions (when known) of the specimens tested are presented in the following tables accompanied by pertinent data on blending procedure and firing temperatures.

Table I.

MATERIALS USED IN EXPERIMENTAL BODIES

A. Grade and Supplier

Chemicals:

Al_2O_3 - (500 mesh, acid washed) Norton Company
SiO_2 - (see flint)
$BaCO_3$ - (C.P. grade) Baker's Analyzed Chemicals
$CaCO_3$ - (C.P. grade) Baker's Analyzed Chemicals
Co_3O_4 - (C.P. grade) Gen. Chem. Div., Allied Chem. & Dye Corp.
Cr_2O_3 - (C.P. grade) Gen. Chem. Div., Allied Chem. & Dye Corp.
K_2CO_3 - anhydrous (reagent grade) Merck & Company
Li_2CO_3 - (reagent grade) Merck & Company
MgO - (reagent grade) Merck & Company
$MgCO_3$ basic - (reagent grade) Baker's Analyzed Chemicals
NiO - (C.P. grade) Baker's Analyzed Chemicals
ZrO_2 stabilized - Titanium Alloy Manufacturing Company
ZrO_2 - (C.P. grade) Baker's Analyzed Chemicals

Minerals:

Flint - (200 mesh quartz) Pennsylvania Pulverizing Company
E.P.K. - (air floated) Edgar Plastic Kaolin Company
OM No.4 - (Kentucky ball clay, Old Mine No.4 air floated) Kentucky-Tennessee Clay Company
Vlvc. - (Velvacast, air floated) Georgia Clay Company
No.56 Spar - (No.56 glaze feldspar, 200 mesh) Consolidated Feldspar Corporation
Bk. Spar - (Buckingham feldspar, 200 mesh) Consolidated Feldspar Corporation
Ptl. - (Petalite, 100 mesh) Foote Mineral Company
Talc - (Sierra Hi-grade, 325 mesh) Sierra Talc Company

Table I. (cont.)

B. Oxide Composition of Minerals

(typical analyses provided by supplier as weight percent)

Mineral	SiO_2	Al_2O_3	K_2O	Na_2O	Li_2O	CaO	MgO	Fe_2O_3	TiO_2	Loss Ign.
E.P.K.	46.95	36.75	0.24	0.24		0.15	0.20	0.80	0.18	14.95
OM No.4	51.65	31.24	0.94			0.20	0.50	1.17	1.72	12.13
Vlvc.	45.12	38.12	0.13	0.31		0.03	0.22	0.63	1.35	13.75
No. 56 spar	68.4	19.4	3.0	8.4		0.8	tr.	0.09		0.2
Bk. spar	65.7	18.6	12.7	2.5		0.2	tr.	0.06		0.3
Ptl.	76.16	17.24	0.39	0.16	4.49	0.21	0.24	0.18		0.8
Talc	59.90	1.75	0.54	0.54		0.41	30.64	0.63		6.13
Flint	99.5 +									

Table II. COMPOSITION AND PREPARATION OF EXPERIMENTAL BODIES
A. Non-silicates

Identification	Oxide Comp. (wt %)	Batch Comp. (wt %)	Firing
80 Al, 20 Co	80 Al_2O_3, 20 CoO	79 Al_2O_3, 21 Co_3O_4	3100°F
$CoO \cdot Al_2O_3$	68 " 42 "	56 " 44 "	"
80 Al, 20 Cr	80 " 20 Cr_2O_3	80 " 20 Cr_2O_3	"
60 Al, 40 Cr	60 " 40 "	60 " 40 "	"
Cr_2O_3	0 " 100 "	0 " 100 "	"
80 Al, 20 Ni	80 " 20 NiO	80 " 20 NiO	"
60 Al, 40 Ni	60 " 40 "	60 " 40 "	"
80 Al, 20 Sr	80 " 20 SrO	74 " 26 $SrCO_3$	3000°F

Batches (25 gm) mixed dry for 10 minutes in automatic mortar, dampened, pressed as 1/2 in. diameter discs, fired for one hour in gas-air kiln. All samples were porous.

Identification	Oxide Comp. (wt %)	Batch Comp. (wt %)	Firing
ZrO_2 (Z-1)	100 ZrO_2	100 ZrO_2 (stabilized)	3500°F
90 Zr, 10 Ca (Z-6)	95 ZrO_2, 5 CaO	93 ZrO_2, 8 $CaCO_3$	"
50 Zr, 50 Ca (Z-7)	69 " 31 "	55 " 45 "	"

Batches (12.5 gm) blended dry in automatic mortar, dampened, pressed as 1/2 inch diameter discs, fired 1/2 hour in propane-oxygen fired kiln. Specimens somewhat porous.

Identification	Al_2O_3	MgO	Li_2O	Al_2O_3	MgO	Li_2CO_3	Firing
80 Mg, 20 Al	20.0	80.0	--	20.0	80.0	--	3100°F
$MgO \cdot Al_2O_3$ (L-1)	71.7	28.3	--	71.7	28.3	--	"
$(Mg,Li)O \cdot Al_2O_3$ (L-2)	71.7	28.1	0.2	71.5	28.0	0.5	"
" " (L-6)	72.2	25.7	2.1	70.0	24.9	5.1	"

Batches (25 gm) mixed as thin slip with acetone, dried, pressed as discs (1/2 inch diameter, 1/4 inch thick), fired one hour in gas-air kiln. All samples were porous, specimen L-2 developed cracks.

Table II (cont.)

B. Alkali-earth Aluminum Silicates

Identification		Oxide Comp. (wt %)			Batch Comp. (wt %)			Firing
		BaO	Al_2O_3	SiO_2	Calc*	Al_2O_3	SiO_2	°F
BaAlSi	(B-5)	84	4	12	100.0			2750
"	(B-2)	66	6	28	78.5	2.9	18.6	2300
"	(B-3)	53	19	28	63.1	16.5	20.4	2300

*Calcine batch: 870 gm $BaCO_3$, 30 gm Al_2O_3, 100 gm SiO_2: blended dry in baffle mill for 30 minutes, calcined at 2300°F, pulverized and stored for use. Hydrates readily.

Batches (25 gm) mixed dry for 1/2 hour in automatic mortar, dampened slightly, pressed as discs, fired at indicated temperature for one hour in gas-air kiln. All bodies somewhat porous; B-5 tended to hydrate at room temperature.

		CaO	Al_2O_3	SiO_2	$CaCO_3$	Al_2O_3	SiO_2	°F
CaAlSi	(C-9)	36	40	24	50.0	31.2	18.7	2525
"	(C-7)	21	38	41	32.2	32.6	35.2	2740
"	(C-1)	20	37	43	31.0	31.6	37.4	2740
"	(C-4)	18	41	41	28.2	35.9	35.9	2740
"	(C-15)	17	70	13	26.8	61.7	11.5	2525

Batches (25 gm) mixed dry for 1/2 hour in automatic mortar, dampened, pressed as discs fired at indicated temperature for 1/2 hour. All matured; C-1 slightly overfired.

		MgO	Al_2O_3	SiO_2	Calc**	Al_2O_3	SiO_2	°F
MgAlSi	(M-5)	50	10	40	66.7	5.3	28.0	2500
"	(M-4)	46	11	43	61.3	6.7	32.0	2500
"	(M-3)	46	7	47	61.3	2.7	36.0	2485
"	(M-11)	36	35	29	48.0	31.6	20.4	2520
"	(M-1)	36	7	57	48.0	4.0	48.0	2485
"	(M-13)	30	50	20	40.0	47.2	12.8	2520

**Calcine batch: 470 gm basic $MgCO_3$, 21 gm Al_2O_3, 54 gm SiO_2; blended dry in baffle mill 2 hours, calcined at 2500°F 2 hours, pulverized and stored for use.

Batches (25 gm) prepared as in C-series above. All specimens well matured.

Table II (cont.)

C. Alkali Aluminum Silicates

Identification		Oxide Comp. (wt %)			Batch Comp. (wt %)			Firing
		K_2O	Al_2O_3	SiO_2	Calc*	Al_2O_3	SiO_2	°F
KAlSi	(K-5)	5	75	20	33.3	61.7	5.0	2600
"	(K-4)	5	65	30	33.3	51.7	15.0	2600
"	(K-8)	7	53	40	46.7	34.3	19.0	2450
"	(K-3)	10	60	30	65.4	34.6	0	2450
"	(K-1)	10	50	40	66.7	23.3	10.0	2400
"	(K-9)	10	45	45	66.7	18.3	15.0	2400
"	(K-7)	12	40	48	80.0	8.0	12.0	2400
"	(K-2)	13	47	40	86.7	12.3	1.0	2400
"	(K-6)	15	40	45	100.0	0	0	2400

*Calcine batch: 110 gm K_2CO_3, 200 gm Al_2O_3, 225 gm SiO_2; blended dry in baffle mill for 2 hours, calcined at 1800°F for 2 hours, pulverized, and stored for use in composition batches.

Batches (25 gm) mixed dry in automatic mortar for 1/2 hour, dampened, pressed as discs, fired as indicated above.

Specimens K-4 and 5 were slightly porous; specimen K-2 slightly overfired; other bodies were well matured.

Table II (cont.)

D. Alkali Porcelain Bodies Employing Natural Minerals

Identification	Oxide Comp. (Approx. wt %)				Batch Comp. (wt %)				Firing
(Sodium-type)	(NaK)$_2$O	MgO	Al$_2$O$_3$	SiO$_2$	No.56 spar	Talc	EPK	Flint	°F
Cone 14	3.0	1.0	20.7	75.3	22.3	2.9	40.7	34.0	2535
Cone 14A	3.1		21.3	75.6	23.0		42.0	35.0	2535
Cone 12	6.2		26.0	67.8	40.0		45.0	15.0	2390

Batches (25 gm) blended dry, dampened, pressed as discs, fired for one hour at the temperature indicated.

Cone 14 body also prepared as 2000 gm batch, blended as plastic mass in Lancaster mixer, micro-pulverized, extruded (with de-airing) as long rods 1/8 inch diameter. These were fired as indicated then cut to 3/4 inch lengths and fabricated as thermistors for testing at the National Bureau of Standards.

(Lithia-type)	(KNa)$_2$O	Li$_2$O	Al$_2$O$_3$	SiO$_2$	Bk. spar	Ptl.	OM No.4	Vlvc.	Flint	°F
Li-K-1	2.2	0.7	21.6	75.5	11.47	14.04	10.64	31.93	31.91	2200
" -2a	2.8	0.7	29.1	67.3	14.28	14.28	7.15	50.00	14.29	2300
" -2b	2.4	0.6	32.3	64.7	11.43	11.43	5.72	60.00	11.43	2450
" -2c	1.9	0.4	35.5	62.2	8.57	8.57	4.29	70.00	8.57	2450
" -2d	1.8	0.4	30.6	67.2	8.57	8.57	4.29	60.00	18.57	2450
" -2e	1.8	0.4	25.8	72.0	8.57	8.57	4.29	50.00	28.57	2550

Batches (200 gm), non-plastics wet milled 12 hours, clays added, complete batch milled as heavy slip for 3 hours, dried at 180°F, dampened, granulated, pressed as discs (3/4 inch diameter), fired one hour at temperature indicated.

Table III

SOURCE AND PROBABLE COMPOSITION OF SPECIMENS RECEIVED AS FIRED BODIES

Identification	Probable Composition (wt %)				Source
(single crystals)					
Al_2O_3	100 Al_2O_3				Linde Air Products Co.
Ruby	98 Al_2O_3, 2 Cr_2O_3				Linde Air Products Co.
$CoO \cdot 2Fe_2O_3$	19 CoO, 81 Fe_2O_3				Dr. W.H. Bauer, Rutgers
(BeO bodies)	BeO	Al_2O_3	ZrO_2	MgO	
$48BeO \cdot Al_2O_3 \cdot ZrO_2$	81.0	6.9	8.3	3.8	Dr. R.F. Geller, Nat'l Bur. Stand.
88% BeO	88.0	10 -	other?		Spark plug manufacturer
65% BeO	65.0	35 -	other?		Spark plug manufacturer
(ZrO_2 bodies)					
$ZrO_2 + MgF_2$ (S-1)	94.5 ZrO_2, 5.5 MgO?				Mr. Richardson, Materials Laboratory, WADC
ZrO_2 (S-2)	100 ZrO_2 (stabilized)				Dr. Weber, Materials Laboratory
Zircon porcelain	$ZrO_2 \cdot SiO_2$, + other?				Ceramic dielectric manufacturer
Low Zircon (18-4 body)	Complex zirconium silicates				Mr. E.J. Smoke, Rutgers(7)
(alk.-earth porcelains)	MgO	BaO	Al_2O_3	SiO_2	
$MgO \cdot Al_2O_3$ + 25% SiO_2	23	--	57	20	Mr. E.J. Smoke, Rutgers(8)
" + 11% "	25	--	65	10	" " " " "
Cordierite	14±	--	35±	51±	Ceramic dielectric manufacturer
" (self-glazed)	(cordierite + feldspar)				" " "
" (F-25)	17	--	34	49	Dr. H.R. Wisely, Rutgers(9)
" (G-10 N)	11	2	36	53	" " " " "
Ba-C	14	6	20	60	" " " " "
Ba-C 6	10	5	23	62	" " " " "
Ba-C 15	5	8	20	67	" " " " "
Complex alk.-earth body	clay + calcine containing: BaO, MgO, CaO, and SrO				Dr. M.D. Rigterink, Bell Telephone Laboratory

Table III (cont.)

Identification	Probable Composition (wt %)	Source
(Potassia-porcelains)		
Shenango bodies:		
Nos. 1,2,4,6,9	(cone 12-14 china)	Shenango Pottery Company
Hall China body	" " "	Hall China Company
	15-25% Orthoclase feldspar 35-40% Flint 0-3% Talc balance, clays	
samples:		
AAB, W-2, KEP-6	(electrical porcelain) 30-35% Orthoclase feldspar 20-25% Flint 0-3% Talc balance, clays	Low-tension electrical porcelain manufacturers
(Lithia porcelains)		
Burner tip body	80 Petalite, 20 clay	Stupakoff Mfg. Company
285 A	50 " 50 "	Ceramic dielectric manufacturer
QC6-F-1	61 QC6 frit, 39 clay	Mr. E.J. Smoke, Rutgers(10)

III. PREPARATION OF SPECIMENS FOR TESTING

Most specimens were shaped as wafers, having an area/ thickness value greater than one. Within limits, the resistance of the specimen could be adjusted to fall within a more desirable range by decreasing the sample thickness or area. The faces were ground to within 0.005 inch of parallel. The average distance between faces, before electrode application, was taken as the sample thickness. Following electrode application, the edges of the sample were ground reasonably perpendicular to the faces to simplify the determination of the electrode area and to eliminate the possibility of a metallized conductive path between the electrodes, which completely covered the faces of the specimens.

Several methods for applying electrodes were tried:

1. Ammonium platino-chloride (NH_4PtCl_6) suspended in organic oils (varnish) was painted on the sample face. A layer of platinum foil (0.0005 inch thick) was placed on top, and the assembly was fired at the maturing temperature of the ceramic specimen. Fair to good adhesion between platinum foil and ceramic body was obtained. Following the electrode application firing, the specimens were held overnight at approximately 2000°F to allow the ceramic body to approach equilibrium for that temperature and thus minimize any tendency to change during subsequent tests at elevated temperatures.

2. Pure platinum paste was, later, used to provide the bond between foil and ceramic surfaces. Some platinum pastes contain ceramic fluxes which aid in bonding them to the ceramic. This feature, though advantageous in producing adhesion, introduces the problem of increased electrical resistance in the coating and a probable wide variation of resistance with change in temperature. To avoid these detrimental properties, the platinum pastes chosen for use were formed of extremely fine particles of pure metallic platinum in a vehicle of organic oils and resins. The "thin" paste was less viscous at room temperature than the "thick" paste. A coating of "thin" platinum paste (Hanovia, No. 232) was painted on the sample face. The coating was fired on at the maturing temperature of the body. A coating of "thick" platinum paste (Hanovia, No.012) was then applied, dried at room temperature to tacky consistency, and a layer of the platinum foil firmly pressed

on top. The platinum coated specimen was placed between two alumina discs and the assembly fired at the maturing temperature of the body. Fair to excellent electrode adhesion was achieved.

3. The specimen was warmed on a hot plate before application of a coating of "thick" platinum paste. The specimen was then fired at approximately 2100°F. A second coating of the "thick" paste was applied and the specimen gently heated to drive off most of the volatile oils. At this stage the coating was tacky when hot but quite hard when cooled to room temperature. A layer of platinum foil was carefully pressed over the face of the heated sample which was then placed between two alumina discs and re-fired at approximately 2100°F. Good to excellent electrode adhesion was obtained.

Examination of the results of electrode application disclosed several factors which seem to be involved in obtaining satisfactory electrode contact. The adhesion of the first coating of platinum paste to the face of the specimen was most important. Adhesion depended upon mechanical bonding and required that the coating fill the microscopic hollows on the ceramic surface. This condition was defeated if: the paste, either when applied or during later heating, did not have a low enough viscosity to allow proper "wetting" of the ceramic surface; heat was applied so rapidly that the escape of volatiles caused bubbling; the application was so heavy that during firing-on, the natural tendency of the platinum particles to agglomerate overcame the initially weak bond holding them to the ceramic; the temperature employed in firing the platinum was sufficiently high that the ceramic surface became slightly glassy, thus destroying the mechanical bond. Bonding of the platinum foil electrode to the thin initial platinum film was quite successful if care was taken not to disturb the foil before firing, and if a slight, even, pressure was applied during the firing process, as by the weight of an alumina disc.

When properly attached, the platinum electrode could not be pulled away from the ceramic without tearing the foil. Slightly less successful application allowed the foil to be peeled from the specimen face by using gently applied force, but left a continuous platinum coating on the ceramic that could not be removed by scraping with a sharp blade. With fair adhesion, the foil did not loosen under normal handling but when forcibly removed revealed small patches of the ceramic surface.

Although no specific tests were made, it was assumed that the platinum paste, when fired, produced a continuous metallic film having very low electrical resistance. Platinum to ceramic contact resistance was minimized by achieving the best possible mechanical bond. The platinum foil layer was shaped to partially or completely cover the specimen face, with a tab of reasonable length and width extending beyond. Lead-wires were joined to these tabs by welding. Despite these attempts to provide negligible electrical resistance due to electrodes, lead-wires, and contacts, the results of tests on specimens having less than 30 ohms resistance at elevated temperatures indicated a probable electrode plus lead-wire resistance amounting to several ohms at temperatures approaching 2000°F.

For special tests some specimens were provided with electrodes consisting only of platinum paste which was used, also, to attach short platinum lead-wires. Difficulty was encountered in building an appreciable thickness of platinum by using the paste, and it was found to have rather low mechanical strength. As a result, such specimens required reasonable care in handling and, probably could not remain intact under any appreciable tensile stress.

The best means found for producing a specimen with strongly attached electrodes and leads was accomplished by coating the lead-wires with platinum paste, dried on, and casting the ceramic body (prepared as a slip) around the properly positioned wires. On firing the body to maturity, a suitable combination of paste and body shrinkage produced a tight ceramic to metal contact. The strength of such an assembly would be limited only by the strength of the lead-wires employed.

In mounting thermistors for experimental testing, the electrodes were welded to conducting wires leading to the resistance measuring bridge by widely separated paths. For testing under simulated service conditions, the thermistor required mounting in a probe. Swaged MgO insulation between the parallel lead-wires within the probe shaft was found to affect observed resistance measurements due to its tendency to hydrolize at room temperature with subsequent fluctuations in resistance values on being heated. Vitrified Al_2O_3 tubing gave more satisfactory results, being quite stable and providing much higher resistance than the thermistors tested.

IV. DETERMINATION OF SPECIMEN TEMPERATURE DURING TESTS

The experimental work done during this investigation may, roughly, be divided into two phases: the preliminary survey in which many dissimilar compositions were tested to determine, approximately, their resistivity vs. temperature characteristics; and a more careful study of compositions which were found to have resistivity values within the range suitable for thermistor use (i.e., 10^7 to 10^5 ohm cm at 1000°F, and 10^4 to 10^2 ohm cm at 2000°F).

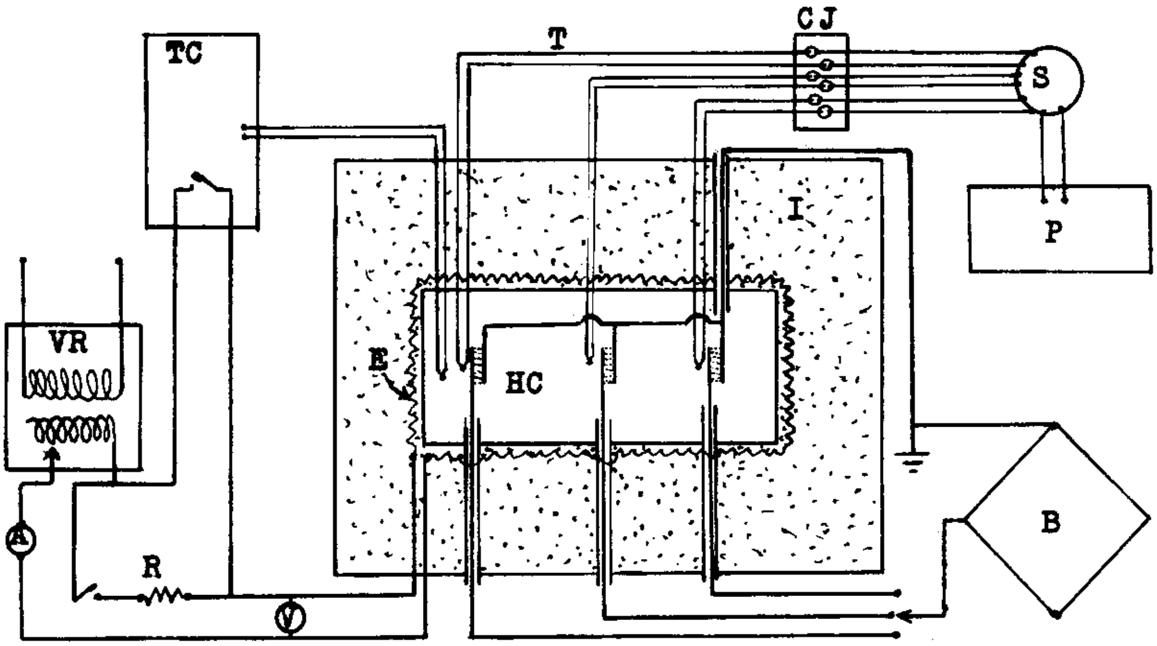
For the preliminary survey work, an exact knowledge of the temperature of the specimen was considered unnecessary. In making these tests the specimens were supported by their lead-wires within the chamber of an electrically heated kiln. The specimen temperature was considered to be that indicated by a protected thermocouple located several inches from the specimen position. This thermocouple temperature was shown on the scale of an automatic temperature controller which was employed to hold any set temperature with a maximum fluctuation of ± 15°F. Due to this fluctuation in kiln temperature, the lag difference in thermocouple and specimen response to change of kiln temperature, the existance of appreciable thermal gradients within the kiln chamber, and the difference in positions of thermocouple and test specimen, the error in determination of the specimen temperature could have been as much as ± 25°F. This inaccuracy was considered as unimportant in establishing the general resistivity range of a material.

Specimen temperature, at the time the resistance measurement was being made, could never be known with certainty under actual test conditions. The closest approximation of the true specimen temperature would be possible only if a standardized thermocouple very nearly touched the test specimen located in a kiln position free of thermal gradients and at a time during which the kiln temperature had been stabilized for several minutes. These ideal conditions were approached in the small electrically heated kiln which was constructed for the resistance vs. temperature tests. The essential features of this kiln are shown, schematically, by Figure 1.

It should be noted that temperature gradients were minimized by supplying adequate thermal insulation throughout and by providing heating elements for each face of the small heated chamber. Provision was made for mounting three test specimens within the chamber. Each specimen was within one inch of its individual 28 gauge chromel-alumel thermocouple. These thermocouples were renewed frequently but not standardized. The temperature of these couples was obtained from a

Figure 1

TEST KILN DESIGNED FOR TESTING RESISTANCE
AT ELEVATED TEMPERATURES



VR = Transtat voltage regulator, 3.9 Kva, 15 amp maximum
A = Ammeter, 15 amp maximum
V = Voltmeter, 150 volt maximum
R = Auxiliary resistance, 1 ohm
E = Heating elements, surrounding all faces of the chamber including removable door
TC = Automatic temperature controller, Brown Instrument Co., with Pt-Pt 10% Rh thermocouple
I = Insulation brick
HC = Heating chamber, 7 inches wide by 3 high and 3 deep, showing arrangement of test specimens
T = Chromel-alumel thermocouples (28 gauge)
CJ = Ice bath cold junction
S = Selector switch
P = Precision potentiometer, Leeds and Northrup (model 8662)
B = AC bridge for determining specimen resistance

precision potentiometer employing an ice bath as the cold junction. Any set kiln temperature was controlled automatically, with a ±10°F fluctuation. The rate of temperature change was manually adjusted by altering the power input. With care it was possible to hold a given temperature to a change of less than 1°F in five minutes. This latter feature was not fully employed, however, until most of the compositions had been tested.

Under the test conditions usually employed, the resistance measurements were made as the kiln temperature was changing slowly, thus introducing a slight error due to the slower temperature response rate of the test specimen. The three thermocouples frequently indicated a temperature gradient across the test chamber of as much as 10°F allowing a further slight variation between observed and actual specimen temperature. Temperature readings were probably within ±5°F of the true specimen temperature.

V. INSTRUMENTATION FOR RESISTANCE MEASUREMENTS

Measurements Using Direct Current:

For the measurement of the electrical resistance of specimens to direct current, two bridges were employed in order to span the wide range of resistance encountered. Resistance from 10^6 to 10^{10} ohms was measured by means of a General Radio Company megohm bridge which applied a potential of approximately 500 volts DC to the sample. This bridge is essentially a Wheatstone bridge with a vacuum tube voltmeter detector. Resistance below 10^6 ohms was measured with a laboratory built Wheatstone bridge which applied approximately 6 volts to the sample.

Testing with direct current proved to be unsatisfactory due to polarization effects which became noticeable as the specimen temperature exceeded 800°F. Polarization of a specimen held at a constant temperature was evidenced by steadily increasing resistance values from the time the potential was applied. Reversal of the polarity of the applied potential returned the resistance to its original value, whereupon it again increased.

The use of very low current flow (10^{-6} amps) would decrease the obvious resistance variations due to polarization, but would tend to change the sample composition through electrolysis over long periods of time. Because of the changing resistance of the sample under a constant applied potential, the DC measurements lacked precision and this test method was abandoned early in the investigation.

Measurements Using Alternating Current:

The determination of the electrical resistance of a specimen to alternating current not only allowed an improvement in the precision of the measurements, but allowed measurements to be made on easily polarized materials such as alkali porcelains. This method introduced a number of complexities. In obtaining resistance measurements with alternating current the following instruments were employed:

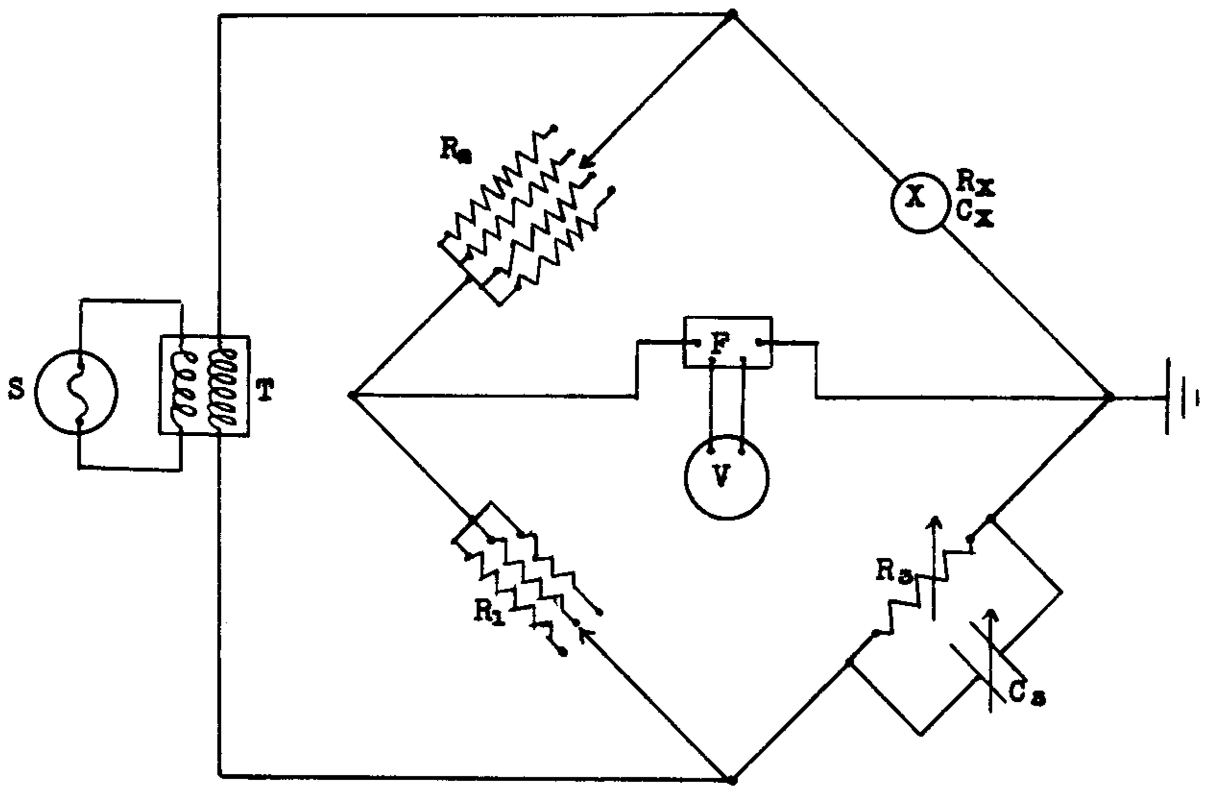
1. A Hewlett-Packard audio oscillator (model 200-CD) capable of generating a 10 volt signal of any selected frequency from 5 cycles to 6×10^5 cycles/second. Frequencies of 40, 400, and 1000 cycles were employed.
2. The signal produced was passed through a shielded transformer giving an output of approximately 75 volts, 0.006 amps AC which was fed into the measuring bridge circuit.

3a. An experimental AC bridge of the Wheatstone type, capable of measuring resistance up to 10^{10} ohms was built in the laboratory. A Heathkit decade condenser was placed in parallel with the variable resistance leg of the bridge to compensate for the capacity of the test specimen which provided the resistance in the fourth leg of the bridge, as shown by the schematic diagram, Figure 2. Conditions for bridge balance were that: $R_1 R_x = R_2 R_3$, also, $C_3 R_1 = C_x R_2$. Difficulty in providing adequate insulation for very high resistance within the bridge, particularly when high frequency AC was employed, probably accounted for a 50 megohm leak which developed in this bridge. Measurement errors attributable to this cause varied in magnitude with the resistance involved and the frequency of the signal used. With 40 cycles/sec, resistance measurements as high as 10^8 ohms were reasonably accurate. With 400 cycles/sec, readings above 2×10^7 ohms were subject to over 10% error but the error dropped below 1% for measurements of 10^6 ohms or less.

Further errors were introduced by electrical conduction through the heated atmosphere surrounding the specimen being tested. The electrical resistivity of the normally contaminated air in the kiln drops with increasing temperature until, at 1000°F, its resistivity may become of the same, or lower, order of magnitude as the test specimen. When specimens had observed resistance values higher than 5×10^5 ohms, at or above 1000°F, the possibility of error due to atmospheric conduction was introduced. With specimens having observed resistance values of 10^7 ohms or more, such errors may amount to 50% or more. As the kiln temperature increases the resistivity of the specimen material decreases more rapidly than the resistivity of the air surrounding the specimen so that errors in resistance observations probably become negligible as specimen resistance falls below 10^5 ohms.

Figure 2

AC BRIDGE CIRCUIT



S = Hewlett-Packard audio oscillator (model 200-CD)
T = Shielded transformer
F = High pass filter
V = Hewlett-Packard vacuum tube volt meter (model 400-C) and/or ear phones
C_3 = Heathkit decade condenser (model DC-1)

R_1, R_2, R_3 = General Radio impedance bridge (type 650-A) or Experimental bridge in which:

R_1 = 10^3, 10^4, or 10^5 ohms
R_2 = 10^4, 10^5, 10^6, or 10^7 ohms
R_3 = 0 to 10^6 ohms

X = Test specimen having R_x resistance, C_x capacitance

3b. A General Radio Company impedance bridge (type 650A) capable of determining resistance values up to 10^6 ohms was also used. This bridge model is equipped with a kilocycle signal source or may be operated with an external oscillator. As above, the bridge circuit was modified by providing a variable condenser in parallel with the variable resistance leg of the bridge.

4a. A Hewlett-Packard vacuum tube volt meter (model 400 C) was most often used as the null point indicator for determining bridge balance. When specimens were tested at a frequency higher than 100 cycles/sec, the sensitivity of the volt meter was improved by placing a laboratory built high-pass filter in series with the volt meter. This filter effectively removed the 60 cycle disturbance picked up chiefly by the test specimen within the electrically heated test kiln.

4b. Bridge balance, or null point, could also be identified by means of ear-phones when the General Radio bridge was used. Very precise measurements were obtainable with this method of detection since the presence or absence of the distinctive test signal (400 or 1000 cycles/sec) usually could be identified in the presence of the hum due to 60 cycle pick up. Most of the later measurements were made with the General Radio impedance bridge using a 400 cycle/sec signal which is generally available in air craft.

An effort was made to produce test specimens having dimensions such that their resistance, when heated to 1000°F, did not exceed 10^6 ohms. Some specimens were encountered that produced very low resistance values when their temperature was increased to 2000°F. As the measured resistance fell below 30 ohms, a noticeable error in the determination of true specimen resistance was introduced due to the constantly increasing ratio of contact plus lead-wire resistance to that of the ceramic specimen alone.

VI. RESISTIVITY VS. TEMPERATURE TESTS

Reliability of Data:

As the experimental work progressed, the technique for determining the resistance values and temperature of specimens of the various ceramic compositions was changed in an effort to improve the reliability of the results. Reliability of the data depended upon: the condition of the specimen being tested (non-porous structure, free of cracks); ceramic-electrode contact (good electrode adherence providing a negligible contact resistance);

and the conditions under which the data were obtained.

As previously discussed, any measurements made with direct current lacked precision due to the effects of polarization of the specimen on the observed resistance. When alternating current was employed, minor errors may have occurred due to difficulty in obtaining precise resistance readings as specimens approached the higher test temperatures and 60 cycle pick-up became troublesome. More obvious errors may be attributed to: failure of the experimental AC bridge to measure resistance greater than 10^8 ohms at 40 cycles or 10^6 ohms at 400 cycles/sec with reasonable accuracy; and the increasing significance of contact, electrode, and lead-wire resistance in measurements made on specimens having less than 30 ohms resistance, as some did at high temperatures.

During the earlier survey tests, made in a kiln having poor temperature control and steep thermal gradients, difference between actual and observed specimen temperatures may have been as much as 25°F. Temperatures observed during later tests, employing the kiln designed for testing resistance at high temperatures, were probably within 5°F of the true specimen temperature. When care was taken to stabilize the kiln temperature and to allow time for the specimen to reach thermal equilibrium, the error in temperature measurement was probably negligible, or at least constant for any one test.

Presentation of Data:

Due to the above uncertainties, the resistance vs. temperature data must be evaluated in the light of the test conditions under which it was obtained. Therefore, the possible variation in the specimen temperature from that indicated by the thermocouple is given along with the range of specimen resistance observed and the frequency of the current employed for the test.

In reporting the results, a plot of log resistivity vs. 1/°K was chosen as the best means of presenting the data since it allowed direct comparison of one material with another and demonstrated the characteristics of essential interest. As previously discussed, these were: resistivity range, with resistivity of useful thermistor materials falling between 10^7 ohms at 1000°F and 10^2 ohms at 2000°F; sensitivity of resistivity to temperature change (as shown by the slope of the log R vs. 1/°K plot) with a 10^3 fold drop in resistivity between 1000° and 2000° F being desirable; and approximate linearity of the log R vs. 1/°K plot, indicating no abrupt phase changes due to change in temperature.

Results:

The observed resistivity vs. temperature characteristics of the various ceramic compositions that were tested are presented graphically in the sections of Figure 3 which are arranged to allow comparison of bodies having related chemical compositions. This division of the data resulted in some inevitable jumbling of the earlier, survey, tests with the more accurate later determinations. These data must be considered as indicative of resistivity magnitudes and not as absolute values.

True resistivity values for the entire 1000° to 2000°F temperature range were probably approached only with vitrified specimens having resistance values of 5×10^5 ohms or less at 1000°F and 10^2 ohms or more at 2000°F when tested with 400 cycle AC in the kiln allowing temperature of the specimens to be determined within ±5°F. Very few of the specimens tested met all of these requirements, but many provided reasonably reliable results over a portion of the temperature range studied.

The following generalizations may be drawn from the data obtained:

1. The resistivity values of Al_2O_3, $MgO \cdot Al_2O_3$, $CoO \cdot Al_2O_3$, ZrO_2 and BeO, even in compositions providing appreciable additions of contaminating oxides, were too high for practical application as thermistor material for the 1000°to 2000°F range.
2. Very low resistance was encountered with specimens of Cr_2O_3 or $CoO \cdot 2Fe_2O_3$. Progressively larger additions of Cr_2O_3 to Al_2O_3 lowered resistivity and decreased the log R vs. 1/°K slope.
3. Zirconium silicate (zircon) compositions should be further investigated as thermistor material.
4. Alumina-silica systems containing BeO, MgO, CaO or BaO, though not completely represented by the series of specimens tested, seem to hold slight promise for the temperature range of immediate interest. Rather high resistivity values were accompanied by indications of non-linearity in some of the members of the series.
5. Resistivity values of useable magnitude, and linear relationship of log R vs. 1/°K were characteristic of most of the compositions of the alkali-alumina-silica series that were tested. A progressively steeper slope was obtained as the predominating alkali was changed from sodium to potassium to lithium.

The relative magnitude of resistivity and the characteristic slope of log R vs. 1/°K, as observed for a number of dissimilar compositions, are presented in Figure 4. It may be noted that the BeO body shows not only a very high resistance but also an extremely steep slope, making it of interest for further investigation at somewhat higher temperatures. The complex alkali-earth body (Ba-C6) and the high temperature portion of the cordierite ($MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) body also have steep slopes and high resistivity values. These compositions are not sufficiently refractory to be useful in a much higher temperature range but indicate that a body near the more refractory celsian ($BaO \cdot Al_2O_3 \cdot 2SiO_2$) composition might have interesting possibilities. Among the alkali porcelains shown, the potassium aluminum silicate (composition K-8) may be seen to have a somewhat steeper slope and higher resistivity values than found with the allied porcelain bodies which employ feldspar ($(KNa)_2 \cdot Al_2O_3 \cdot 6SiO_2$) as the alkali source. The potassium feldspar body (AA-B) typical of the many similar porcelains tested, provided resistivity values within the desired range. The lowest resistivity values represented in Figure 4 were obtained from the alkali porcelain made with petalite ($Li_2O \cdot Al_2O_3 \cdot 8SiO_2$). The lithia content appeared to produce an excellent log R vs. 1/°K slope. This body would be useful as thermistor material in a slightly lower temperature range. Further exploration of the system should reveal a composition retaining the steep slope characteristic of the lithia porcelains yet having the required resistivity values for thermistor applications between 1000° and 2000°F.

Fig 5

On several occasions test results at different frequencies were obtained on the same specimen during the same heating run. Under these conditions, quite different resistivity values were noted at the lower temperatures if the resistance of the specimen was high. This apparent sensitivity to frequency probably reflected the errors inherent in the measurement of high resistance values. Specimens of cone 14 porcelain, having resistance values within the range of accurate observation, were insensitive to alteration of the test frequency from 60 cycles/sec to 400 or 1000 cycles/sec, as shown in Figure 5.

The position of bodies in the K-series(composed of K_2O-Al_2O_3-SiO_2) are shown on the weight percent phase equilibrium diagram of that system, page 32. Since the high silica portion of the phase equilibrium diagram of that system and the system Na_2O-Al_2O_3-SiO_2 are quite similar, except for somewhat higher temperatures, the porcelain compositions that employed feldspars as the alkali source may logically be projected to fall on the same weight percent diagram, though in actuality their position lies in the four-component system K_2O-Na_2O-Al_2O_3-SiO_2. The position of a body composition on the phase equilibrium diagram serves only to indicate the phase composition which the body was approaching when fired to maturity since most ceramic bodies represent a state of arrested, or incomplete, reaction between their initial components. Such diagrams are of limited use in predicting the properties of a body which has been fired to vitrification.

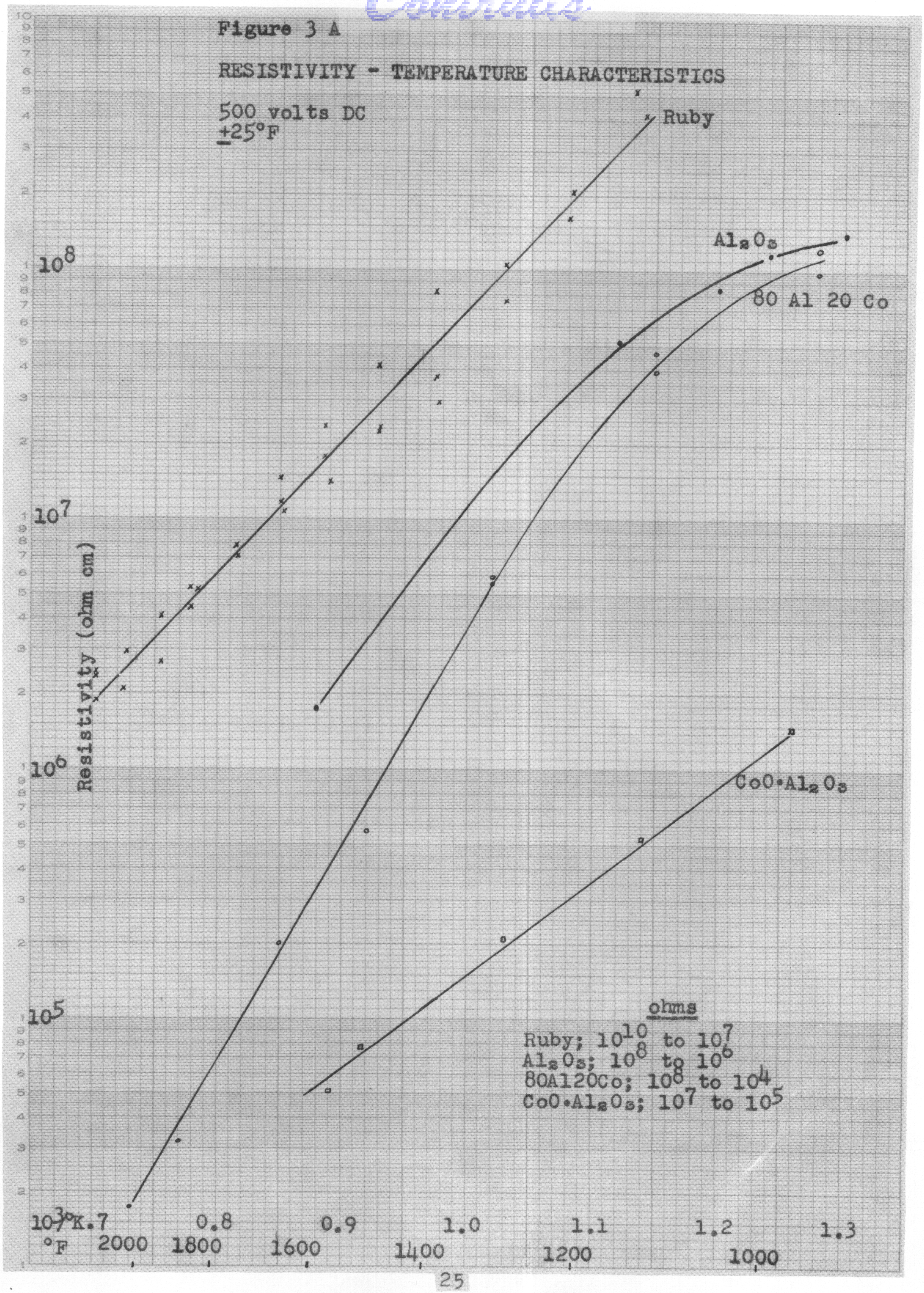


Figure 3 A

RESISTIVITY - TEMPERATURE CHARACTERISTICS

500 volts DC
±25°F

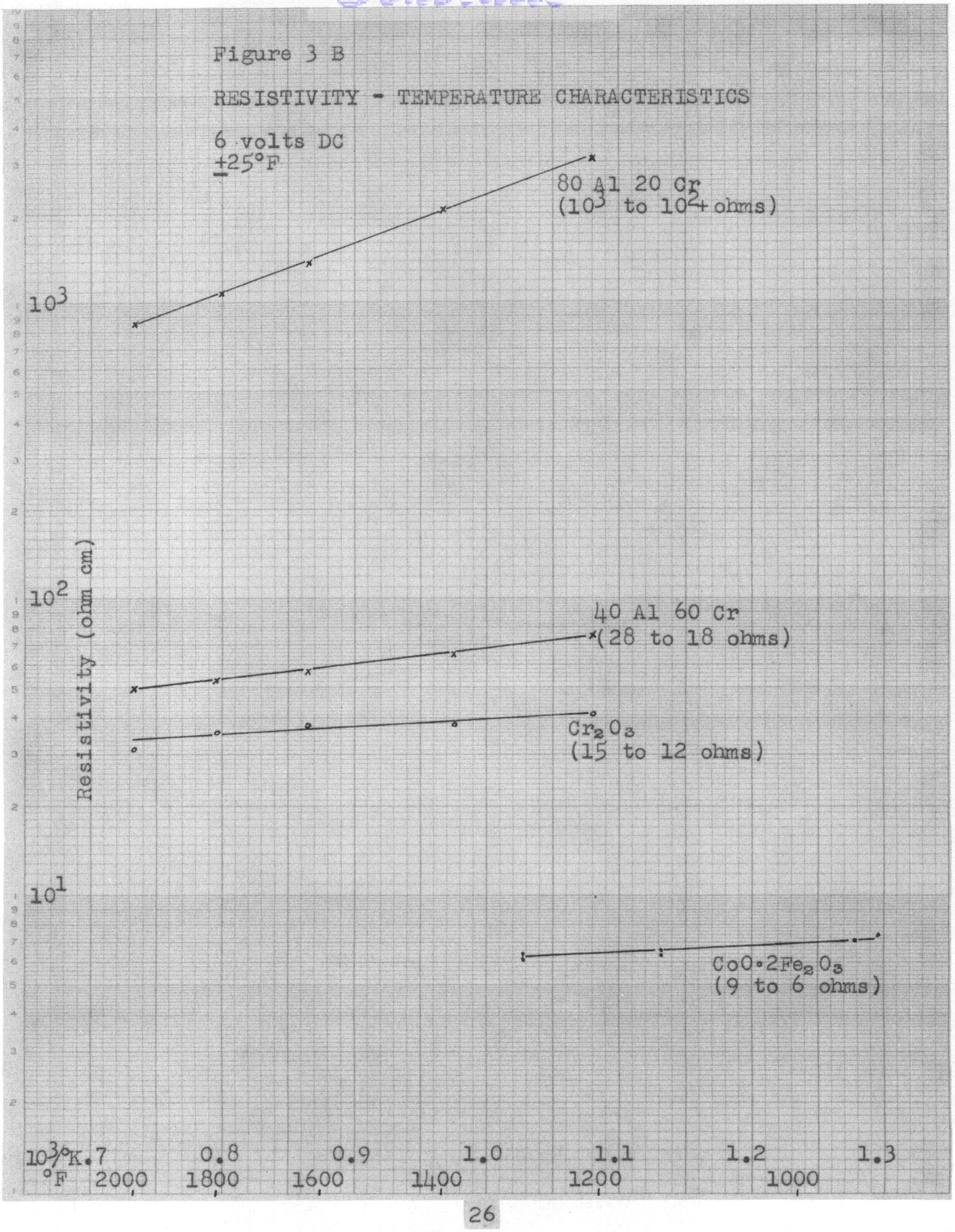


Figure 3 B

RESISTIVITY - TEMPERATURE CHARACTERISTICS

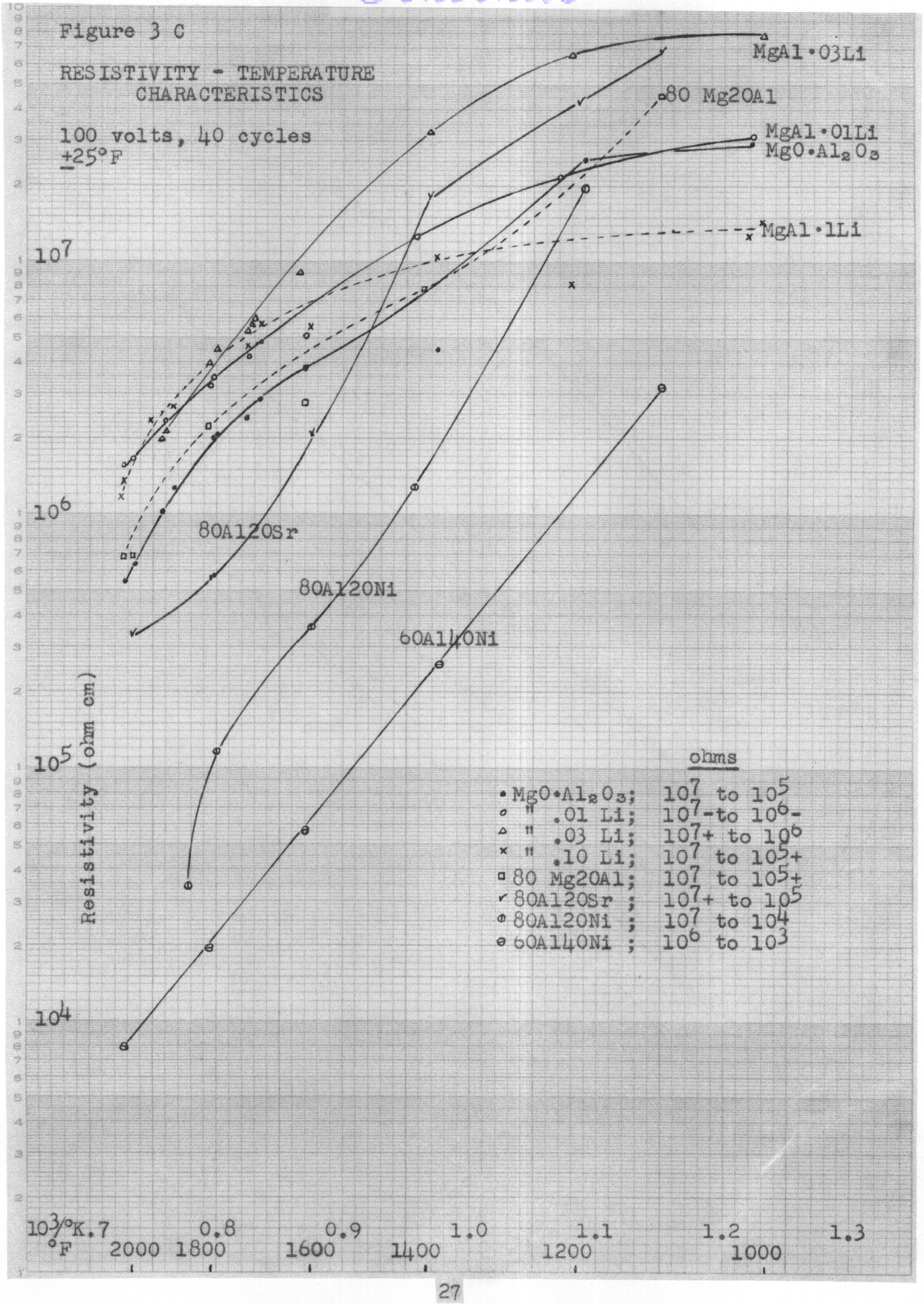


Figure 3 C

RESISTIVITY - TEMPERATURE CHARACTERISTICS

100 volts, 40 cycles
±25°F

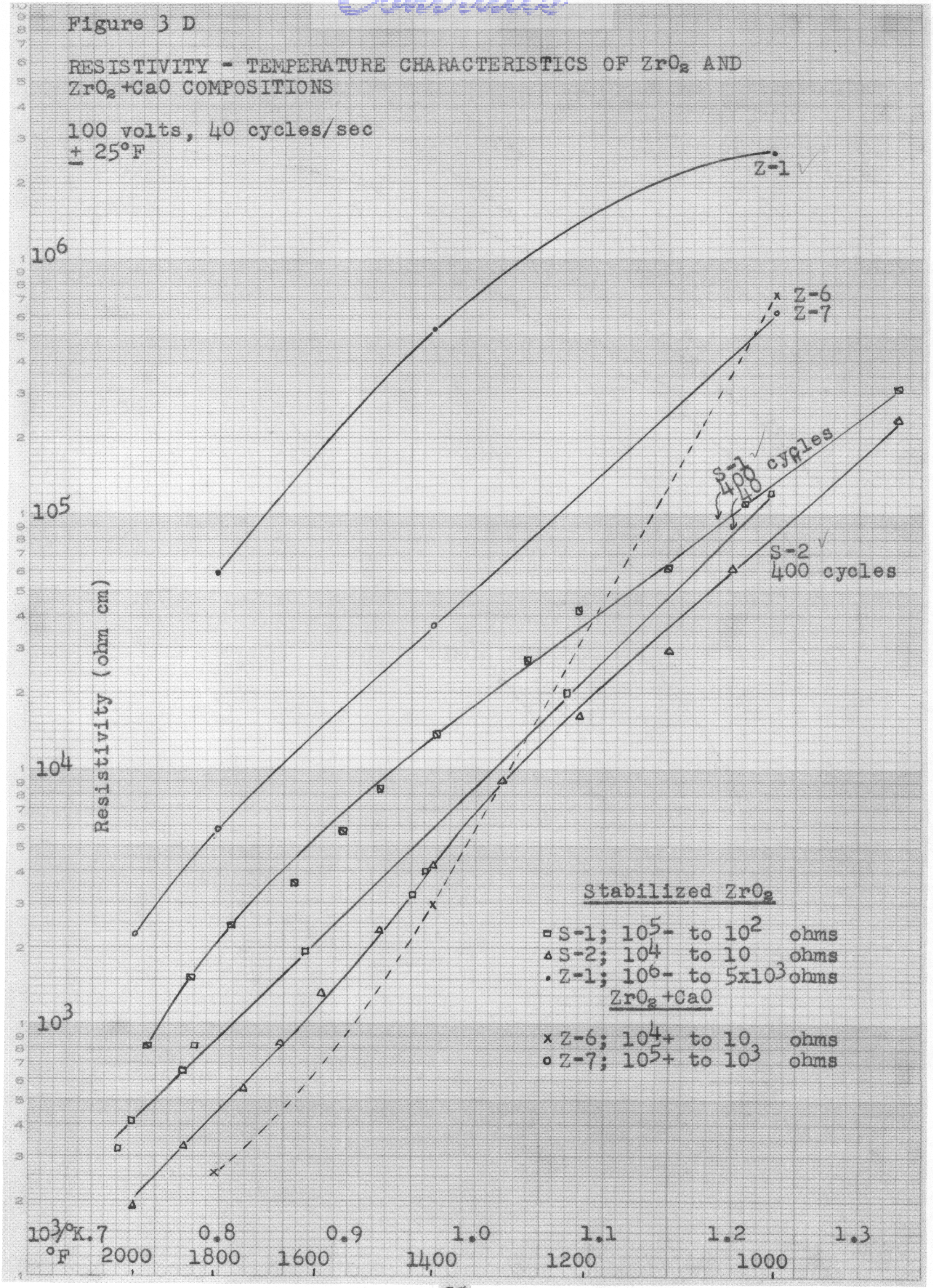


Figure 3 D

RESISTIVITY - TEMPERATURE CHARACTERISTICS OF ZrO_2 AND ZrO_2+CaO COMPOSITIONS

100 volts, 40 cycles/sec
± 25°F

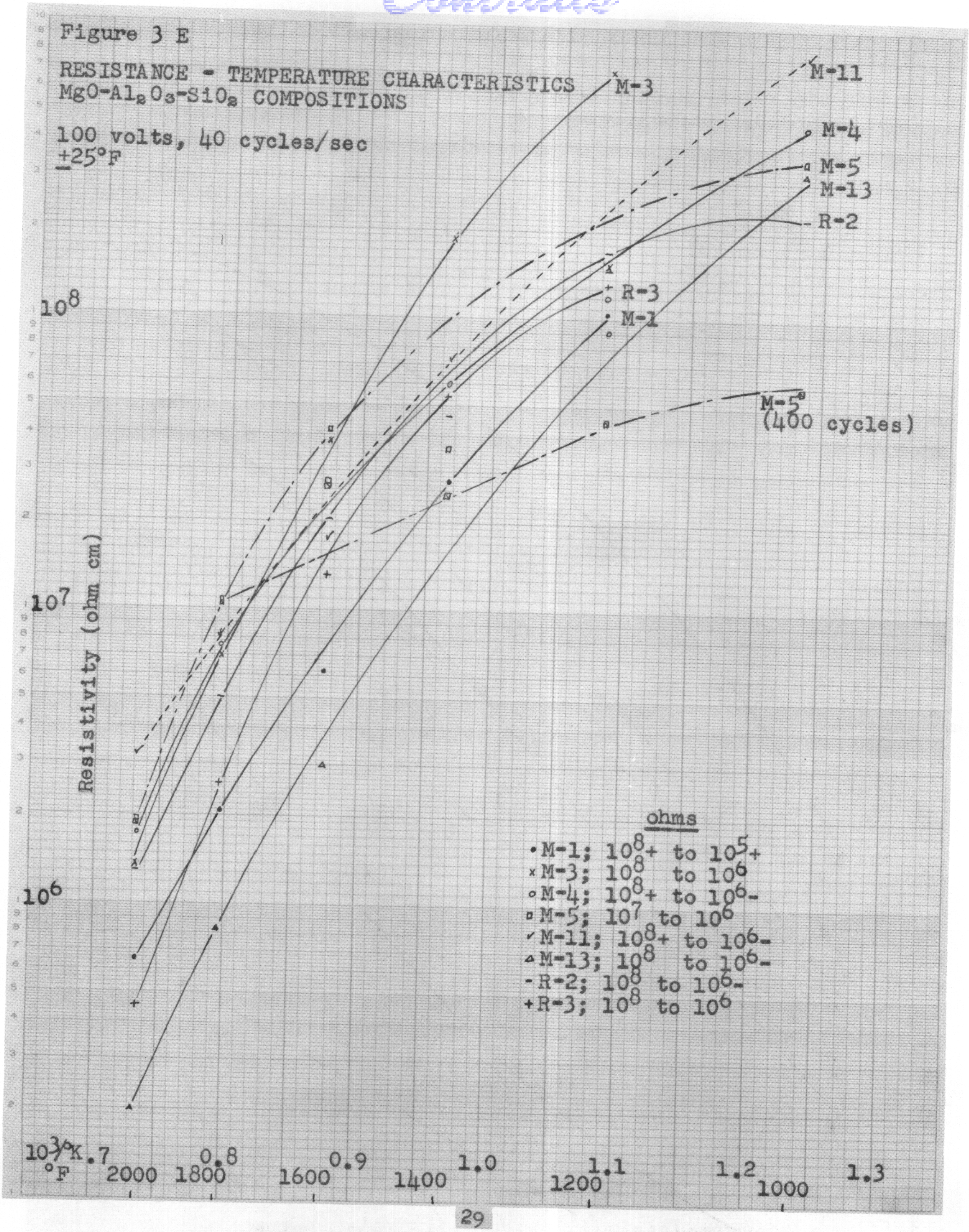


Figure 3 E

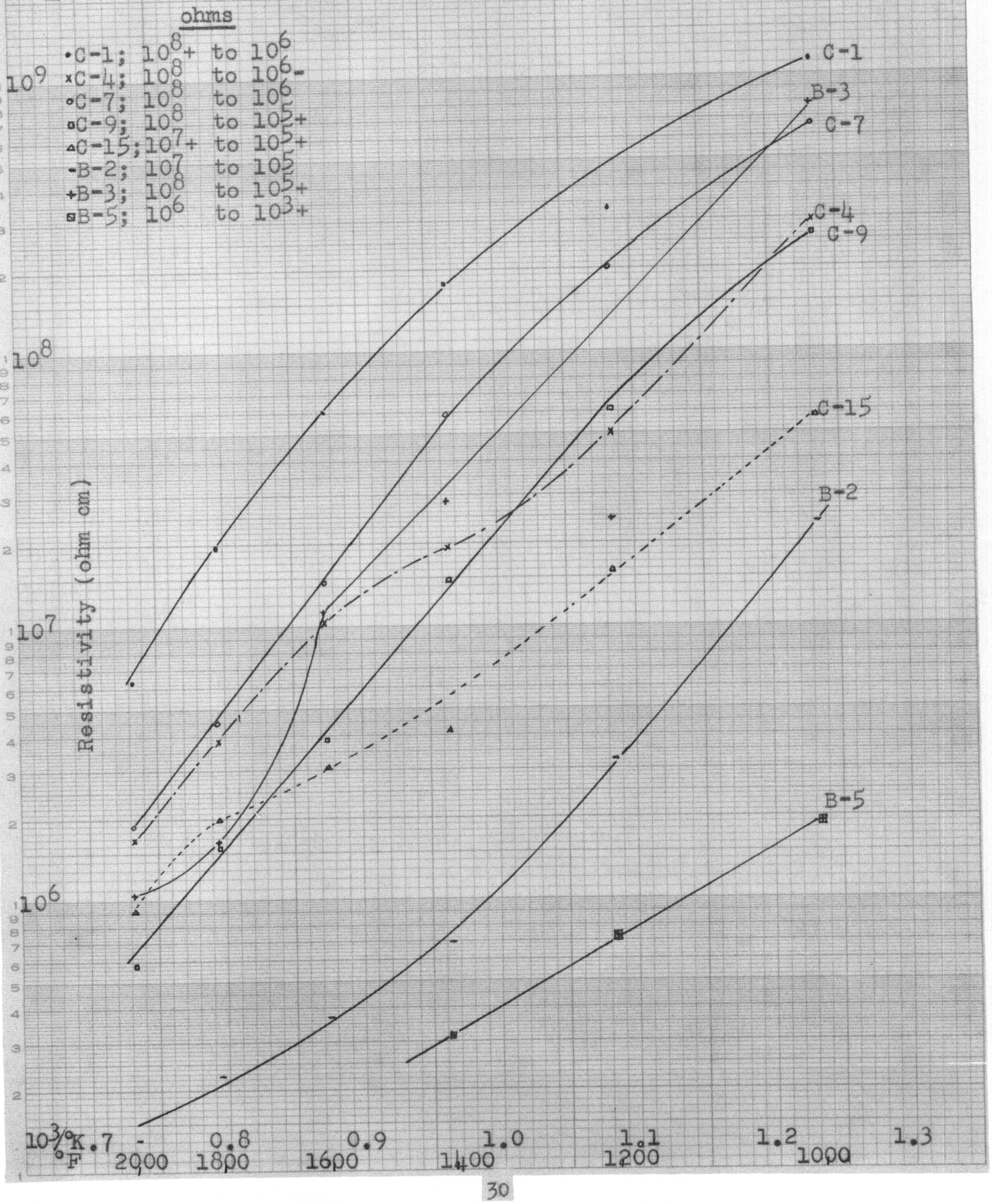
RESISTANCE - TEMPERATURE CHARACTERISTICS
$MgO-Al_2O_3-SiO_2$ COMPOSITIONS

100 volts, 40 cycles/sec
±25°F

Figure 3 F

RESISTANCE - TEMPERATURE CHARACTERISTICS $CaO-Al_2O_3-SiO_2$ AND $BaO-Al_2O_3-SiO_2$ COMPOSITIONS

100 volts, 40 cycles
± 25°F



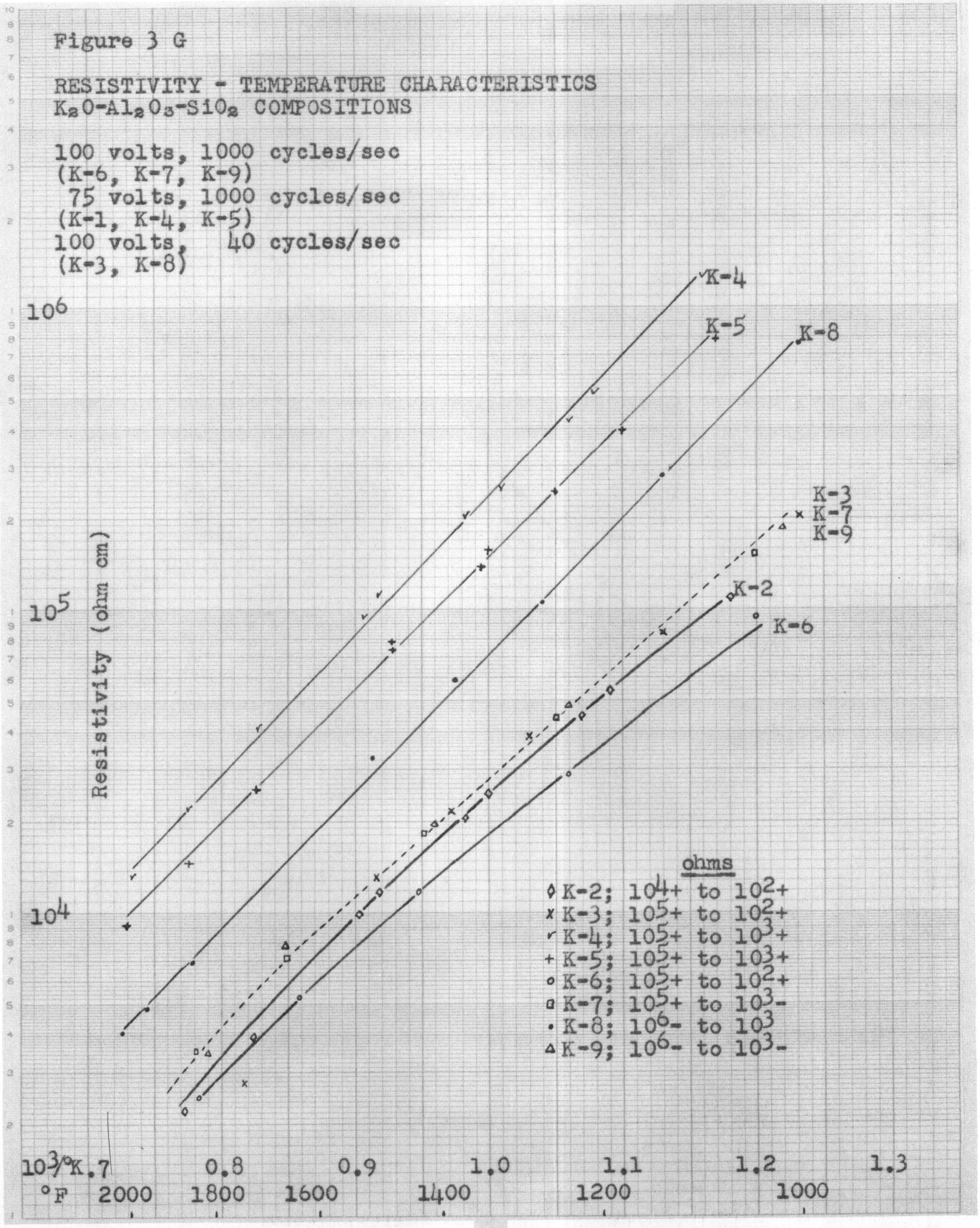


Figure 3 G

RESISTIVITY - TEMPERATURE CHARACTERISTICS
$K_2O-Al_2O_3-SiO_2$ COMPOSITIONS

100 volts, 1000 cycles/sec
(K-6, K-7, K-9)
75 volts, 1000 cycles/sec
(K-1, K-4, K-5)
100 volts, 40 cycles/sec
(K-3, K-8)

Figure 3 G (cont'd.)

POSITION OF COMPOSITIONS ON THE PHASE EQUILIBRIUM DIAGRAM OF THE SYSTEM $K_2O-Al_2O_3-SiO_2$

(weight percent)

	m.p. °F
o	1805±35°
p	2085±35°
q	2400±20°
r	2825±10°

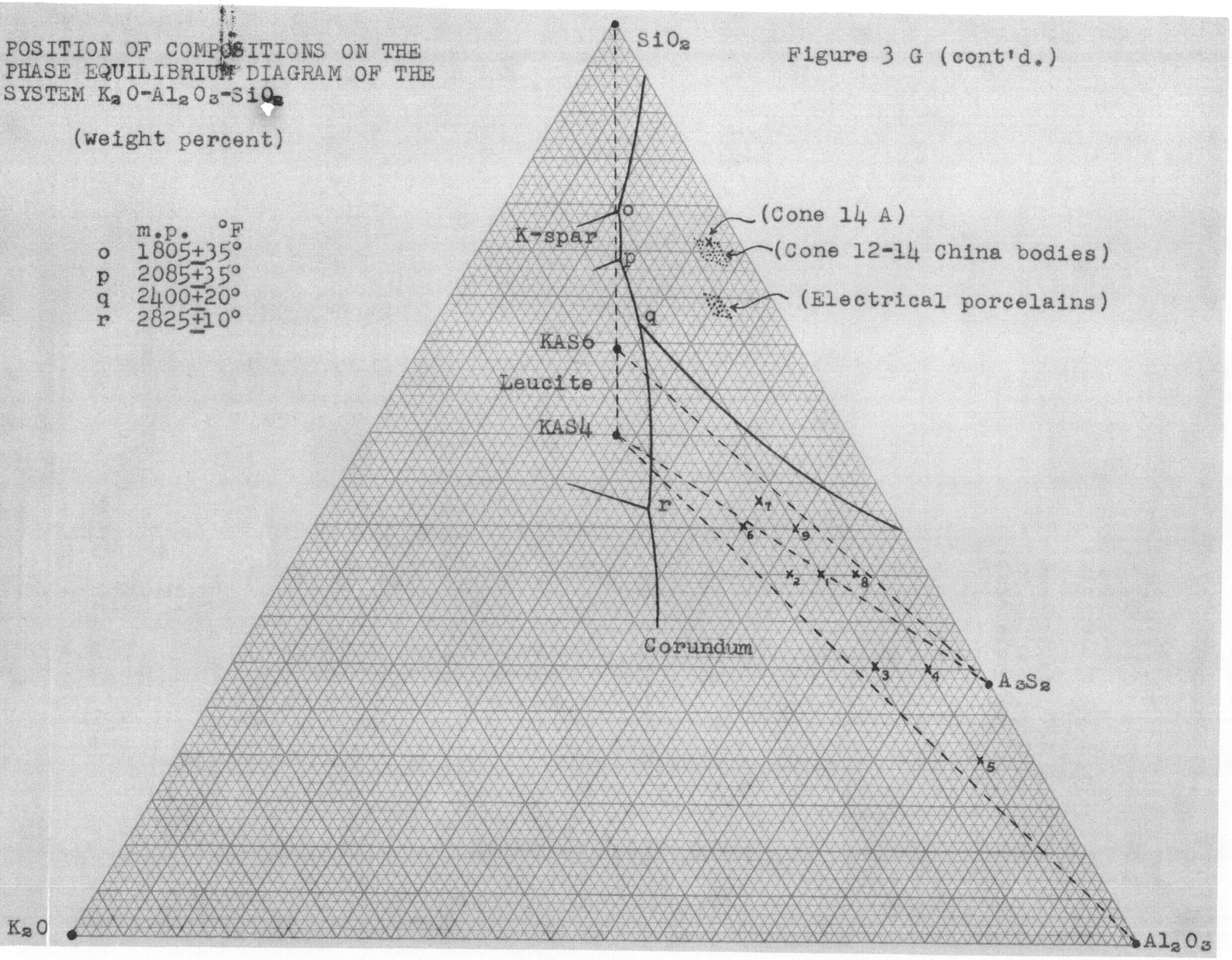


Figure 3 H

RESISTIVITY - TEMPERATURE CHARACTERISTICS ZIRCON PORCELAINS

100 volts, 40 cycles/sec
± 25°F

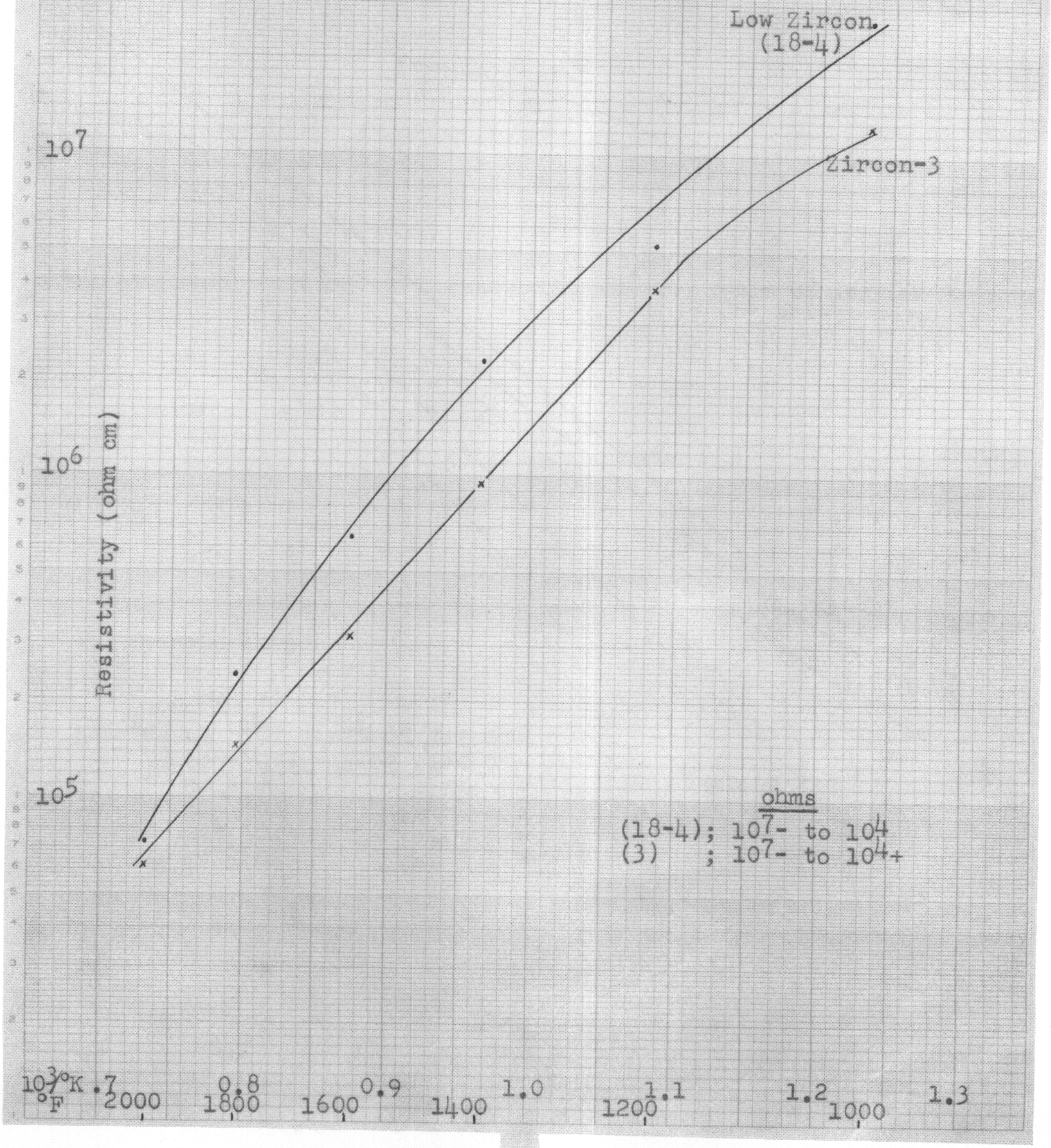


Figure 3 I

RESISTIVITY - TEMPERATURE CHARACTERISTICS PETALITE ($Li_2O \cdot Al_2O_3 \cdot 8SiO_2$) BODIES

75 volts, 400 cycles/sec
±5°F

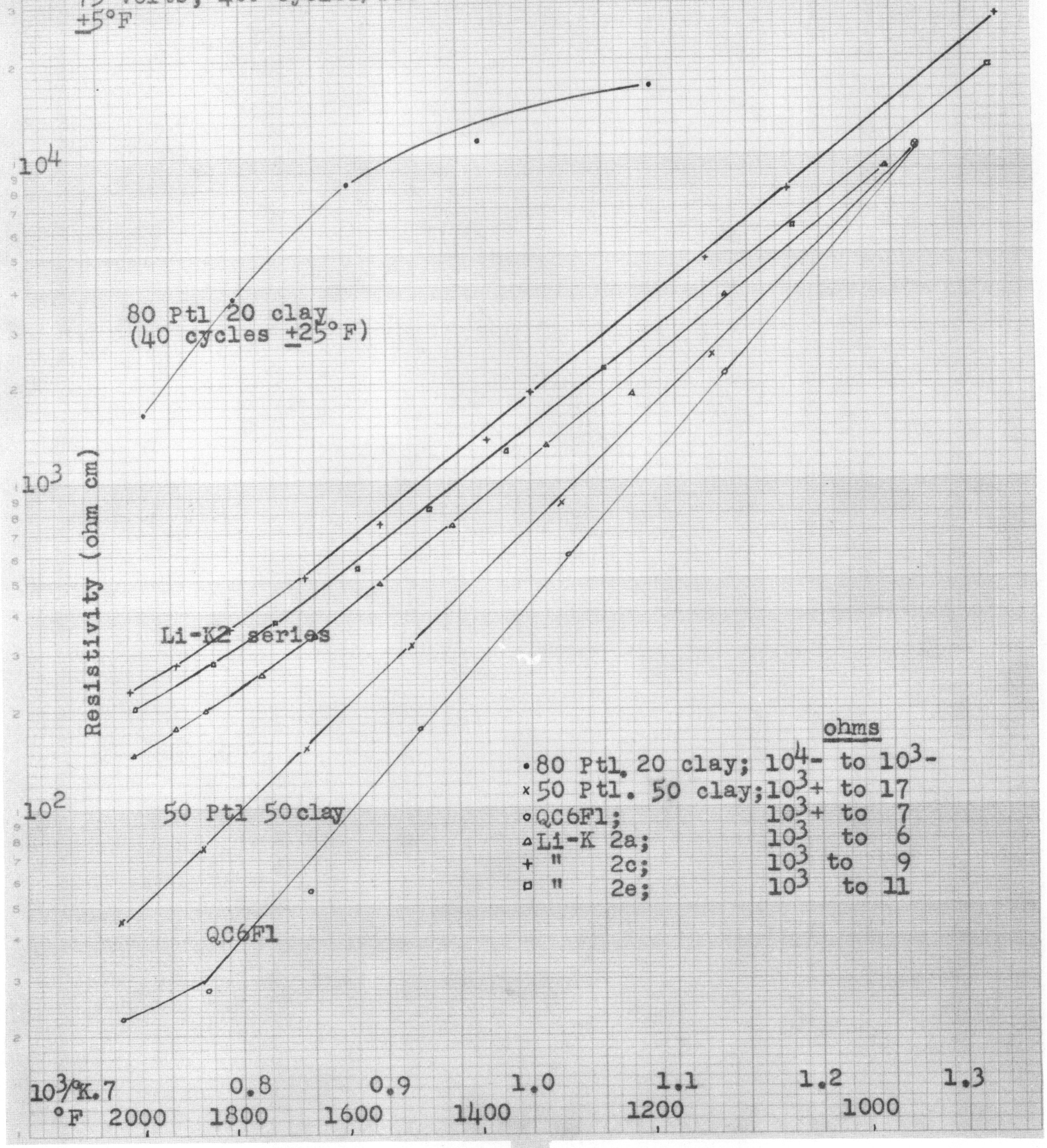


Figure 3 J

RESISTIVITY TEMPERATURE CHARACTERISTICS
SODIUM-FELDSPAR PORCELAINS

100 volts, 40 cycles/sec
±5°F

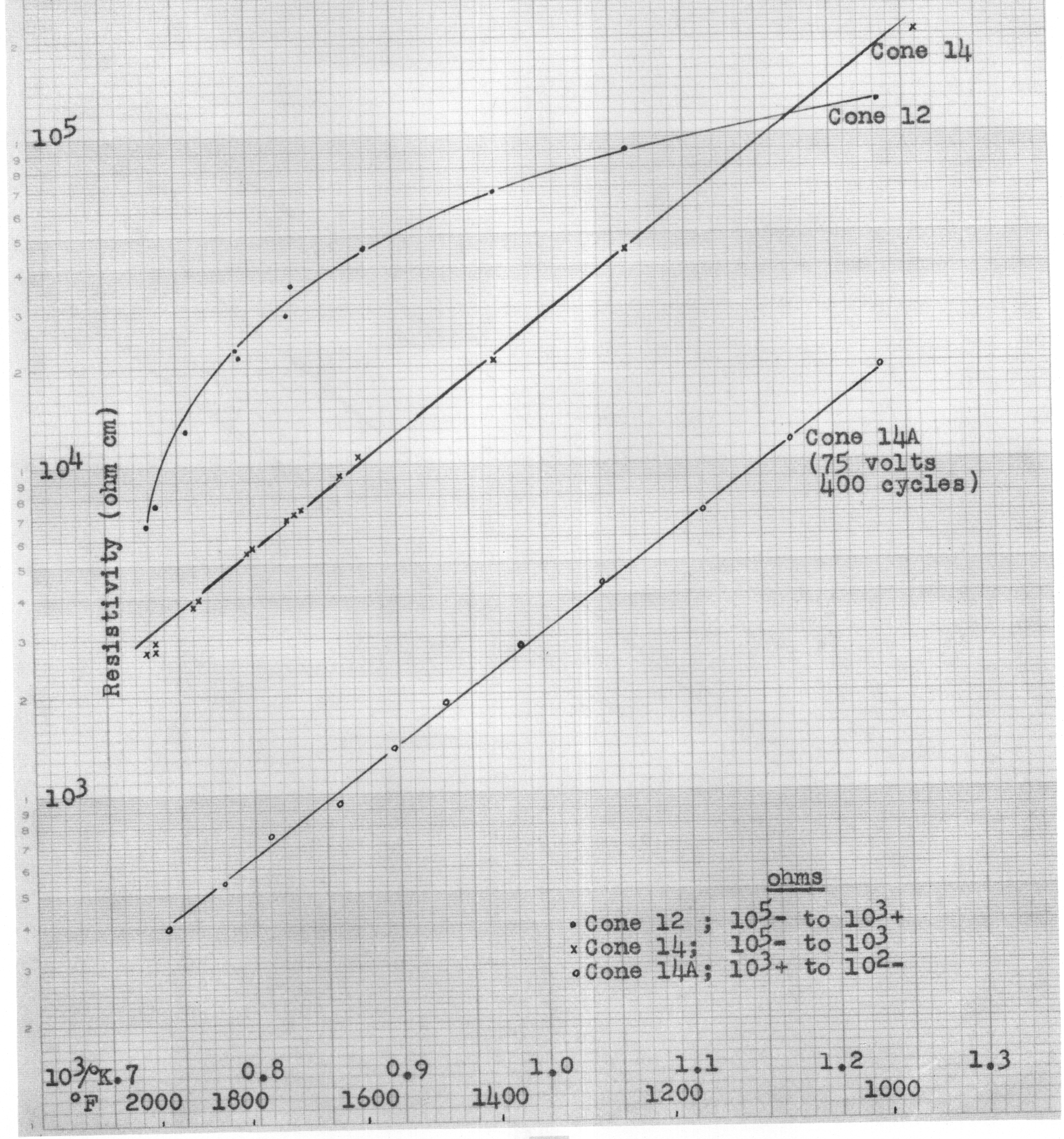


Figure 3 K

RESISTIVITY - TEMPERATURE CHARACTERISTICS POTASSIUM FELDSPAR BODIES

75 volts, 400 cycles/sec
±5°F

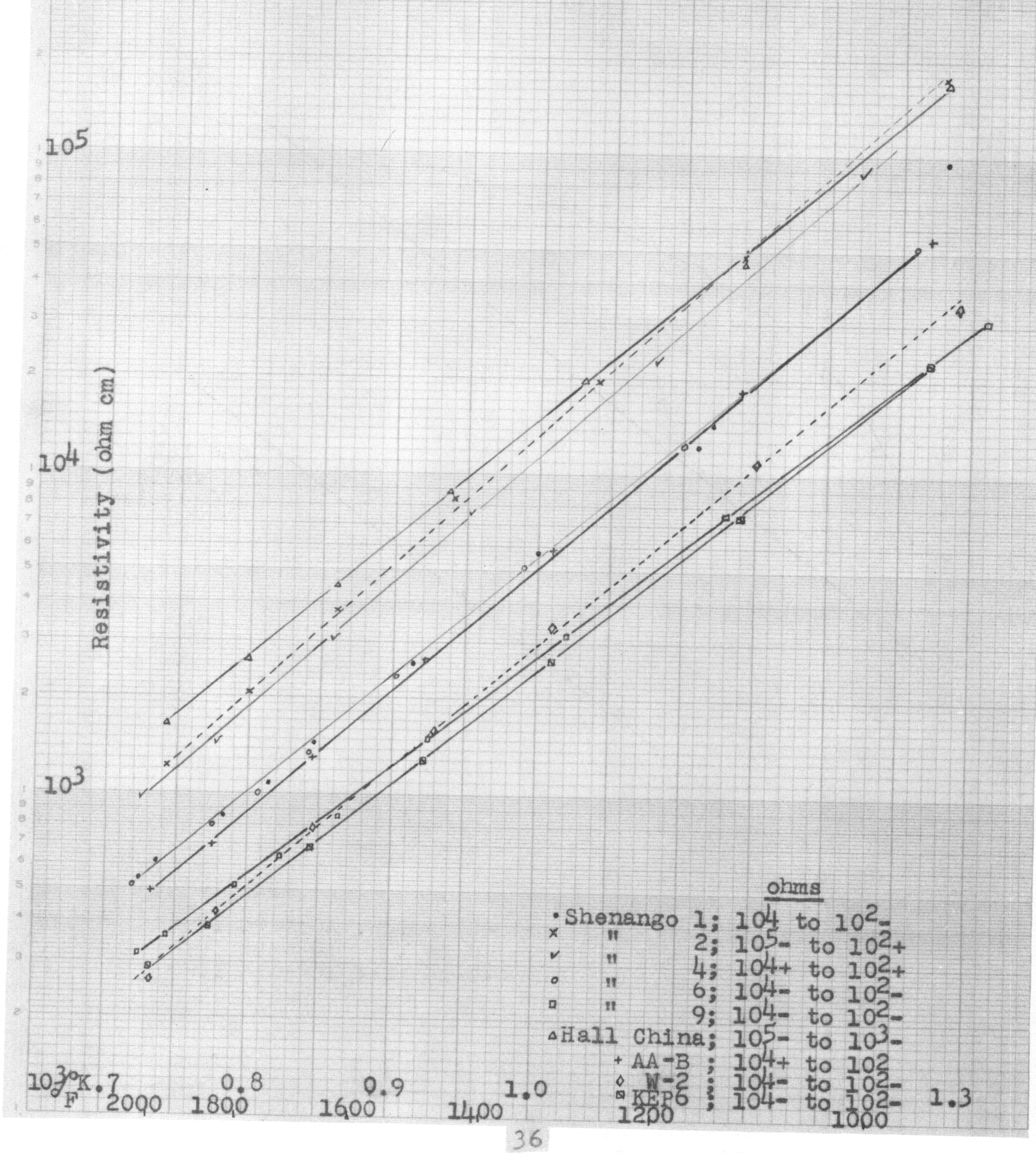


Figure 3 L

RESISTIVITY - TEMPERATURE CHARACTERISTICS BeO BODIES

75 volts, 400 cycles/sec
±5°F

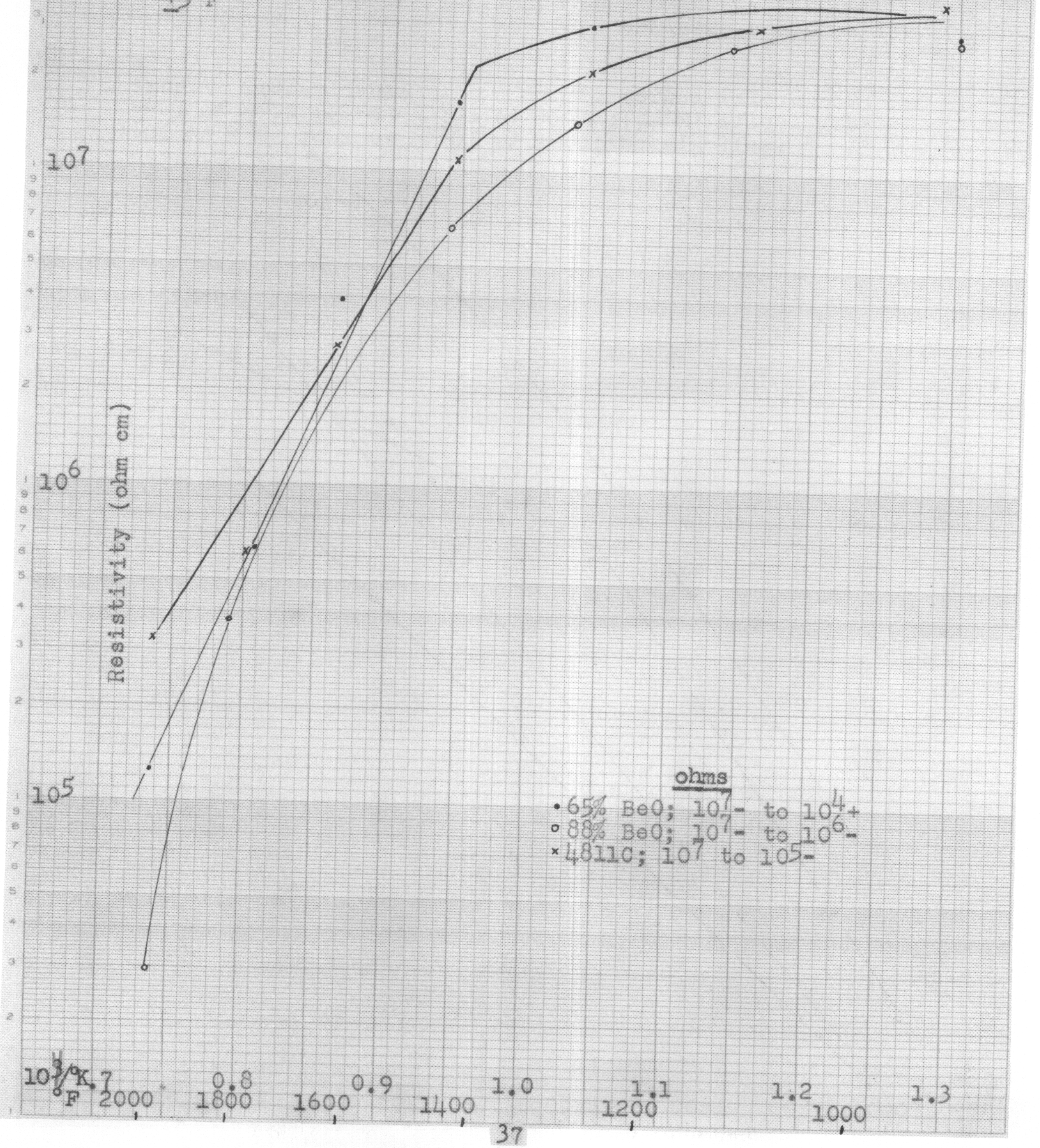
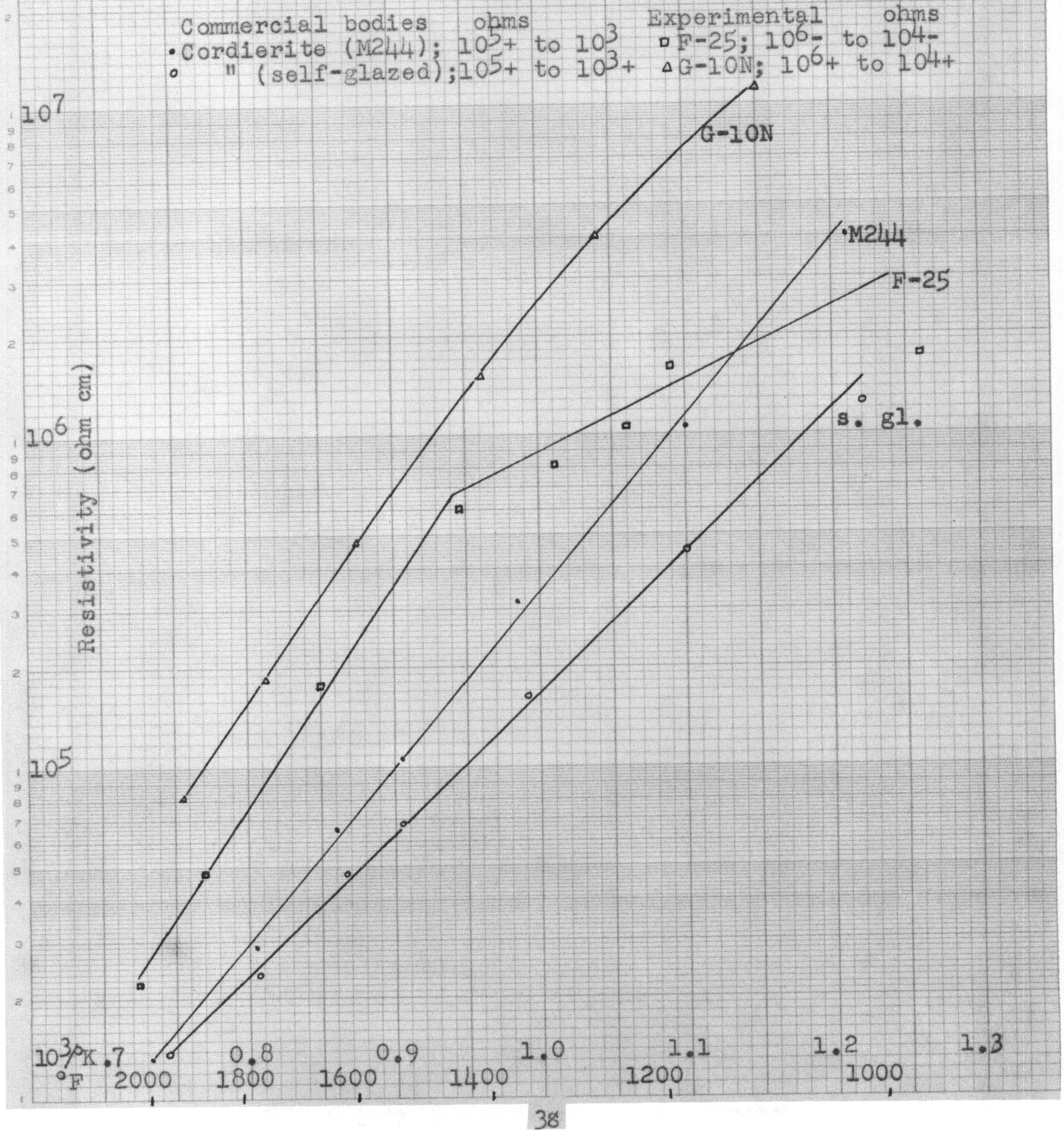


Figure 3 M

RESISTIVITY - TEMPERATURE CHARACTERISTICS CORDIERITE ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) BODIES

75 volts, 400 cycles/sec
±5°F



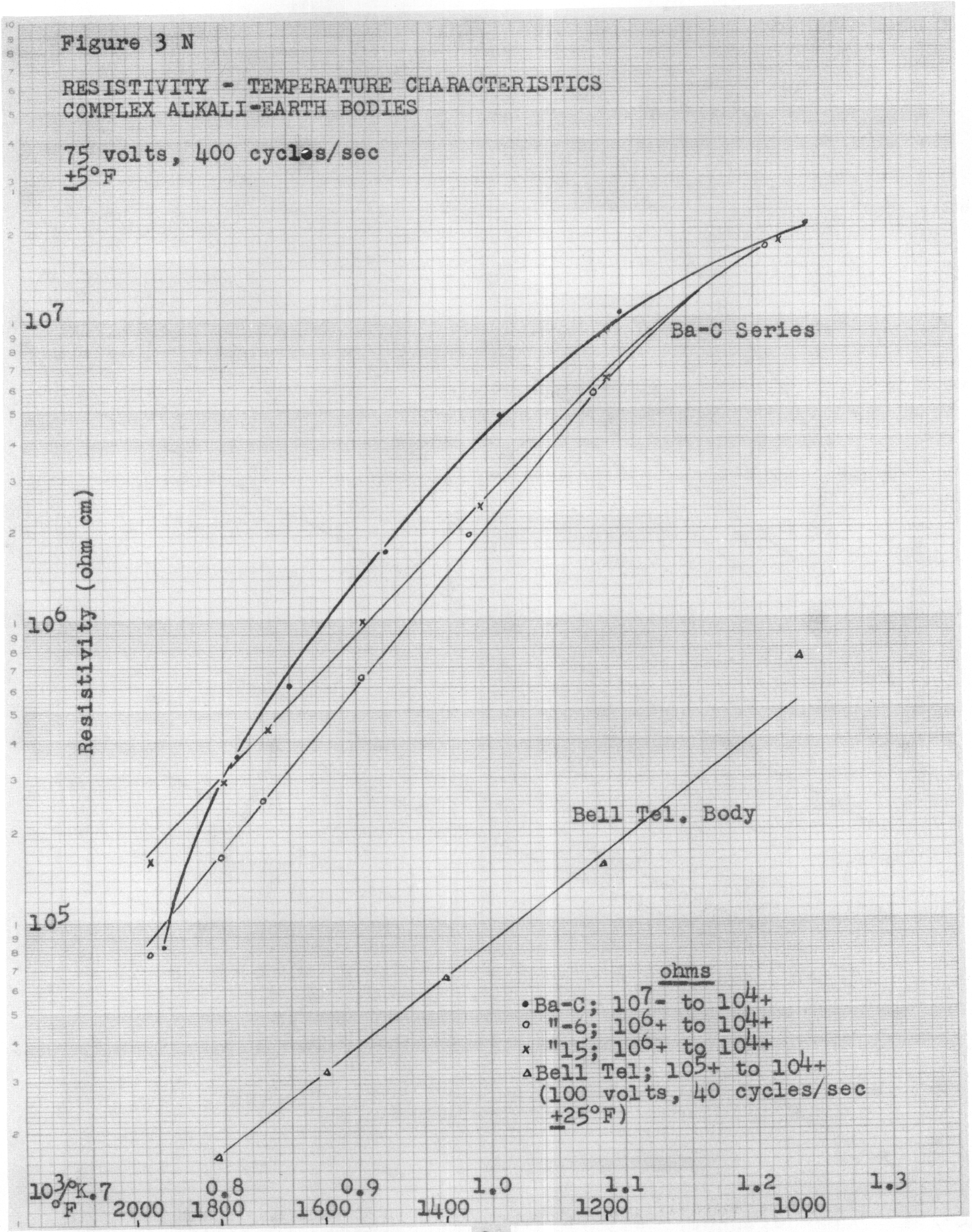


Figure 3 N

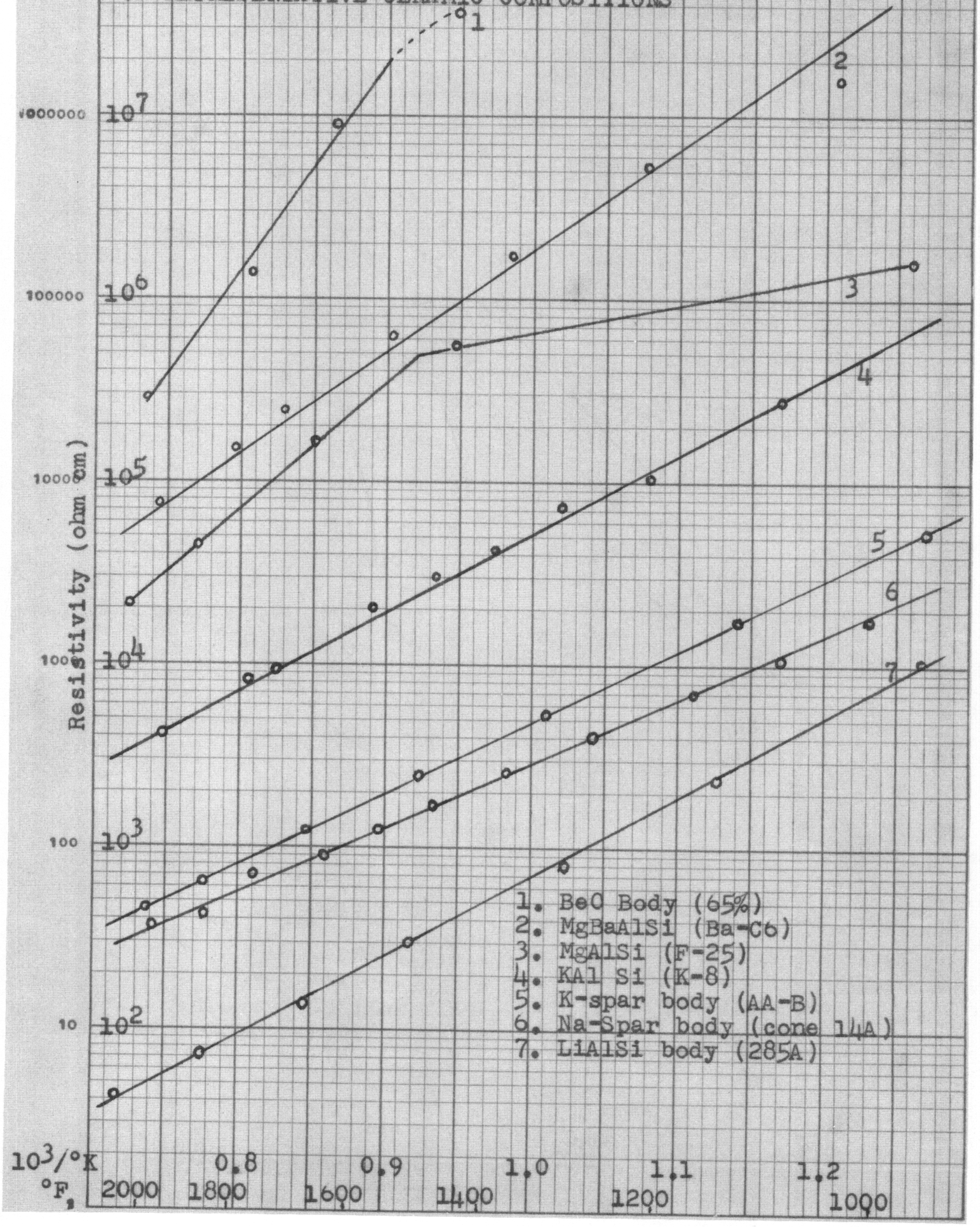
RESISTIVITY - TEMPERATURE CHARACTERISTICS
COMPLEX ALKALI-EARTH BODIES

75 volts, 400 cycles/sec
±5°F

MODEL DATE

Figure 4

RELATIONSHIP OF RESISTANCE - TEMPERATURE CHARACTERISTICS OF REPRESENTATIVE CERAMIC COMPOSITIONS



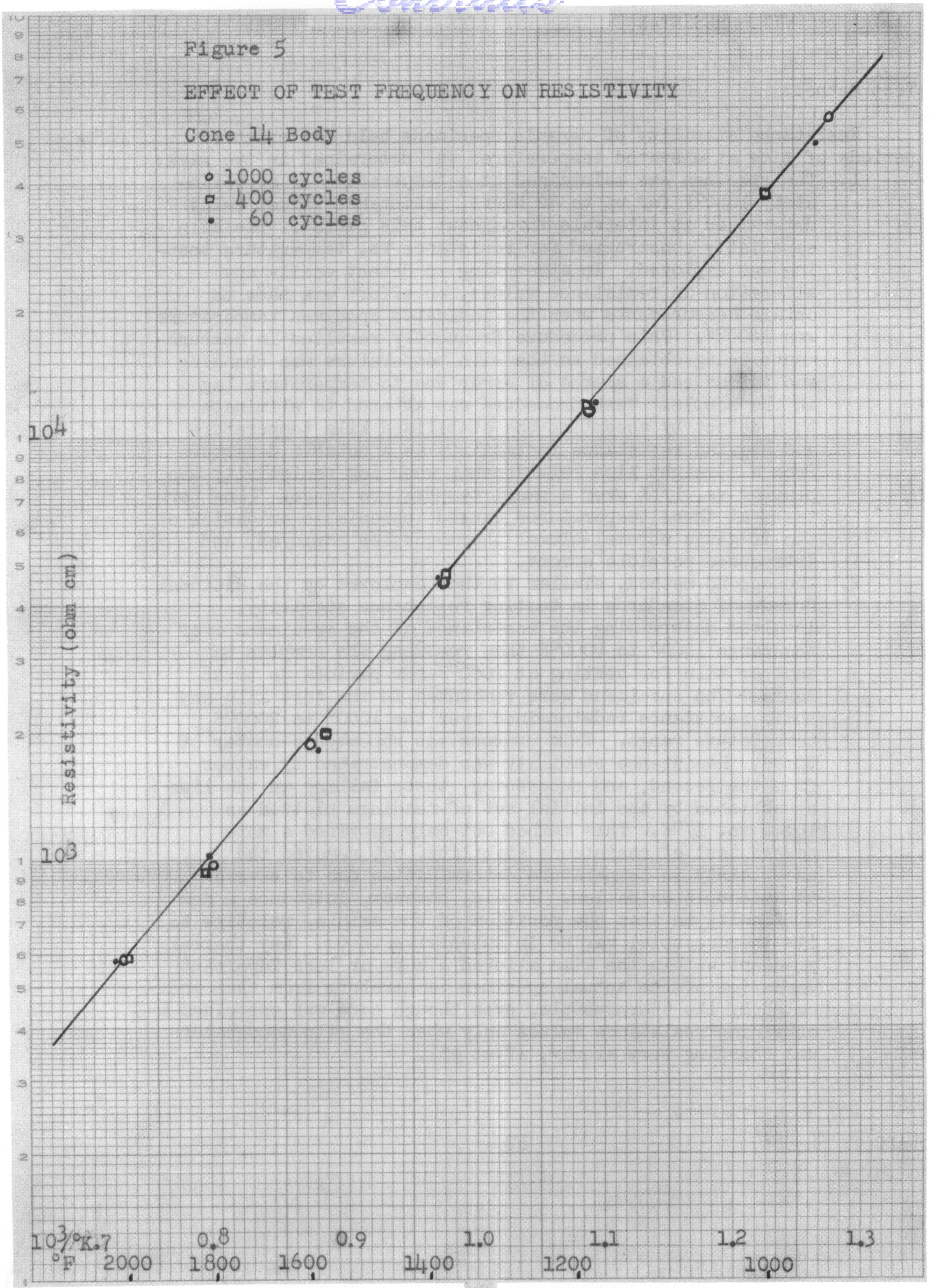


Figure 5

EFFECT OF TEST FREQUENCY ON RESISTIVITY

Cone 14 Body

VII. RESISTANCE STABILITY TIME-TEMPERATURE TESTS

Test Method:

Resistance stability of ceramic specimens held for extended periods of time at elevated temperatures was determined in two ways:

1. The specimen was maintained at a temperature of approximately 1800°F for up to 72 hours, resistance values being determined at intervals throughout this period. The kiln especially constructed for resistance vs. temperature testing was employed. In attempting to detect easily any alteration in resistance values, an effort was made to obtain measurements when the indicated specimen temperature was 1800°F. This procedure frequently resulted in measurements being obtained as the kiln temperature was changing and introduced a source of error due to temperature lag in the sample. Test procedure was altered to eliminate this defect by accepting the stabilized kiln temperature and showing resistance instability as a notable departure from a straight line relationship when log resistivity was plotted vs. 1/°K over a small temperature range. Long term tests at these temperatures caused appreciable oxidation of the 28-gauge chromel-alumel thermocouples employed, and introduced possible errors.
2. The second method, similar to that employed by the National Bureau of Standards in testing resistance stability, involved determining the resistance of the specimens over the range 1000° to 2000°F then removing the samples to another kiln for heating at 2000°F for periods up to 48 hours. The specimens were remounted in the test kiln and their resistance redetermined over the 1000° to 2000°F temperature range. This process was repeated a number of times. Resistance stability was demonstrated by values from the second, and succeeding, tests falling on the line established by the initial set of readings plotted as log R vs. 1/°K. This method not only provided a more severe test of resistance stability, but removed the uncertainty in temperature determination due to severe thermocouple oxidation. It did, however, introduce a new difficulty in that the position of the sample, relative to its thermocouple, varied in successive tests. Any thermal gradient within the kiln allowed a more or less important variation of the actual specimen temperature from that indicated by the thermocouple, even though care was exercised in obtaining resistance values only when the kiln temperature was changing very slowly, if at all.

Table IV

RESISTANCE STABILITY WITH TIME AT ELEVATED TEMPERATURES

Hours elapsed:	2	24	40	48	64	
Temp. °F :	1873	1873	1871	1873	1871	
CaAlSi-7	2.19	2.21	2.16	2.17	2.81	(x 10^5 ohms) torn electrode
80% Petalite	1.30	1.30	1.30	1.18	1.21	(x 10^2 ohms)
Cone 14 body	1.47	1.46	1.48	1.46	1.48	(x 10^3 ohms)

Hours elapsed:	2	8	23	32	50	
Temp. °F :	1780	1800	1800	1797	1800	
Zirconia S-1	4.30	4.20	4.70	4.70	4.80	(x 10^2 ohms)

Hours elapsed:	0	24	48	72	
Temp. °F :	1800	1800	1800	1800	
Zirconia S-1, rerun	--	6.28	8.51	9.98	(x 10^2 ohms)
Zirconia S-2	--	4.1	6.1	7.5	(x 10 ohms)
KAlSi 1	1.56	1.58	1.72	1.75	(x 10^3 ohms)
" 6	0.95	0.99	1.04	1.02	(x 10^3 ohms)
" 7	1.34	1.42	1.34	1.43	(x 10^3 ohms)
" 8	2.87	2.74	2.85	2.97	(x 10^3 ohms)
" 9	1.46	1.47	1.41	1.44	(x 10^3 ohms)
Cone 14 A body	--	1.41	1.42	1.42	(x10^2 ohms)
Shenango 1	5.70	5.80	5.80	5.80	(x 10^2 ohms)
" 2	6.40	6.40	6.80	6.90	(x 10^2 ohms)
" 4	5.60	5.56	5.50	5.55	(x 10^2 ohms)
Hall China	0.99	0.99	1.01	1.01	(x 10^3 ohms)
W-2	1.30	1.29	1.30	1.30	(x 10^2 ohms)
KEP 6	1.24	1.22	1.25	1.24	(x 10^2 ohms)
AA-B	3.06	3.05	3.10	3.06	(x 10^2 ohms)

Table IV (cont.)

Hours elapsed:	0	24	48	72	
Temp. °F :	1800	1800	1800	1800	
88% BeO	1.76	1.78	1.40	1.46	(x 10^5 ohms)
Cordierite self-gl.	3.21	3.10	3.10	3.07	(x 10^3 ohms)
Cordierite M-244	3.24	3.61	4.11	4.25	(x 10^3 ohms)
Cordierite G-10 N	4.27	4.06	3.60	3.06	(x 10^4 ohms)
Cordierite F-25					
sample (a)	2.56	2.59	2.58	2.55	(x 10^4 ohms)
sample (b)	1.67	1.66	1.49	1.51	(x 10^4 ohms)
Ba-C	8.60	9.50	(x 10^4 ohms)		
Ba-C 6	3.69	4.54	(x 10^4 ohms)		
Ba-C 15	5.44	5.47	(x 10^4 ohms)		

Hours elapsed:	0	24	41	72	90	
Temp. °F :	1800	1800	1800	1800	1800	
*Cone 14 A	1.53	1.52	1.58	1.54	1.54	(x 10^2 ohms)
(rerun)	1.57	1.52				(x 10^2 ohms)
**Shenango 4	5.90	5.50	5.80	5.90	5.98	(x 10^2 ohms)
(rerun)	5.50	5.59				(x 10^2 ohms)
Petalite body 285A	3.97	4.00	3.97	3.95	3.97	(x 10 ohms)
(rerun)	3.64	3.77				

* Cone 14 a specimen, previously held at 1800°F for 72 hours. Held at 2000°F for 24 hours prior to rerun above.

** Shenango 4 specimen previously held at 1800°F for 70 hours. Held at 2000°F for 24 hours prior to rerun above.

Table V

THERMAL HISTORY OF PORCELAIN SPECIMENS SHOWN IN FIGURES 6A TO 6C

Date	Heat Treatment	C-14 A	Shgo. No.4	285 A
--	r.t. to 2000°F (approx)	x	x	x
--	2000° to 1800°F, held :	72 hrs.	70 hrs.	---
Feb. 5	r.t. to 1980°F	---	x	---
Feb. 18	r.t. to 1935°F	x	x	x
Feb. 18-22	1935° to 1800°F held 90 hrs. at 1800°F	x	x	x
Feb. 22	1800°F to r.t.	x	x	x
Feb. 24-25	r.t. to 2000°F held 24 hrs. at 2000°F	x	x	x
Feb. 26	r.t. to 2015°F	x	x	x
Feb 26-27	2015° to 1800°F held 19 hrs. at 1800°F	x	x	x
Mar. 2-3	r.t. to 2000°F held 24 hrs. at 2000°F	x	x	x
Mar. 4	r.t. to 1980°F	x	x	x

Example summary of thermal history of Shenango No.4 specimen:

7 cycles heated from room temperature to 2000°F (approx.)
Held at 1800°F for a total of 179 hours.
Held at 2000°F for a total of 48 hours.

Figure 6 A

RESISTANCE STABILITY OF CONE 14A BODY (1000° to 2000°F)

75 volts, 400 cycles/sec
±5°F

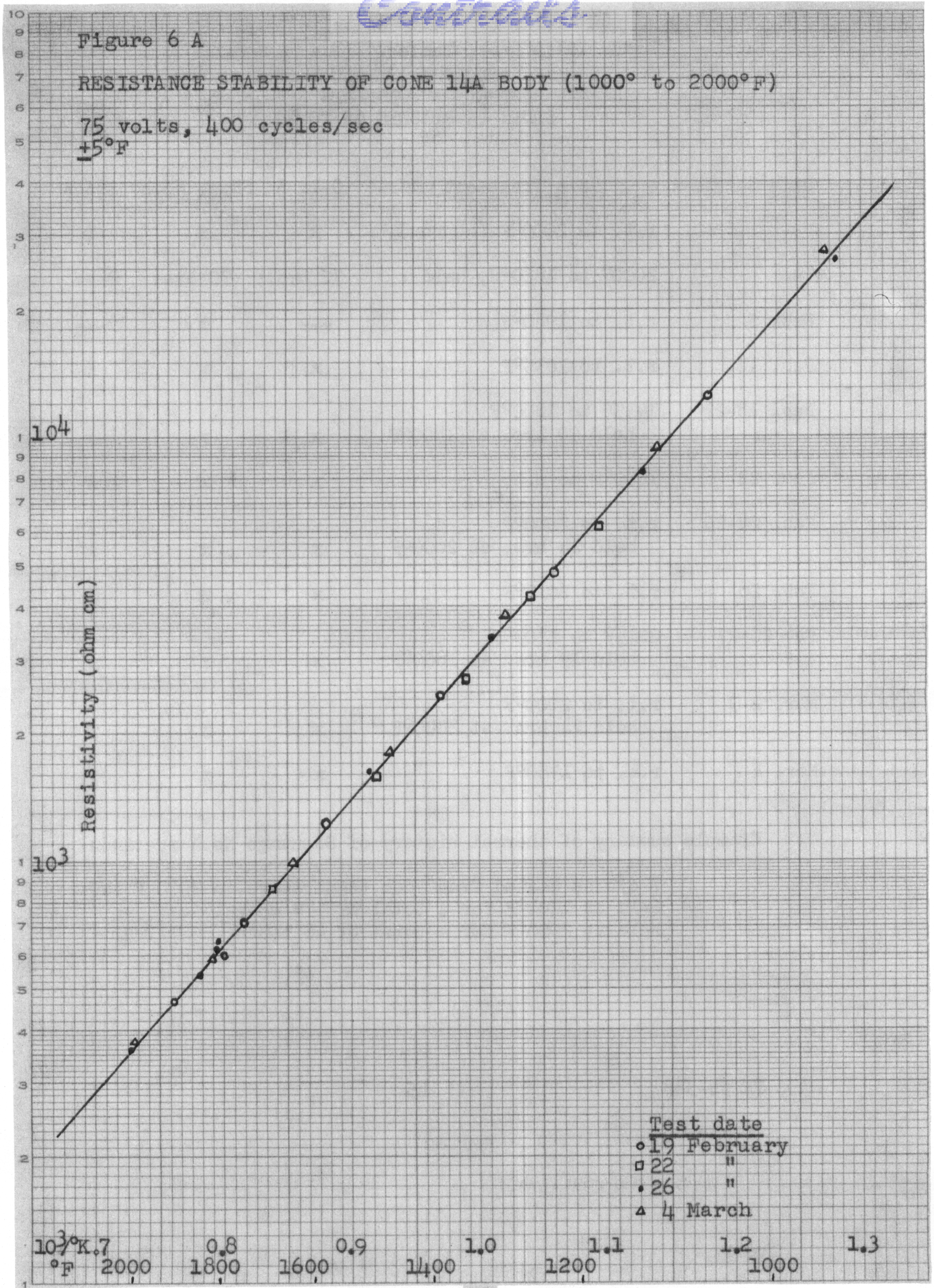


Figure 6 B

RESISTANCE STABILITY OF SHENANGO NO. 4 BODY (1000° to 2000°F)

75 volts, 400 cycles/sec
±5°F

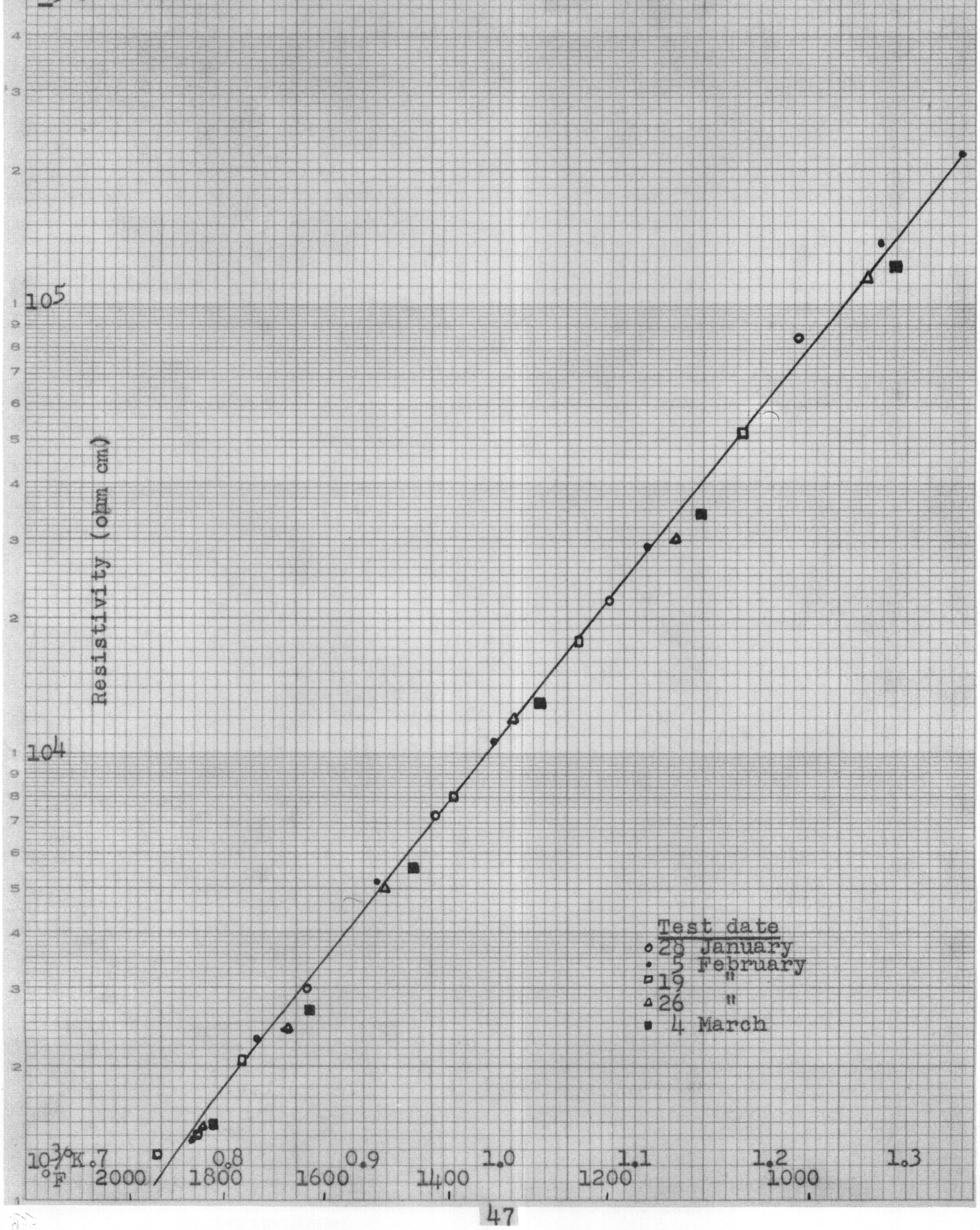


Figure 6 C

RESISTANCE STABILITY OF PETALITE 285A BODY (1000° to 2000°F)

75 volts, 400 cycles/sec
±5°F

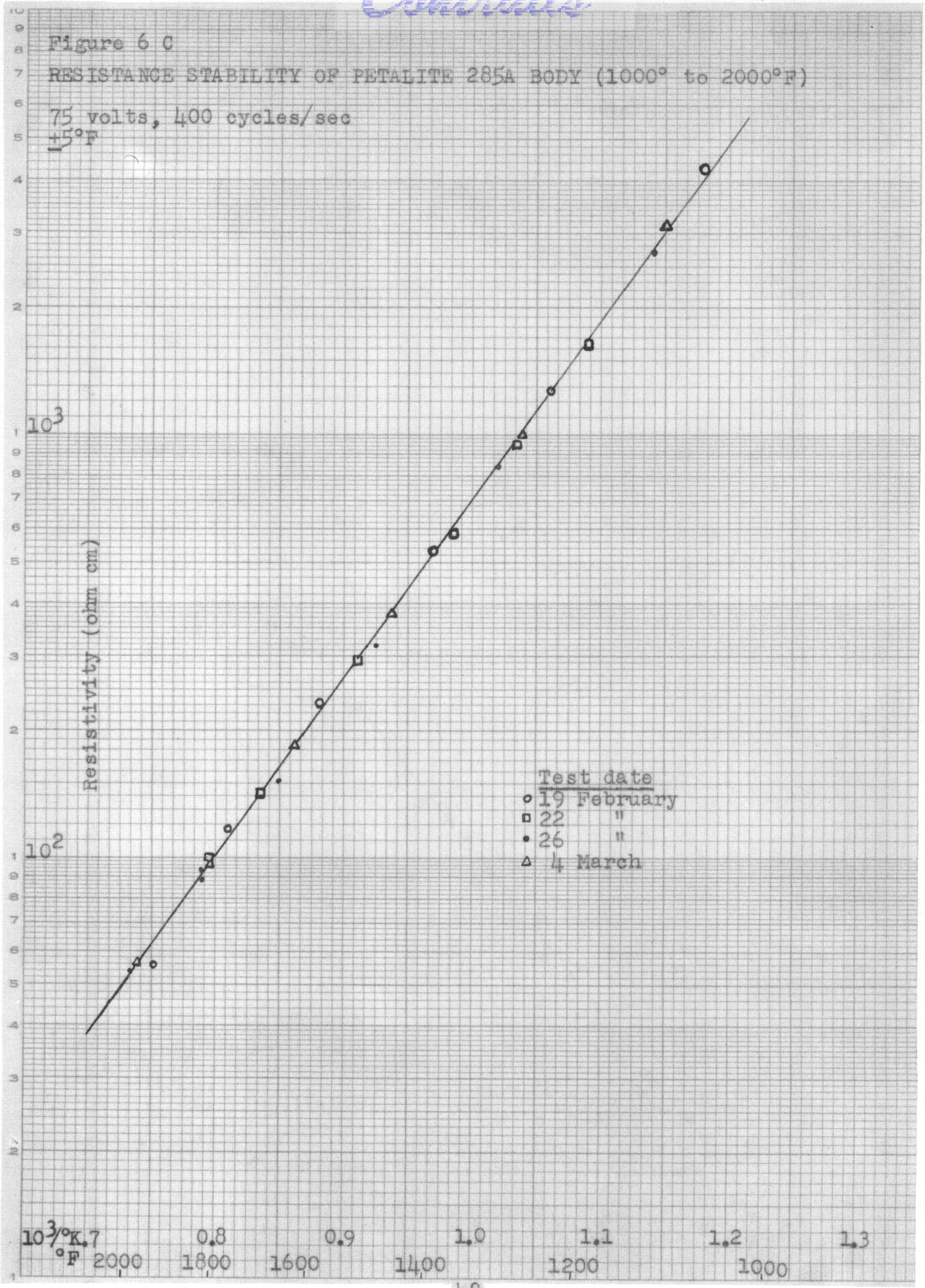
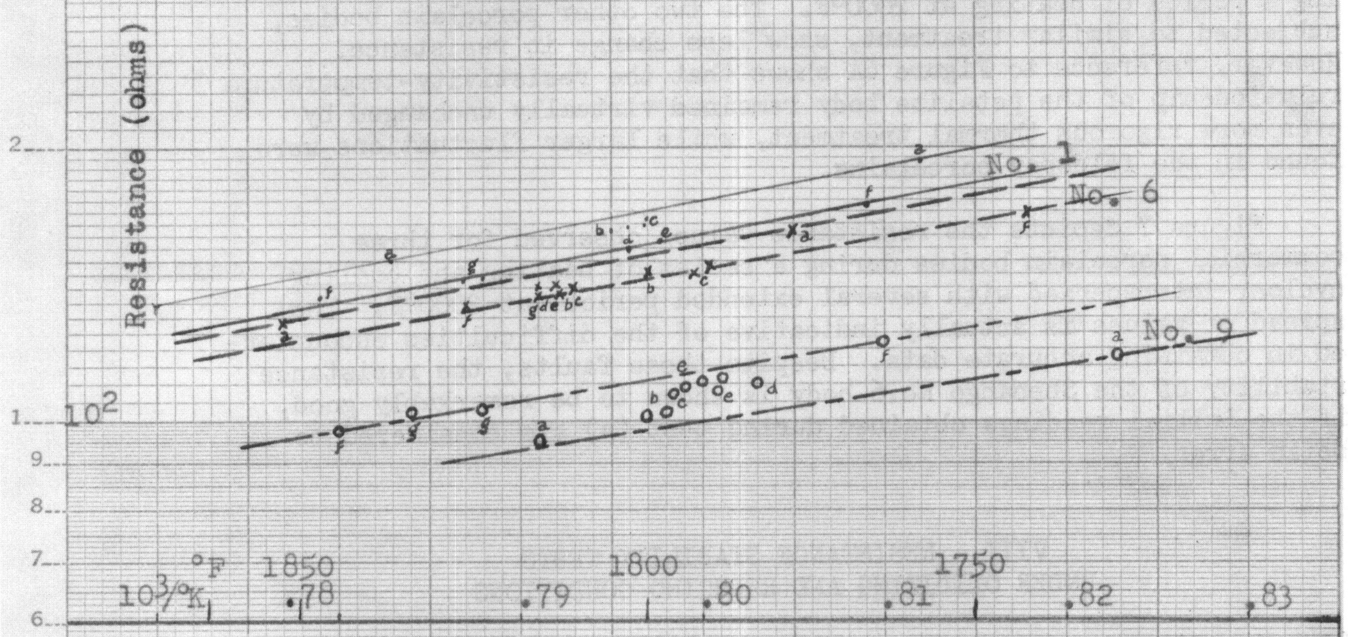


Figure 7

RESISTANCE STABILITY OF SHENANGO BODIES BETWEEN 1750° and 1850°F

75 volts, 400 cycles/sec
±5°F



Thermal History of Specimens

Test	
a	Room temp. to approx. 2000°F. Cooled to room temp. Heated 12 hrs. at 2000°F. Cooled to r.t.
b	Room temp. to approx. 2000°F. Cooled to approx. 1800°F.
c	5 determinations at approx. 1800°F over 48 hr. period. Cooled to r.t. Heated 66 hrs. at 2000°F. Cooled to r.t.
d	Room temp. to approx. 2000°F. Cooled to approx. 1800°F.
e	2 determinations at approx. 1800°F over 30 min. period. Cooled to r.t. Sample positions switched.
f	Room temp. to approx. 2000°F. Cooled to approx. 1800°F.
g	2 determinations at approx. 1800°F over 30 min. period.

Results of Tests:

Data obtained from specimens tested by the first method are given in Table IV, Results from later tests are shown in Figures 6 and 7. Considering the possible sources of error involved, the tests were capable of indicating resistance stability but, in borderline cases, did not prove instability.

From Table IV it may be seen that the sodium feldspar porcelain bodies (Cone 14 and Cone 14A) were quite stable when held for up to 72 hours at 1800°F or higher. The commercial porcelain bodies were generally good in this respect as well, particularly W-2, KEP6, and AA-B, the electrical porcelain specimens tested. The commercial petalite body (285A) seemed quite stable when held at 1800°F, but may change at a higher temperature, as indicated by the short test following a period of heating at 2000°F. The two other porcelain bodies, subjected to similar treatment, show less change in resistance. However, reference to Figure 6A shows that the resistivity-temperature relationship of the petalite body remained virtually unchanged by even more rigorous thermal treatment, while larger fluctuations were found in the feldspar porcelains.

Figure 7 depicts the resistance values observed for three commercial porcelain bodies during a series of heating and cooling cycles, interspersed with several extended periods at 2000°F. The spread of values is actually indicative of the difficulties encountered in obtaining accurate data. Despite these faults, the resistance stability of the Shenango No.6 body is shown to be remarkably good, if the initial readings obtained during test (a) are considered to be in error.

VIII. RESISTANCE STABILITY TESTS UNDER OXIDIZING AND REDUCING CONDITIONS

Test Methods:

The chemical stbility of a ceramic composition in the presence of strongly oxidizing or reducing gases at elevated temperatures, as reflected by the stability of resistance values, was one of the prime requisites to be met by a material suitable for thermistor use in the exhaust gases of a jet engine.

Early tests for the determination of stability under these conditions employed a small kiln fired by city gas and compressed air. By altering the gas : air ratio it was possible to achieve a variation in atmosphere from strongly oxidizing to strongly reducing.

An Orsat gas analyzer was used to determine the gases present in the kiln atmosphere during the test. One composition was tested by comparing resistance values obtained before and after the specimen had been annealed 4 hours at 1900°F in an oxygen atmosphere.

Later stability tests were made by placing the test specimen in a gas-tight tube furnace heated by Glo-bars. Within this tube, any selected atmosphere could be maintained. Reducing conditions were produced by supplying CO and CO_2 from compressed gas tanks. Sufficient CO was added to the CO_2 to support a flame at the tip of the exhaust tube. Oxidizing conditions were obtained through the introduction of O_2 after the tube had been flushed with CO_2.

Resistance values obtained during the test under reducing conditions were compared with the values originally observed when the specimen was tested from 1000° to 2000°F in air. Further testing was done by holding the temperature constant for an hour or more and observing the change in specimen resistance as the atmosphere was alternated between strongly reducing and strongly oxidizing.

Test Results:

The two compositions containing readily reducible oxides proved to be readily affected by strongly oxidizing atmosphere. The single crystal specimen of $CoO \cdot 2Fe_2O_3$ displayed a marked increase in resistance at room temperature following a four hour treatment at 1900°F in an oxygen atmosphere. At elevated temperatures the observed resist- was so low that it may be attributed to the resistance of the mounting, thus, the agreement of resistance at moderate temperatures tends to be misleading. As shown in Section B of Table VI, the porous specimen of the mixture 20% CoO, 80% Al_2O_3 sharply increased its resistance as the atmosphere was changed from oxidizing to reducing. A similar test on the BaAlSi composition B-5 produced no noticeable change in resistance, as shown by the data presented in Section C of Table VI.

A more rigorous test was employed in further studying the effects of a reducing atmosphere on bodies of the alkali porcelain type. As shown in Section E of Table VI, specimens fabricated with exposed electrodes displayed a gradual decrease in electrical resistance when held for a period of time at 1100°F in the reducing atmosphere provided in the tube furnace. The resistance rapidly approached the original value upon introduction of oxidizing conditions. As demonstrated by data in Section D of Table VI, when reducing conditions were maintained through the heating cycle 800° to 1800°F, the initial deterioration in resistance (which occurred between 800° and 1200°F) tended to disappear as the temperature approached 1600°F and was negligable at 1800°F. Evidence of carbon deposition at the lower test temperatures was found.

Table VI

ELECTRICAL RESISTANCE OF COMPOSITIONS SUBJECTED TO STRONGLY OXIDIZING OR REDUCING ATMOSPHERES AT ELEVATED TEMPERATURES

A. $CoO \cdot 2Fe_2O_3$ (single crystal)

Tested in neutral atmosphere with 6 volts DC.

Temperature °F	Ohms Resistance	
	Original	Annealed*
80	2.74×10^3	
86		4.58×10^3
392		1.17×10^2
435	5.51×10	
572	2.13×10	
608		1.89×10
770	9.3	9.8
932		7.4
941	7.2	
1121	6.5	
1130		6.5
1292	6.2	6.2

Resistance values observed at the higher temperatures are undoubtedly affected to a large extent by the resistance of electrodes and lead-wires.

*Specimen annealed 4 hours at 1900°F in O_2 before being tested in air.

Table VI (cont.)

B. 20% CoO, 80% Al_2O_3 (porous body)

Tested in gas-air kiln with 6 volts DC.

Time (Min.)	Temp. °F	Resistance (ohms)	Atmosphere (%)		
			CO_2	O_2	CO
0	1783	7.42×10^4	0.5	19.8	0
90	1810	8.35 "			
115	1804	8.20 "			
123	1804	8.26 "	0.4	19.8	0
130	1840	6.00 "			
155	1795	9.80 "			
170	1801	9.00 "			
200	1811	8.20 "	1.0	20.0	0
212	1812	8.00 "			
257	1815	1.32×10^6	9.8	0	0.6
277	1818	1.30 "			
290	1823	1.24 "	9.7	0	0.6
304	1821	8.6×10^4	0.8	20.1	0
315	1820	8.3 "			
322	1815	8.4 "			
324	1815	1.30×10^6	9.7	0	0.7
326	1815	1.30 "	9.7	0	0.7

Table VI (cont.)

C. B-5 Body (84 BaO, 4 Al_2O_3, 12 SiO_2 wt. %)

Tested in gas-air kiln with 400 cycle AC.

Temp. (°F)	Resistance (ohms)	Atmosphere
1703	1.79×10^4	oxidizing
1704	1.79 "	"
1743	1.49 "	"
1780	1.22 "	"
1785	1.20 "	reducing
1783	1.22 "	"
1777	1.23 "	"

D. Electrical porcelain (body AA-B)

Results from test in tube furnace under constantly reducing conditions, compared with initial values obtained on testing specimen in air, using 400 cycle AC.

Temp.	Resistance (ohms)	
(°F)	Oxidizing	Reducing
1025	3.89×10^3	9.30×10^2
1200	1.24 "	4.65 "
1400	4.40×10^2	2.50 "
1600	2.10 "	1.80 "
1800	1.00 "	1.04 "
2000		0.67 "
1600		2.30 "

Table VI (cont.)

E. Electrical porcelain (body KEP 6)

Results from test with 400 cycle AC in tube furnace under alternating reducing and oxidizing conditions, compared with original values obtained in air.

Temp. (°F)	Time (min.)	Resistance given in ohms (Reducing)	(Oxidizing)	(Air)
830	20	15,600 ?		13,000
1015	65	2,360		4,300
1065	95	1,320		3,200
1130	130	471		2,200
"	240	269		
"	<10		1,780	
"	50		1,800	
"	<20	1,800		
"	75	1,800		
"	85	4,060		4,700
"	110	2,600		
"	<10		4,120	
"	35		4,200	
1000	25	4,250		
"	40	4,100		
"	60	2,000		
1800	0		132	128
"	15		125	
"	50		130	
"	<10	128		
"	70	127		
"	<10		123	
"	35		128	
1600	<20	249		240
"	40	249		

Table VI (cont.)

F. Petalite body (Li-K 1):

Specimen designed to protect electrodes; tested with 400 cycles AC in tube furnace.

Time (min.)	Temp. (°F)	Resistance (ohms)	Atmosphere
0	r.t.		air
60	1025		"
165	1078	7.5×10^2	"
190	"	"	"
200			CO_2 introduced
205	1078	7.6×10^2	CO_2
210	"	8.00 "	CO introduced
280	"	8.20 "	CO_2 and CO
365	"	8.20 "	" "
435	"	8.25 "	" "

Although the platinum electrodes may have served to catalyze the deposition of carbon, it occurred readily when specimens without electrodes were subjected to the heated reducing gases. This reaction may be expressed as:

$$2\ CO \underset{\text{above } 1400^{\circ}F}{\overset{\text{to } 1400^{\circ}F}{\rightleftarrows}} CO_2 + C$$

Following extended testing under alternating atmosphere the specimen and tube interior were liberally coated with finely divided iron oxide. This iron contamination was found to come from the compressed CO gas, probably carried as $Fe(CO)_5$ vapor. It has been suggested that the deposition of carbon was catalyzed by the iron impurity. Undoubtedly the iron, under reducing conditions, aided the deposited carbon in forming a conductive path between electrodes.

As shown in Section F of Table VI, one porcelain specimen that was designed to protect the path between electrodes from carbon deposition gave quite stable resistance values even though subjected to strongly reducing conditions in the temperature range below 1400°F.

In general, the results of tests on alkali porcelains and on the BaAlSi composition B-5 indicated that these materials remained inert under strong oxidation or reduction in the 1000° to 2000°F temperature range. This insensitivity is probably characteristic of all aluminum silicate compositions containing the relatively chemically stable alkali or alkali-earth oxides.

IX. SUMMARY OF RESULTS

During the course of the investigation, a number of variations were employed in the method used for determining the resistance of ceramic specimens. Use of direct current was found to be unsatisfactory due to polarizing effects that became particularly troublesome at high temperatures. An alternating current of 400 cycles/sec was eventually adopted since it is generally available in aircraft The capacity of specimens subjected to alternating current at elevated temperatures made it necessary to include a variable capacitor in the measuring bridge circuit so that the true resistance of the system could be determined.

The measured resistance was not only that of the temperature sensitive material but included the contact resistance between the sensitive body and applied metal electrodes as well as the resistance of all wires leading to the measuring bridge. Although contact resistance was minimized by using platinum foil electrodes applied with platinum paste, and welded joins between electrodes and lead-wires, the extraneous sources of resistance proved to be sources of appreciable error in evaluating specimens having less than 30 ohms resistance.

Observed resistance values above 10^6 ohms were of doubtful accuracy since such measurements required the use of an experimental bridge having a known resistance leak whose source could not be located. Fortunately, most specimens had dimensions such that their resistance over the temperature range 1000° to 2000°F fell between 10^6 and 10^2 ohms. Within this range the experimental bridge gave reasonably reliable results or the General Radio impedance bridge could be used.

In tests conducted during the early phases of the study the specimens were heated in kilns having steep temperature gradients and coarse temperature control. These conditions made it difficult to determine the specimen temperature within 25°F. Subsequent tests, employing a specially constructed kiln and improved testing procedure, produced more reliable data with the error in specimen temperature probably not exceeding 5°F. The gradual oxidation of the chromel-alumel thermocouples used for temperature determination probably introduced a significant error only during long term tests of resistance stability at elevated temperatures.

Some of the specimens, which were subjected to a strongly reducing atmosphere, indicated that the observed change in resistance at the lower test temperatures was due to the deposition of a carbon deposit which formed a conductive path between the electrodes. This source of apparent instability under reducing conditions was eliminated by enclosing the electrodes within the ceramic specimen.

Thermistors to be tested under simulated service conditions required mounting in thermocouple-type probes. The insulation, used between lead-wires within the probe, introduced a second resistance in parallel with the specimen. In order to obtain an observed resistance which was at least 90% of the true specimen resistance it was necessary to provide a probe resistance at least ten times higher than that of the specimen. The commonly used swaged magnesia insulation between the lead-wires within the probe shaft proved to be unsatisfactory due to insufficient resistance coupled with resistance instability. Vitrified alumina thermocouple tubing gave reasonably good results.

Probe-mounted thermistors fabricated from selected compositions were sent to the National Bureau of Standards for further investigation, including tests conducted in exhaust gases from a jet engine, as described in an excellent paper by Dahl and Fiock(6). Other thermistors have been fabricated from the commercially available Shenango No.6 porcelain. These were sent to the Wright Air Development Center for testing under service conditions.

Extensive preliminary testing had revealed vitrified alkali porcelains as a group of ceramic compositions which met the requirements of: linearity of log resistivity vs. 1/°K; resistance stability for at least 72 hours at 1800°F; and indifference to oxidizing and reducing atmospheres.

Data obtained from those porcelain bodies that were studied indicated that the particular alkali used as a flux in the body influenced the slope of the log R vs. 1/°K line. Both the identity and quantity of alkali present in the body influenced the relative resistivity of the composition. Resistivity values typical of the alkali porcelain bodies tested at 400 cycles/sec had approximate ranges as follows:

	Na-type	K-type	Li-type	
(1000°F)	2×10^4	1×10^5	7×10^3	ohm cm
(2000°F)	4×10^2	1×10^3	5×10	ohm cm

The resistivity vs. temperature characteristics of the many ceramic compositions which were tested over the temperature range of 1000° to 2000°F are summarized in Table VII along with pertinent data obtained from the available literature. Resistivity data for other ceramic compositions, taken from reports issued by Lear, Inc., and the Armour Research Foundation, are appended.

Table VII

RESISTIVITY VS. TEMPERATURE CHARACTERISTICS OF SOME CERAMIC COMPOSITIONS

References Cited:

Rogener, H. <u>Resistivity of Sintered Al_2O_3</u> Z. Elektrochem. <u>Vol. 46</u> January 1940. p. 25.

Navias, L. General Electric Research Laboratory Report No. RL-833, April 1953.

Davenport, et al. <u>Oxide Resistors</u> Jour. Amer. Ceramic Society <u>Vol. 33</u> November 1950. p. 335.

Ford, F.W. and White, J. <u>Electrical Properties of Oxide Mixtures</u> Trans. British Ceramic Society <u>Vol. 51</u> January 1952. pp. 1-77.

Terminology:

1. Linearity or non-linearity of the plot of log resistivity vs. 1/°K was frequently questionable due to errors in measurement of specimens having very high or very low resistance values.

2. Slope of the line obtained by plotting log R vs. 1/°K should be steep, indicating a large change in resistance with change in temperature.

3. Stability of resistance at 1800°F, or higher, for a period of time exceeding 48 hours.

4. Sensitivity of specimen resistance to alternately oxidizing and reducing (CO and CO_2) atmosphere.

Table VII
RESISTIVITY VS. TEMPERATURE CHARACTERISTICS OF SOME CERAMIC COMPOSITIONS

Composition	Test Conditions freq.	bridge voltage	Approx. Resistivity (ohm cm) 1000°F	2000°F	Characteristics
Al_2O_3 (single crystal)	D.C.	500	$1x10^8$	$3x10^5$	(1)linear? high values (poor contacts)
Al_2O_3 (sintered)	?	?	$2x10^{10}$	$2x10^8$	linear? (values extrapolated, data by Rogener)
Al_2O_3 (body)	D.C.	500	$5x10^8$	$3x10^5$	linear (Gen. Elec. Body 2548, data by Navias)
98 Al_2O_3, 2 Cr_2O_3 (wt%) (ruby single crystal)	D.C.	6	$1x10^9$	$3x10^6$	linear? high resistance values
80 Al_2O_3, 20 CoO (wt%)	D.C.	6	$5x10^8$	$2x10^4$	linear, stable with time,(3) atmosph.-sensitive(4) (porous)
" " 20 Cr_2O_3	D.C.	6	$5x10^3$	$8x10^2$	linear, slight slope(2) (porous)
" " 20 NiO	40	100	$8x10^7$	$4x10^4$	linear
" " 20 SrO	D.C.	6	$1x10^8$	$3x10^5$	non-linear?
60 " 40 NiO	40	100	$1x10^7$	$8x10^3$	linear
BaO Al_2O_3 SiO_2 (wt%)					
84 4 12	40	100	$2x10^6$	$8x10^3$	non-linear, hydrates at r.t.
66 6 28	40	100	$2x10^7$	$1x10^5$	non-linear
53 19 28	40	100	$8x10^8$	$1x10^6$	linear? high values
$48BeO \cdot 1Al_2O_3 \cdot 1ZrO_2$ + 4% MgO	40	100	$2x10^9$?	$3x10^5$	linear? (Body 4811-C supplied by Bur. of Stand.)
" " " "	400	75	$3x10^7$?	$3x10^5$	non-linear?
88% BeO (commercial body)	400	75	$3x10^7$?	$3x10^4$	non-linear? unstable with time at 1800°F
65% BeO (commercial body)	400	75	$7x10^7$?	$2x10^5$	non-linear? high resistance values
$CoO \cdot Al_2O_3$	D.C.	6	$1x10^6$	$2x10^4$	linear (porous body)
$CoO \cdot 2Fe_2O_3$ (single crystal)	D.C.	6	$7x10^0$	$6x10^0$	linear? low values, atmosph.-sensitive

Table VII (cont.)

Composition	Test Conditions freq.	bridge voltage	Approx. Resistivity (ohm cm) 1000°F	2000°F	Characteristics
Cr_2O_3	D.C.	6	5x10	3x10	linear? slight slope (porous body)
60 Cr_2O_3, 40 Al_2O_3 (wt%)	D.C.	6	9x10	5x10	linear, slight slope (porous body)
$MgO\cdot Al_2O_3$	40	100	$5x10^{7}$	$6x10^{5}$	non-linear
$(MgO)_{.99}(Li_2O)_{.01}(Al_2O_3)_{1.0}$	40	100	$2x10^{7}$	$2x10^{5}$	non-linear?
$(MgO)_{.9}(Li_2O)_{.1}(Al_2O_3)_{1.0}$	40	100	$4x10^{7}$	$2x10^{6}$	non-linear?
$MgO\cdot Al_2O_3$ + 11% SiO_2	40	100	$2x10^{8}$	$1x10^{6}$	non-linear, high values (body R-2 from Sig. Corps Project, Rutgers)
$MgO\cdot Al_2O_3$ + 25% SiO_2	40	100	$3x10^{8}$	$5x10^{5}$	non-linear, high values (body R-3, source as above)
80 MgO, 20 Al_2O_3 (wt%)	40	100	$1x10^{8}$	$7x10^{5}$	linear? high values
$2MgO\cdot SiO_2$ (Forsterite body)	D.C.	500	$8x10^{9}$	$1x10^{6}$	non-linear (Gen. Elec. body 189-2C, data by Navias)
80 NiO, 20 Al_2O_3 (wt%)	D.C.	6	$1x10^{4}$	$1x10^{2}$	linear? stable with time at high temperature.
ZrO_2	40	100	$3x10^{6}$	$2x10^{4}$	non-linear
ZrO_2 (stabilized)	?	?	$3x10^{4}$	3x10	linear (data from Davenport)
ZrO_2 (stabilized)	400	75	$8x10^{4}$	$3x10^{2}$	linear, unstable with time at 1800°F (sample S-2, obtained from Weber, WADC)
ZrO_2 + 9% MgF_2	40	100	$1x10^{5}$	$4x10^{2}$	linear, unstable with time at 1800°F (sample S-1, obtained from Richardson, WADC)
90 ZrO_2, 10 CaO (wt%)	40	100	$7x10^{4}$	7x10	linear? low values
50 ZrO_2, 50 CaO (wt%)	40	100	$6x10^{5}$	$2x10^{2}$	linear?
$ZrO_2\cdot SiO_2$ (Zircon body)	40	100	$1x10^{7}$	$6x10^{4}$	linear?
Zircon-talc body	D.C.	500	$7x10^{7}$	$2x10^{5}$	linear? (Gen. Elec. body 2618, data by Navias)
Low Zircon body (complex zirconium silicates)	40	100	$3x10^{7}$	$7x10^{4}$	non-linear? (body 18-4 from Sig. Corps Project, Rutgers)

Table VII (cont.)

Composition				Test Conditions		Approx. Resistivity (ohm cm)		
				freq.	bridge voltage	1000°F	2000°F	Characteristics
ALKALI ALUMINUM SILICATES								
K_2O	Al_2O_3	SiO_2	(wt%)					
5	75	20		1000	75	$3x10^6$	$1x10^4$	linear (porous specimen, body K-5)
5	65	30		1000	75	$3x10^6$	$1x10^4$	linear (porous specimen, body K-4)
7	53	40		400	75	$6x10^5$	$4x10^3$	linear, fair stability with time (body K-8)
"	"	"		40	100	$8x10^5$	$5x10^3$	linear
10	60	30		40	100	$2x10^5$	$2x10^3$	linear (body K-3)
10	50	40		400	75	$3x10^5$	$2x10^3$	linear (body K-1)
10	45	45		400	75	$2x10^5$	$3x10^3$	linear, stable with time at 1800°F (body K-9)
12	40	48		400	75	$2x10^5$	$3x10^3$	linear, stable with time at 1800°F (body K-7)
13	47	40		1000	75	$2x10^5$	$2x10^3$	non-linear (body K-2)
15	40	45		400	75	$1x10^5$	$2x10^3$	linear, fair stability with time at 1800°F (body K-6)
Commercial dinner-ware bodies:								
Shenango 1 (old)				400	75	$7x10^4$	$8x10^2$	linear
" 1 (new)				400	75	$4x10^4$	$5x10^2$	linear, fair stability with time at 1800°F
" 2				400	75	$1x10^5$	$1x10^3$	linear, poor stability with time at 1800°F
" 4				400	75	$9x10^4$	$1x10^3$	linear, stable with time at 1800°F, atmosphere insensitive
" 6				400	75	$4x10^4$	$5x10^2$	linear, stable with time at 1800°F
" 9				400	75	$2x10^4$	$3x10^2$	linear, fairly stable with time at 1800°F
Hall China body				400	75	$1x10^5$	$2x10^3$	linear, fairly stable with time at 1800°F

Table VII (cont.)

Composition	Test Conditions freq.	bridge voltage	Approx. Resistivity (ohm cm) 1000°F	2000°F	Characteristics
Low-tension insulator bodies:					
AA-B (Commercially fabricated)	400	75	4×10^4	5×10^2	linear, stable with time, atmosph.-insensitive
W-2 " "	400	75	2×10^4	3×10^2	linear? stable with time at 1800°F
KEP 6 " "	400	75	2×10^4	3×10^2	linear, stable with time at 1800°F
Lithia-type porcelains:					
80 Petalite, 20 clay (wt%)	40	100	3×10^4	2×10^3	non-linear, fair stability with time at high temp.
50 " 50 "	400	75	7×10^3	5×10	linear, stable with time at 1800°F (commercial body)
QC6-F 1	400	75	7×10^3	2×10	linear? (sample from Sig. Corps Project, Rutgers)
Li_2O KNaO Al_2O_3 SiO_2 (mol.%)					
1.5 1.5 14 83	400	75	--	--	linear, stable with time, insensitive to atmosphere (body Li-K 1)
1.6 2.3 20 76	400	75	8×10^3	1×10^2	linear? low resistance values (body Li-K 2a)
1.3 2.0 22 75	400	75	1×10^4	1×10^2	linear? low resistance values (body Li-K 2b)
1.0 1.7 24 73	400	75	1×10^4	2×10^2	linear? low resistance values (body Li-K 2c)
1.0 1.5 21 77	400	75	1×10^4	2×10^2	linear? low resistance values (body Li-K 2d)
0.9 1.4 17 81	400	75	1×10^4	2×10^2	linear? low resistance values (body Li-K 2e)
Sodium-type porcelains:					
Cone 14 body	40	100	2×10^5	3×10^3	linear, stable with time at high temp. insensitive to atmosphere
" "	60, 400, 1000	75	4×10^4	7×10^2	as above
Cone 14 A body	400	75	2×10^4	4×10^2	as above
Cone 12 body	40	100	1×10^5	7×10^3	non-linear

Table VII (cont.)

Composition			Test Conditions		Approx. Resistivity (ohm cm)		Characteristics
			freq.	bridge voltage	1000°F	2000°F	
ALK.-EARTH ALUMINUM SILICATES							
CaO	Al_2O_3	SiO_2 (wt%)					
45	10	45	475	?	---	$(2x10^5)k$	linear to 2190°F (data by Ford and White)
36	40	24	40	100	$3x10^8$	$6x10^5$	non-linear, variable, high values (body C-9)
20	37	43	40	100	$6x10^8$	$2x10^6$	non-linear, high values (body C-1)
18	52	30	40	100	$(2x10^7)k$	$(1x10^5)k$	linear? high values (body C-16, resistance given)
18	41	41	40	100	$3x10^8$	$2x10^6$	non-linear, high values (body C-4)
17	70	13	40	100	$6x10^7$	$4x10^5$	linear? high values (body C-15)
12	70	18	40	100	$(4x10^7)k$	$(1x10^5)k$	linear? high values (body C-17, resistance given)
11	55	34	40	100	$(3x10^7)k$	$(3x10^5)k$	linear, high values (body C-6, resistance given)
MgO	Al_2O_3	SiO_2 (wt%)					
50	10	40	40	100	$3x10^8$	$2x10^6$	non-linear? high values (body M-5)
46	11	43	40	100	$5x10^8$	$2x10^6$	non-linear (body M-4)
46	7	47	40	100	$1x10^9$	$1x10^6$	non-linear? high resistance values (body M-3)
36	35	29	40	100	$8x10^8$	$3x10^6$	linear? high resistance values (body M-11)
36	7	57	40	100	$5x10^8$	$7x10^5$	non-linear (body M-1)
30	50	20	40	100	$3x10^8$	$2x10^6$	non-linear (body M-13)
23	57	20	40	100	$3x10^8$	$5x10^5$	non-linear ($MgO \cdot Al_2O_3$ +25% SiO_2, sample from Sig. Corps Project, Rutgers)
17	34	49	400	75	$2x10^6$	$2x10^4$	non-linear (cordierite body F-25, sample from Sig. Corps Project, Rutgers)
14±	35±	51± (Cordierite)	400	75	$6x10^6$	$1x10^4$	linear? poor stability with time at 1800°F, (body fabricated commercially)
Cordierite + Feldspar			400	75	$2x10^6$	$1x10^4$	linear, fair stability with time at 1800°F (self-glazed body fabricated commercially)

Table VII (cont.)

Composition				Test Conditions		Approx. Resistivity (ohm cm)		Characteristics
MgO	BaO	Al_2O_3	SiO_2 (wt%)	freq.	bridge voltage	1000°F	2000°F	
								(following four bodies from Sig. Corps Project)
11	2	36	53	400	75	$2x10^7$	$5x10^4$	non-linear? unstable with time at 1800°F (body G-10N)
14	6	20	60	400	75	$2x10^7$	$1x10^4$?	non-linear, unstable with time at 1800°F (body Ba-C)
10	5	23	62	400	75	$4x10^7$	$7x10^4$	linear? unstable with time at 1800°F (body Ba-C 6)
5	8	20	67	400	75	$2x10^7$	$1x10^5$	non-linear? fair stability with time at 1800°F (body Ba-C 15)
Complex alk.-earth porcelain				40	100	$7x10^5$	$1x10^4$	linear? poor stability with time at high temperatures (carbon resistor core body from Bell Tel. Lab.)

From the Lear Inc. Reports on the Development of Temperature Measuring Elements for Gas Turbine Control(1)

Discs were formed from 100 mg raw material pressed in 3/16 inch diameter die, then fired in air. AC electrical measurements were reported as specimen resistance (in ohms). Particular difficulty was encountered in achieving a permanent bond between the ceramic body and the platinum electrodes.

Composition	Ohms	(°F)	Ohms	(°F)	Remarks
Fe_2O_3	$4.5x10^5$	(70)	2.0x10	(1350)	metallic fired appearance, rapid resistance drop
50 Fe_2O_3, 50 Cr_2O_3	$1.15x10^2$	(1035)	4.0x10	(1470)	excellent compact, low resistance
97 Cr_2O_3, 3 Fe_2O_3 + 5 Bentonite	$3x10^3$	(1025)	$1.8x10^3$	(1250)	desintegrated at 1472°F during resistance test
90 Cr_2O_3, 10 Bentonite	---	---	---	---	insufficient dry strength, not tested
80 " 20 "	---	---	---	---	" " " " "
70 " 30 "	---	---	---	---	" " " " "
94 ZrO_2, 5 Bentonite	---	---	---	---	poor compaction, not practical

Table VII (cont.)

Composition	Ohms	(°F)	Ohms	(°F)	Remarks
BeO	----	----	----	----	good pellets, poor Pt electrode adherence, no test
75 BeO, 25 Fe_2O_3	1 x 10^6	(1260)	2 x 10^3	(1900)	-----
75 BeO, 25 Cr_2O_3	----	----	2.25×10^4	(1700)	Pt electrodes flaked at high temperature
65 BeO, 25 Fe_2O_3, 10 TiO_2	----	-----	----	----	resistance too high
96.5 BeO, 2.0 TiO_2	4.82×10^4	(1586)	9.24×10^3	(1922)	-----
93.5 " 5.0 "	4.67×10^4	"	9.06×10^3	"	-----
88.5 " 10.0 "	4.44×10^4	"	8.29×10^3	"	-----
83.5 " 15.0 "	4.10×10^4	"	7.34×10^3	"	-----
78.5 " 20.0 "	3.38×10^4	"	5.63×10^3	"	-----
75.0 " 23.5 "	3.04×10^4	"	3.64×10^3	"	-----
48.5 " 50.0 "	2.81×10^4	"	1.89×10^2	"	variable results, non-linear, imperfect Pt adherence
23.5 " 75.0 "	1.27×10^4	"	2.2×10^1	"	-----
95 BeO, 5 CeO_2	----	----	----	----	no success in forming compacts
90 " 10 "	----	----	----	----	" " " " "
85 " 15 "	----	----	----	----	" " " " "
80 " 20 "	----	----	----	----	" " " " "
70 " 30 "	----	----	----	----	compacts well, excessive firing shrinkage and cracking
60 " 40 "	----	----	----	----	as above
50 " 50 "	5.6×10^3 to 1.1×10^4 at 1400°F				as above, brittle, variable results, not reproducible

Table VII (cont.)

From Armour Research Foundation Reports on the Development of Ceramic Materials of High Electrical Conductivity(2)

Material suitable for use as ceramic thermocouple was sought.
Granular material (through 100 mesh) was formed as compacts and tested for resistivity (ohm cm) at room temperature.

Composition	ohm cm	Remarks
Zirconium vanadyl vanadate (14.3 mole % ZrO_2)	2.03×10^2	softened below 700° C, re-oxidized
" " " (33.3 mole % ZrO_2)	1.52×10^2	" " " "
Zirconium vanadate composition (50 mole % ZrO_2)	4.25×10^6	high resistivity
" " " (66.7 mole % ZrO_2)	8.49×10^6	" "
Sodium vanadyl vanadate ($Na_2O \cdot V_2O_4 \cdot 5V_2O_5$) pure	1.6×10^{-2}	softened below 700° C, re-oxidized
" " " " impure	4.04×10^1	" " " "
Sodium vanadyl vanadate ($5Na_2O \cdot V_2O_4 \cdot 11V_2O_5$) pure	1×10^{-1}	" " " "
" " " " impure	3.72×10^2	" " " "
Sodium metavanadate ($NaVO_3$)	1×10^6	high resistivity
Sodium tungsten bronze	3.8×10^{-1}	unstable, re-oxidized on heating in air
" " " , pure	3×10^{-3}	(data from Straumanis)
Aluminum tungsten bronze	6.1×10^{-1}	unstable, re-oxidized on heating in air
Zirconium tungsten bronze	1.7×10^{-1}	" " " " " "
" " " , impure	1.47×10^2	" " " " " "
Zirconyl tungsten bronze	2.4×10^{-1}	" " " " " "
" " " , impure	4.52×10^1	" " " " " "
Titanium tungsten compound ($Ti_2O_3 \cdot WO_2$)	2.36×10^3	" " " " " "
Thorium tungsten composition, impure?	2.36×10^5	high resistivity
Uranium " " "	2.36×10^5	" "
Tungstates	1×10^6	" "
Tungstate, tungstic oxide, tungsten mixtures	1×10^6	" "

X. CONCLUSIONS

1. The production of a temperature sensing element, or thermistor, based upon the change of electrical resistance of a ceramic component with change in temperature from 1000° to 2000°F is quite feasible.

2. Alkali porcelain bodies are available that have the desired straight line relationship between log resistivity and 1/°K. The temperature sensitivity of such bodies is very good, having resistivity values at 1000°F that are at least 100 times greater than the resistivity at 2000°F. These bodies have excellent resistance stability at high temperatures for extended periods of time and remain unaffected by strongly oxidizing or reducing atmospheres.

3. Ceramic compositions having even better resistivity-temperature characteristics may be discovered by further exploration. Lithia compositions deserve additional work as do zircon bodies.

4. By forming the ceramic component around the platinum electrodes and lead-wires then firing the assembly, it is possible to produce a bead-type thermistor element having excellent mechanical strength and good resistance stability even under reducing conditions that produce a carbon deposit. The very small dimensions of such a design should allow a rapid response to temperature change.

5. Probes required for mounting the thermistor in the jet engine must provide suitable insulation. Further investigation of materials and methods of insulating the lead-wires in the probe mountings is required before the advantages to be derived from the ceramic thermistor element can be fully utilized.

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Part II. Performance of the Thermistors

by Paul D. Freeze and Ernest F. Fiock

I. INTRODUCTION

This part of the report presents the results obtained with four thermistors prepared at Rutgers University under WADC Contract AF 33(616)-241. Details as to the composition of these and many other similar units, as to the method used for attaching the platinum lead wires, and as to their performance in furnaces are given in Part I.

Under date of December 17, 1953 an informal report on tests of one of these bodies (cone 14 porcelain) was submitted to WADC by the National Bureau of Standards. A conventional turbojet thermocouple with swaged magnesia insulation served as the mounting for the unit tested, and the resistance between the terminals on the head was found to vary from cycle to cycle. At the time the report was prepared it was not realized that the resistance of the insulation between the two wires leading to the thermistor was variable and low enough to affect the measured resistance of the thermistor itself. The cone 14 material has therefore been reevaluated, along with three other materials submitted at a later date.

II. DESCRIPTION OF THE THERMISTORS AND MOUNTINGS

The thermistor materials tested are described by Rutgers as follows:

No. 1 is a dinner-ware porcelain called Shanango 4;

No. 2 is a low-tension electrical porcelain, AAB;

No. 3 is an experimental sodium-feldspar porcelain called cone 14A; and

No. 4 is cone 14 porcelain identical in composition with cone 14A, except for a minor addition of talc.

Specimens 1, 2, and 3 have the configuration shown in figure 8A, while No. 4 is shown in figure 8B. In all cases the ends of the thermistors were metallized and platinum lead wires were attached thereto at Rutgers. Because of irregularities in the attachment of the leads, the dimensions are difficult to specify with the exactness that might be desired for calculating specific resistances. As closely as could be determined, the dimensions of the four units at room temperature were as follows:

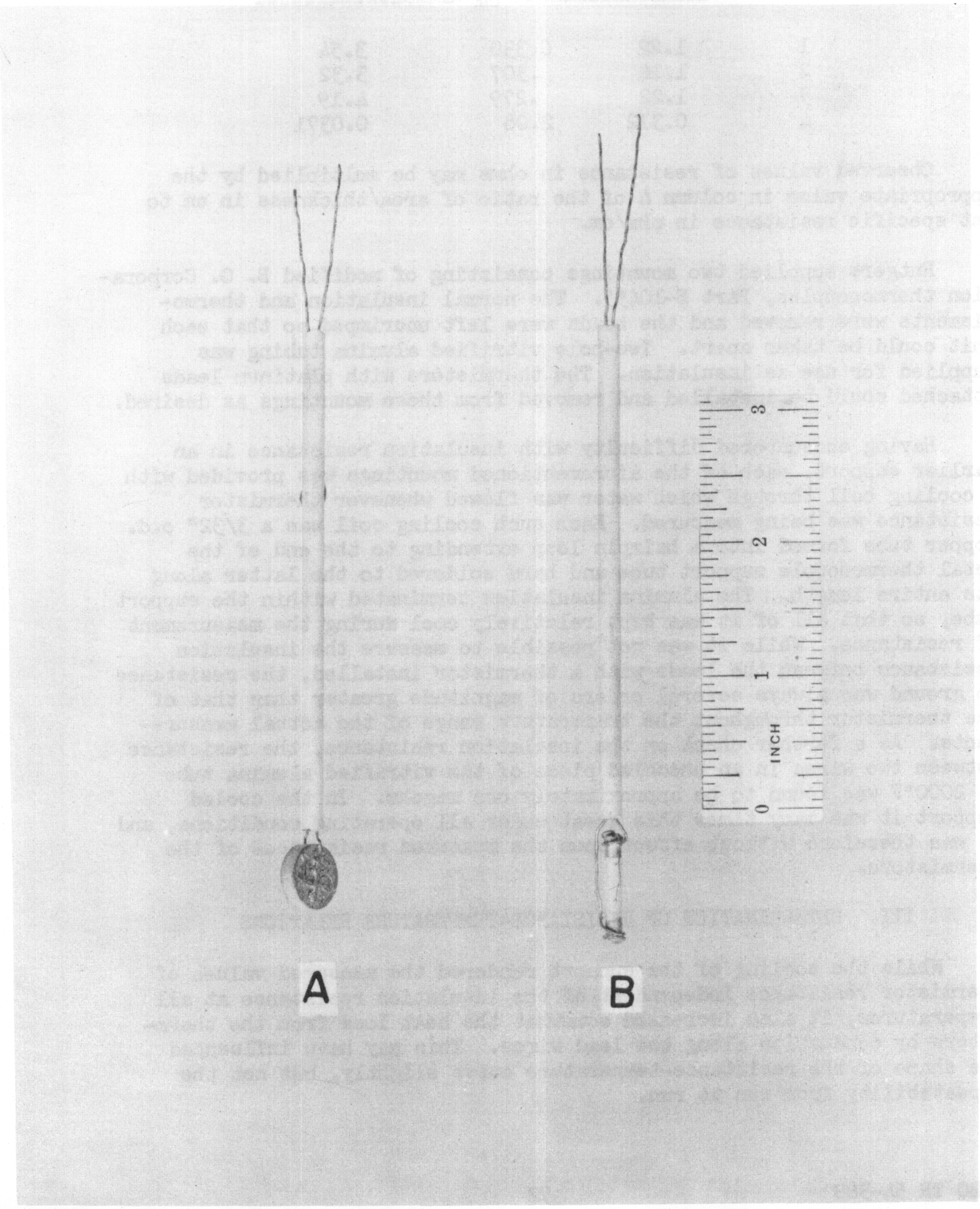


FIGURE 8. TWO TYPES OF THERMISTOR CALIBRATED

Thermistor No.	Diameter	Thickness or Length	Area/Thickness
	cm		
1	1.22	0.330	3.54
2	1.14	.307	3.32
3	1.22	.279	4.19
4	0.312	2.06	0.0371

Observed values of resistance in ohms may be multiplied by the appropriate value in column 4 of the ratio of area/thickness in cm to get specific resistance in ohm/cm.

Rutgers supplied two mountings consisting of modified B. G. Corporation thermocouples, Part B-10455. The normal insulation and thermoelements were removed and the heads were left uncrimped so that each unit could be taken apart. Two-hole vitrified alumina tubing was supplied for use as insulation. The thermistors with platinum leads attached could be installed and removed from these mountings as desired.

Having encountered difficulty with insulation resistance in an earlier support, each of the aforementioned mountings was provided with a cooling coil through which water was flowed whenever thermistor resistance was being measured. Each such cooling coil was a 3/32" o.d. copper tube formed into a hairpin loop extending to the end of the metal thermocouple support tube and hard soldered to the latter along its entire length. The alumina insulation terminated within the support tube, so that all of it was kept relatively cool during the measurement of resistance. While it was not possible to measure the insulation resistance between the leads with a thermistor installed, the resistance to ground was always several orders of magnitude greater than that of the thermistor throughout the temperature range of the actual measurements. As a further check on the insulation resistance, the resistance between two wires in an uncooled piece of the vitrified alumina tube at 2000°F was found to be approximately one megohm. In the cooled support it was many times this great under all operating conditions, and it was therefore without effect upon the measured resistances of the thermistors.

III. DETERMINATION OF RESISTANCE-TEMPERATURE RELATIONS

While the cooling of the support rendered the measured values of thermistor resistance independent of the insulation resistance at all temperatures, it also increased somewhat the heat loss from the thermistors by conduction along the lead wires. This may have influenced the shape of the resistance-temperature curve slightly, but not the repeatability from run to run.

There are three other factors which may possibly influence the shape of the calibration curve, namely catalytic action on the platinum, the rate of heat exchange between the gas and the thermistor by radiation and convection, and size changes due to thermal expansion. From past experience it is expected that the catalytic effect in exhaust gas will cause addition of heat to the thermistors only at temperatures below 1200°F. No such effect will be present when the thermistor is heated in air, as in a furnace. The rate of heat loss by radiation can be made negligible in a furnace, but is important in streams of exhaust gas flowing through systems with cold walls. Size changes due to thermal expansion are probably too small to be of any real consequence in the present considerations.

The effect of a given rate of heat loss by combined radiation and lead conduction upon the steady state temperature attained by the thermistor will vary with the rate at which heat is transferred to the thermistor from the surrounding gas by convection. The latter, in turn, is quite small in quiet gas in a furnace, but may become high in flowing gas. In order to keep the rate of convective heat transfer constant in all tests at a given temperature, all calibration runs in exhaust gas were made at the single mass flow rate of 6 lb/sec ft^2, and in order to keep the radiation loss the same during all repeat runs at a given temperature, the unlagged walls of the test system were always allowed to reach a steady state before measuring thermistor resistance.

Primary interest during the present evaluation was in the ability of the thermistors to maintain a given resistance-temperature relation upon repeated temperature cycling. Since it was not feasible to accumulate long heating time in exhaust gas alone, they were heated in air-filled furnaces between some of the runs in exhaust gas.

In all calibrations, thermistor resistance was measured at 6.3 volts, 60 cycles per sec with an ac bridge shown schematically in figure 9. Balance was detected by a cathode ray oscilloscope during the calibration runs and by a direct-inking oscillograph during determinations of characteristic time. Resistances were not measured at any other voltage or frequency. Figure 5 of Part I indicates that the results would have been essentially the same at any frequency up to 1000 cps, particularly since all of the resistances measured were within the range from 10^2 to 10^6 ohms.

Thermistors Nos. 1 and 2 were calibrated nine times and Nos. 3 and 4 six times each in streaming exhaust gas. All such calibrations were at a mass flow rate of 6 lb/sec ft^2 and at temperature intervals of approximately 100°F throughout the range 1000° to 1700°F. True gas temperatures were determined with gold-shielded chromel-alumel thermocouples, known corrections being applied to the readings of the latter

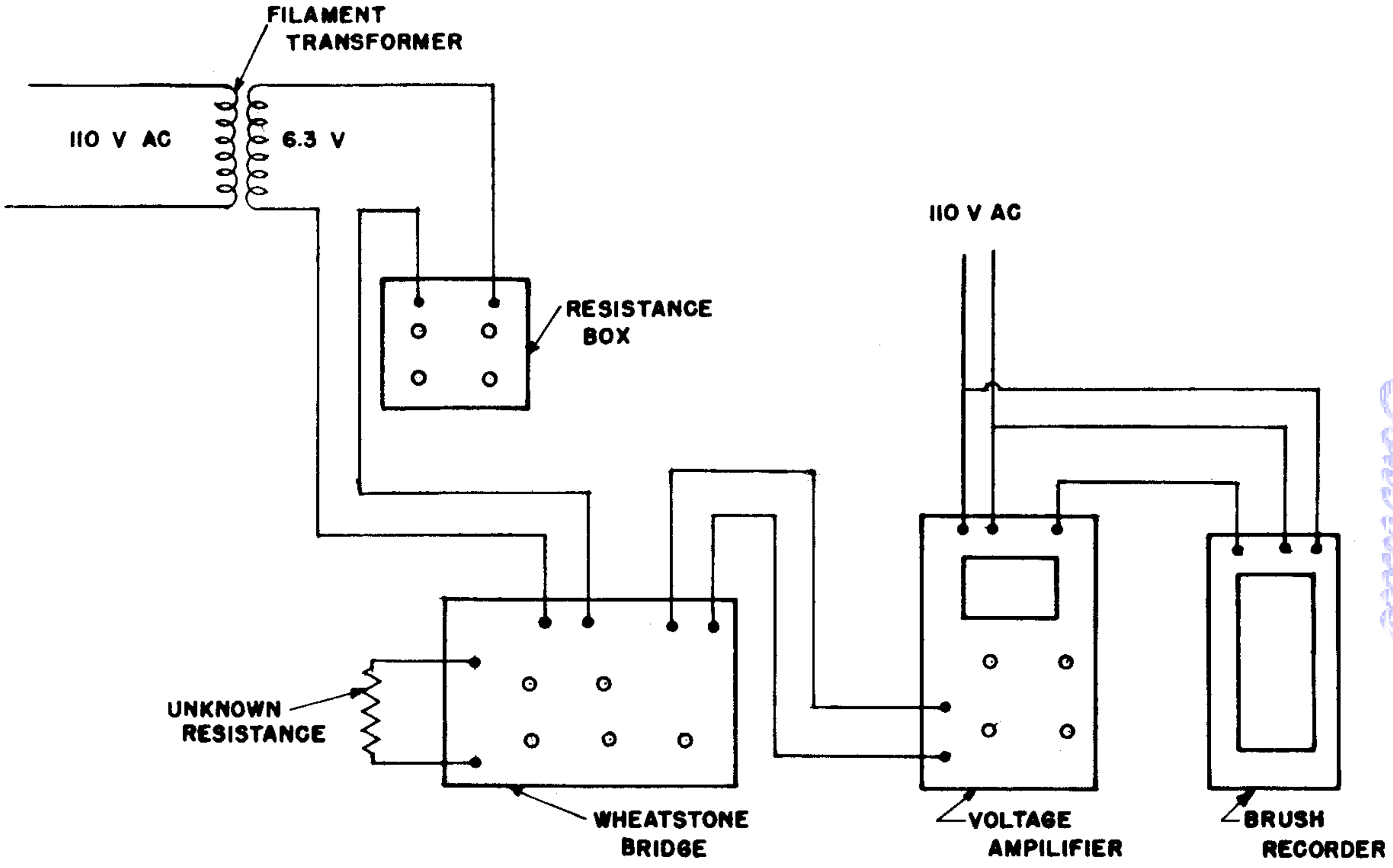


FIGURE 9. SCHEMATIC DIAGRAM OF RESISTANCE MEASURING APPARATUS

for radiation losses. The pipe-wall temperature was kept about the same at each experimental gas temperature throughout successive runs, so that the rate of heat loss by the thermistor, although unknown in magnitude, was always the same in successive measurements at a given gas temperature. The total time of heating for each thermistor was about 90 hr, of which all but about 7.5 hr were spent at approximately 1500°F in a furnace.

After completion of the runs in exhaust gas, each thermistor was calibrated in a furnace. Water cooling was again applied to the support tube. Although the differences between comparable runs in exhaust gas and in a furnace are not due solely to loss by radiation in the former, loss by this process certainly accounts for the major part of the difference.

A final furnace calibration on thermistor No. 1 with an uncooled support gave inconclusive results, since it indicated that the uncooled unit actually ran a little colder in the upper part of the measurement range. It therefore seems probable that the experimental error of the present measurements is as great as the effect of heat loss by conduction along the platinum wires supporting the thermistors, even when the support tube is water cooled.

IV. REDUCTION AND INTERPRETATION OF THE DATA

The specific resistance or resistivity (r) of a semi-conductor having possible application as a thermally sensitive resistor (thermistor) varies exponentially with the absolute temperature of the thermistor, i.e.

$$r = A_1 e^{B/T}, \text{ or } \log_e r = A_2 + B/T. \qquad (1)$$

The ratio of resistivity to resistance (R) is the same as the ratio of area to length or thickness, and if the change in dimensions with temperature is neglected, the ratio r/R is a constant. Thus, on a resistance basis, the theoretical equation for a thermistor becomes

$$\log_e R = A + B/T, \qquad (2)$$

which may be expressed in common logarithms as

$$\log_{10} R = a + B/2.303T = a + b/T. \qquad (3)$$

A thermistor which behaves in accordance with such an equation will have a temperature coefficient of resistance of

$$\frac{1}{R}\frac{dR}{dT} = -\frac{B}{T^2} = -\frac{2.303b}{T^2} \qquad (4)$$

This equation also permits calculation of dR/dT when this quantity is desired for converting small changes in resistance into their equivalent changes in temperature. All of the above quantities except r, R and T are constants. Measuring the resistance at two or more known temperatures permits calculation of two essential constants, for instance a and b, and thus constitutes a calibration of the thermistor.

In the search for materials which might perform satisfactorily as thermistors, application of equations of this type facilitates the comparison of successive results and the search for evidence of physical and chemical instability in the materials. After trying several possible methods of presenting the present results, it was found most satisfactory to proceed as follows for each thermistor:

a. Plot the observed values of R and 1/T on semi-log paper, draw the straight line which is the best representation of all the data, and determine its intercept (a) and slope (b). The uncertainty of selecting the best line to represent the data may be reduced by determining (a) and (b) by the method of least squares, but this was not done to the present results.

b. Calculate R and dR/dT at even intervals of 100°F from 1000° to 1700°F.

c. Using the appropriate values of dR/dT, correct each observed value of R to the even temperatures mentioned in the previous paragraph. In the present runs in exhaust gas, most of the observed values were within 5°F of the even temperatures and the maximum difference was 17°F.

d. For each observed value, get the difference by subtraction between the corrected observed resistance and the resistance called for by the appropriate empirical equation at the same temperature. Again using the proper values of dR/dT, convert these differences in resistance into the corresponding differences in temperature.

The results of such an analysis of the present data are shown in the form of tables and charts. Table VIII gives the constants (a) and (b) for the empirical equations representing the behavior of the four thermistors in exhaust gas and in a furnace.

Table VIII

Empirical Equations Representating Thermistor Behavior in Exhaust Gas and in a Furnace

Type: $\log_{10}R = a + b/T$; R is in ohms and T in deg Rankine

Thermistor Number	a	b
1 in Exhaust Gas	-0.0812	6,664
2 " " "	-0.3826	6,479
3 " " "	-0.2852	5,725
4 " " "	1.4724	6,480
1 in Furnace	-0.5967	7,368
2 " "	-0.5438	6,591
3 " "	-0.4408	5,880
4 " "	1.1334	6,883

The values of resistance calculated from the empirical equations at intervals of 100°F from 1000° to 1700°F are given in Table IX, the first section of which applies to the results in exhaust gas and the second to those in a furnace. Values of dR/dT are also included in the first section, since these were used in correcting the observations in exhaust gas to the even temperatures.

The deviations of the individual observations in exhaust gas from the equations are shown in figure 10. The number in the lower right-hand corner of each strip indicates the number of the test thermistor. The data points for each run are connected by straight lines and, although there are too many points for ready indication of the order in which the runs were made, no consistent pattern of change with the time of heating has been found for any of the thermistors. All four materials follow the theoretical equation well, and none shows evidence of sudden changes in slope which might be indicative of changes in physical or chemical structure.

Thermistors No. 1 and 3 appear to give results that are slightly more consistent than those for the other two. Considering the 207 observations on all four units, the difference from the equations exceeds 20°F for only eight points and exceeds 10°F for only 40 points, there being no consistent trend with either time of heating or temperature.

It is difficult to estimate how much of each existing difference results from experimental error and how much is due solely to thermistor performance, since the thermistor corrections for radiation, conduction

Table IX

Average Behaviour of Thermistors Calculated from Empirical Equations of Table VIII

Gas Temp. °F	No. 1		No. 2		No. 3		No. 4	
	R ohms	dR/dT ohms/°F	R ohms	dR/dT ohms/°F	R ohms	dR/dT ohms/°F	R ohms	dR/dT ohms/°F
Performance in Exhaust Gas								
1000	30,410	219	11,344	79	4,324	27	814,200	5,700
1100	15,500	98	5,894	36	2,424	13	422,900	2,590
1200	8,575	48	3,314	18	1,457	7.0	237,700	1,290
1300	5,074	25	1,990	10	928	4.0	142,700	690
1400	3,173	14	1,225	5.4	620	2.4	90,400	390
1500	2,084	8.1	838	3.2	432	1.5	60,100	233
1600	1,424	5.1	578	2.0	312	1.0	41,500	146
1700	1,010	3.3	414	1.3	232	0.7	29,700	95
Performance in a Furnace								
1000	28,160		9,338		3,856		650,800	
1100	13,370		4,796		2,128		326,200	
1200	6,943		2,669		1,262		177,600	
1300	3,885		1,588		794		103,700	
1400	2,314		999		525		64,120	
1500	1,453		659		362		41,640	
1600	954		452		259		28,200	
1700	652		322		191		19,800	

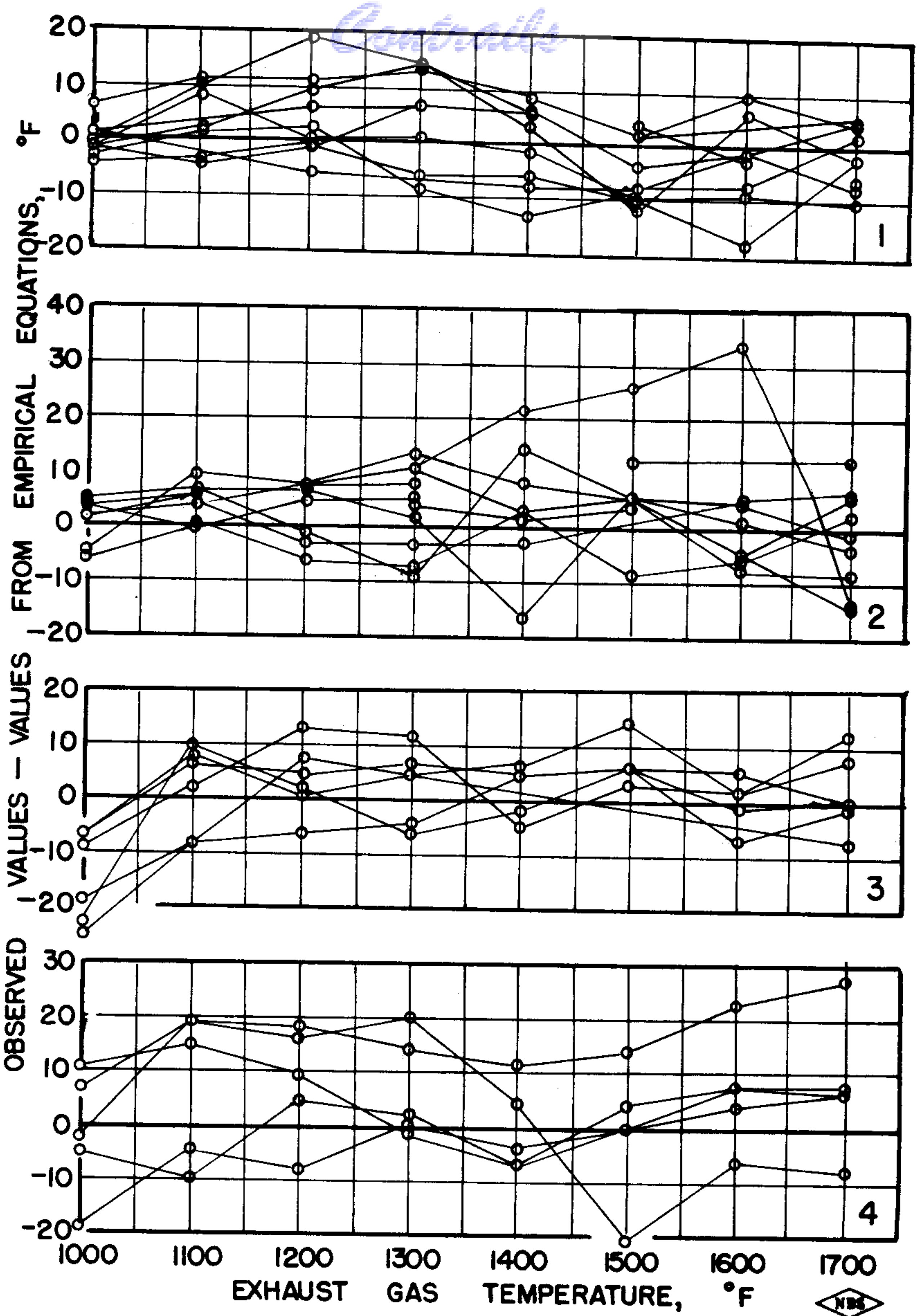


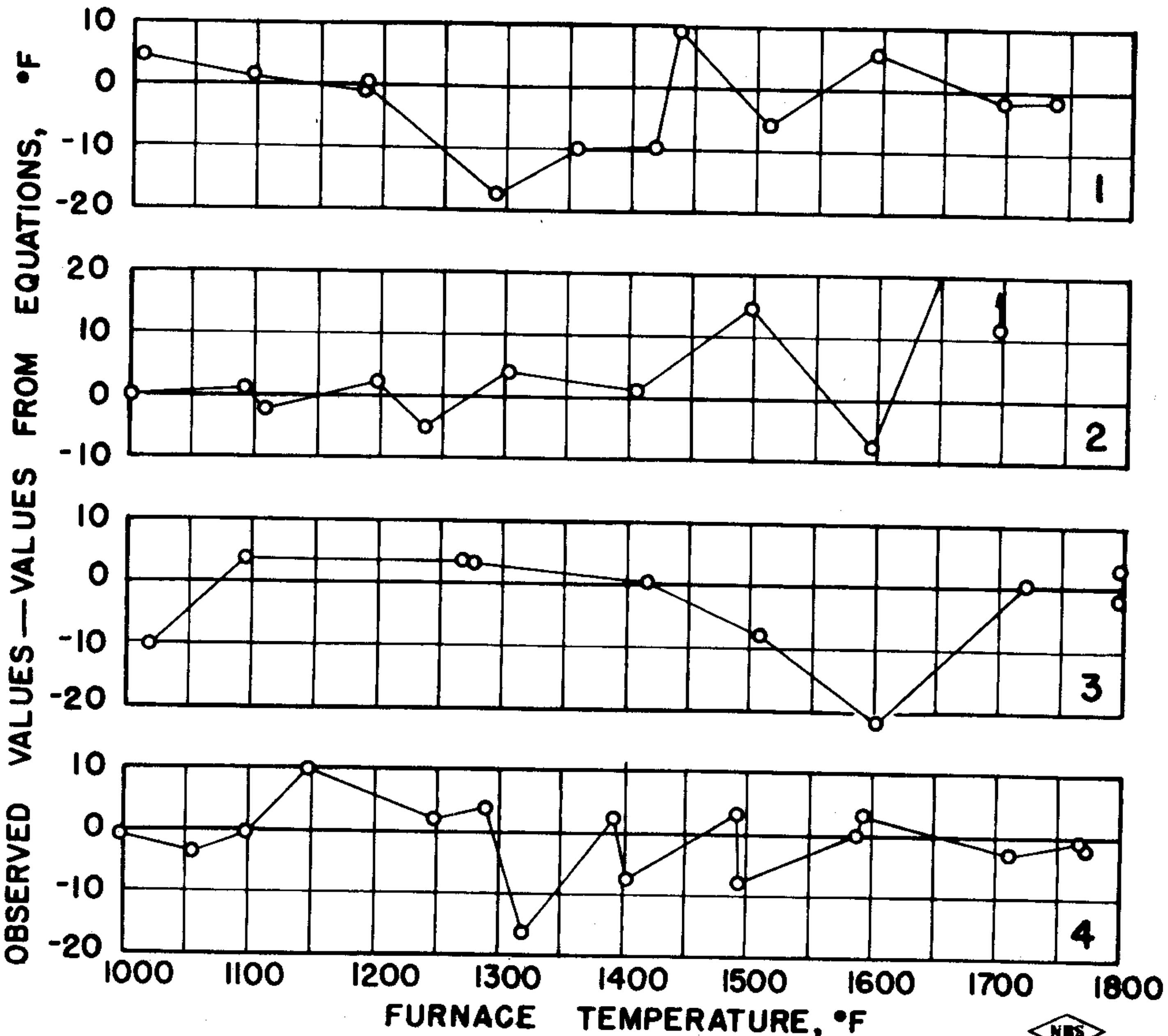
FIGURE 10. DIFFERENCE CHARTS SHOWING PERFORMANCE OF THERMISTORS IN EXHAUST GAS

and recovery are unknown. No account has been taken in figure 10 of the fact that the radiation correction increases with increasing temperature, and for this reason these data do not constitute an accurate calibration of the thermistors. This is more nearly done in the results obtained in a furnace, although even here there is some uncertainty as to the effects of heat loss through the supporting wires to the cooling water.

As will be seen in figure 11, the furnace calibration data are also fitted well by a new set of empirical equations. It is therefore of interest to compare the smoothed data obtained with exhaust gas and in a furnace, as is done in figure 12. The top strip of this curve shows the average temperature of the walls of the test system during runs with exhaust gas, as a function of the temperature of the latter. The curves numbered 1 through 4 in the lower section apply to the thermistors having these same numbers, and define the difference between the temperature attained in the furnace and that attained in exhaust gas, as a function of temperature. As stated previously, this difference is in all cases due primarily to the loss of heat by radiation from the sensing element in exhaust gas, as indicated by the fact that the thermistors always ran considerably hotter in a furnace at a given temperature than in exhaust gas at the same temperature. For comparison, the corresponding differences applicable for a gold-shielded and a platinum-shielded thermocouple in an exhaust gas system having the wall temperatures indicated in the top strip are included as the two bottom curves in this figure. The effective surface emissivity of the thermistors seems to be roughly eight to sixteen times that of gold, or from about two to four times that of platinum.

V. COMPARISON WITH CALIBRATIONS AT RUTGERS

The Rutgers data are presented primarily as semi-log plots of specific resistance (resistivity) as a function of reciprocal temperature. For like materials, these should be comparable with the NBS values of resistance (second section of Table IX), multiplied by the appropriate values of the area-to-thickness ratio of the test unit. Such a comparison of the results from the two laboratories is shown in Table X.



NBS

FIGURE 11. PERFORMANCE OF THERMISTORS IN A FURNACE

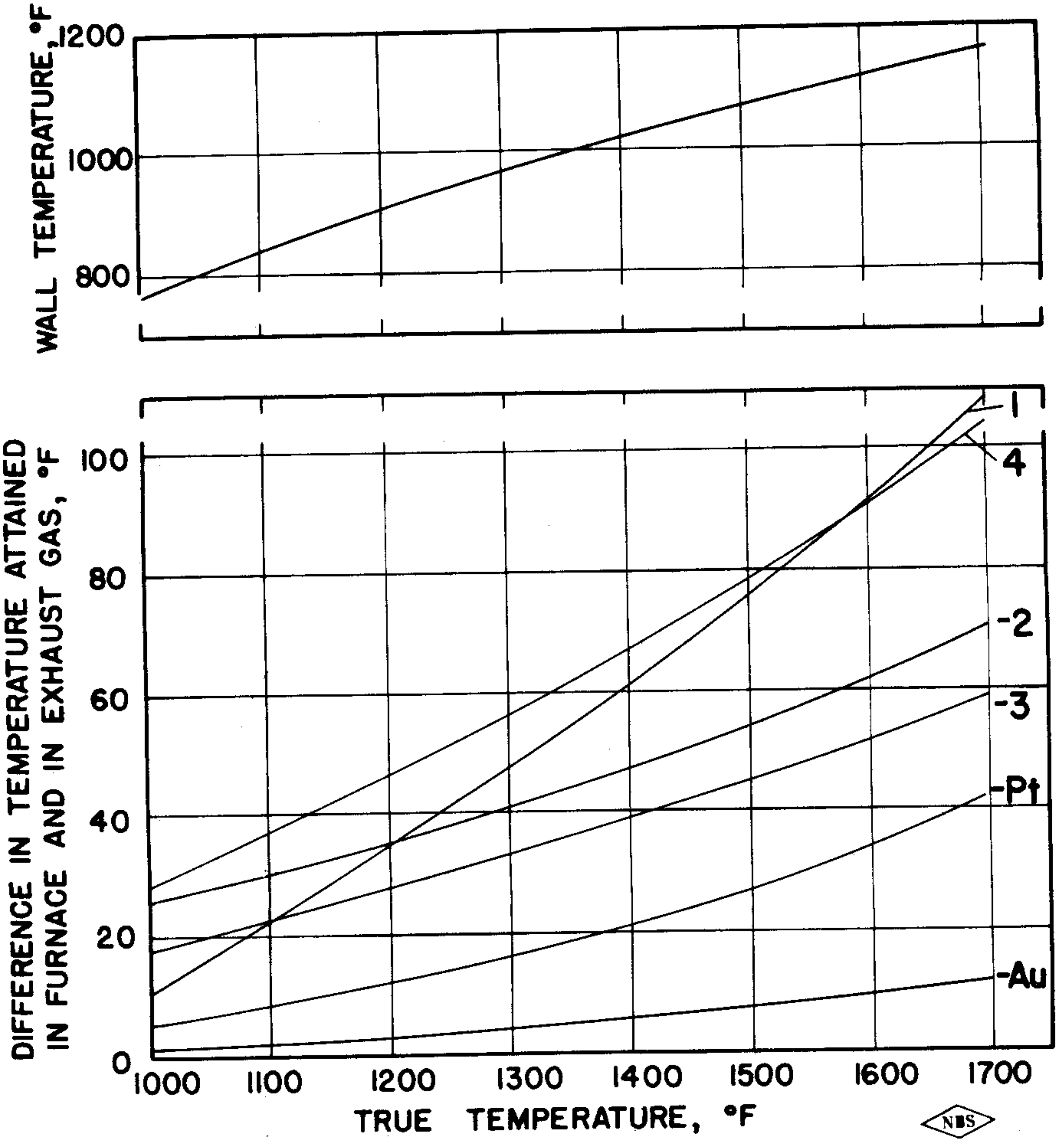


FIGURE 12. DIFFERENCES IN BEHAVIOR IN FURNACE AND IN EXHAUST GAS

Table X

Comparison of Resistivities Measured at NBS and at Rutgers

Temp.	No. 1		No. 2		No. 3		No. 4	
	R.[1]	NBS	R.[2]	NBS	R.[3]	NBS	R.[4]	NBS
°F	Resistivity in ohm centimeters							
1000	89,000	99,700	29,000	31,000	19,000	16,200	184,000	24,100
1200	21,000	24,600	10,500	8,860	5,800	5,800	55,000	6,600
1400	8,200	8,200	3,600	3,320	2,250	2,200	21,000	2,380
1600	3,500	3,380	1,600	1,500	1,070	1,085	9,900	1,050
1700	2,400	2,310	1,100	1,070	800	800	7,200	735

1. Average values from figures 3K and 6B
2. Values from figure 4
3. Average values from figures 3J and 4
4. Values from figure 3J

Considering that different samples of material were calibrated by different methods and under different conditions at the two laboratories, and that there is considerable uncertainty as to what dimensions should be used in calculating resistivity, the agreement is good for all samples except No. 4. The lower values of resistance obtained by Rutgers at low temperatures may be due to the fact that the porcelain bodies appear to be voltage sensitive and that higher voltages were used at Rutgers than at NBS.

With respect to sample No. 4, it is scarcely worth while to attempt a comparison of results because the Rutgers sample was disk-shaped and may have differed somewhat in composition and firing from that tested at NBS. Also the results were obtained before certain improvements had been made in the method of testing at Rutgers.

VI. DETERMINATIONS OF CHARACTERISTIC TIME

The rate of response of each thermistor was measured at a flow rate of 6 lb/sec ft^2 by the method described in Air Force Technical Report A.T.I. No. 42188, with the following results:

Thermistor Number	Characteristic Time at a Flow Rate of 6 lb/sec ft^2 sec
1	7.1
2	6.5
3	5.3
4	9.7[1]

[1] Result reported December 17, 1953

While the thermistors tested respond too slowly for satisfactory use in the control of turbine-type engines, their rates of response can be increased somewhat by decreasing their size.

VII. DISCUSSION

The results reported here are not intended as accurate calibrations of any of the test thermistors. The primary purpose of the study was to determine whether the materials prepared by Rutgers would remain stable upon repeated heating in products of combustion. The upper temperature was limited to about 1700°F, in order not to exceed the melting point of the gold shields of the comparison chromel-alumel thermocouples.

No significant trend in resistance with the time of heating was found at any temperature between 1000° and 1700°F for any of the four samples tested. Run-to-run differences in the observed resistance at a given temperature average considerably less than 10°F and appear to be random in nature. Within the limits of experimental error of the ac bridge and of the calibration methods used, the present results indicate that the thermistors remained physically and chemically stable, and that the platinum lead wires remained in good contact with the ceramic bodies throughout the tests.

The type of support used for the thermistors in these tests is not suitable for use in engines. There the vibration is so great that two-hole insulators into which wires can be slipped and which, in turn, can be slipped into a metal protecting tube, are unsatisfactory. The grinding action, particularly at the end or at any place where the insulator may break, cuts the wires in a relatively short time. The use of platinum, particularly in contact with the thermistor itself, is undesirable because surface heating is known to occur on this metal at temperatures below 1200°F in the presence of unburned fuel or partially burned products of combustion. No such catalytic action has been demonstrated experimentally at higher temperatures, and platinum may not be objectionable if the thermistor so mounted is not used in exhaust gas below 1200°.

Swaged magnesia, such as has proved useful for thermocouples, is far less desirable for insulating the leads to a thermistor because its resistance is not sufficiently high, particularly when moist or at high temperatures. Swaged alumina or thoria could probably be developed as satisfactory insulation for leads to thermistors.

The question as to what is the optimum resistance range for a thermistor is one which requires the consideration of three parallel resistances, namely the thermistor itself, the insulation between the leads to the thermistor, and the gas surrounding the exposed leads to the thermistor. Since thermistor resistance varies exponentially with temperature, an instrument applicable over a wide range of temperature must undergo a very wide change in both resistance and temperature coefficient of resistance.

A control operated by a thermistor must utilize a signal which is linear in log R and 1/T. This means that R varies exponentially with 1/T, as will the current through the thermistor if the applied voltage is kept constant. The maximum current that can be passed through the thermistor without at the same time altering its resistance at a given temperature needs to be investigated, as do the possible effects of varying the voltage and frequency applied to the semi-conductor. It is planned to study some of these factors in future work at NBS, using both the thermistors described herein and others of Shenango No. 6 porcelain prepared jointly by Rutgers and the B. G. Corporation.

The present status of exhaust-gas thermistors may be summarized as follows. In addition to further progress in the development of materials to improve stability, to achieve the desired sensitivity over the complete temperature range of interest, and to extend the useful range upward, much additional work remains to be done in the development of units suitable for application in turbojet engines. Problems of lead attachment and insulation, of mechanical strength, and of rapid response are formidable. Additional information on the effects of varying the applied voltage and frequency, and on how best to utilize the signal which varies exponentially with temperature should be obtained. It would be highly desirable, and probably essential to the use of thermistors in the control of turbojet engines, that circuits be developed for using such instruments in parallel to give average temperatures, and whereby the control system is not rendered inoperable by the failure of a single sensing element.