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DEVELOPMENT OF A HIGH RESISTIVITY PASTE FOR THE SCREENED CIRCUIT PROCESS

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FINAL REPORT

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CONTROL NO. L-3231

SPEER CARBON COMPANY
RESEARCH LABORATORY
NIAGARA FALLS, NEW YORK

Prepared For

National Aeronautics and Space Administration
Langley Research Center
Hampton, Virginia

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ABSTRACT

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The objective of this program was the development of high-value, semiprecision glaze resistors prepared by screen printing suitable pastes on an electroceramic substrate and firing at about 600°C. It has been verified that this objective can be met with previously developed pastes made from mixtures of thallium oxide and glass. The effects of various process and composition variations on resistor properties were investigated. These variations included the proportion of thallium oxide, particle size of paste ingredients, terminal material, firing schedule and glass composition. Resistive elements in values up to one megohm per square were prepared with a high degree of reproducibility. The characteristics included a temperature coefficient of less than 350 ppm/C°, a voltage coefficient of less than 60 ppm/volt, and an instability under various thermal, electrical, and humidity tests of less than 1% in most cases. The properties of the resistors were very uniform.

These pastes are especially compatible with ceramic substrates of higher C. T. E., such as steatite and titanate bodies. Performance on alumina was not completely satisfactory. However, a formulation was devised for use on alumina which provides characteristics only slightly inferior to those cited above.

INTRODUCTION

One of the earliest approaches to integrated microelectronic circuitry was by the screen-printing process. In this technique, various conductive and resistive compositions are printed in selected patterns on ceramic substrates and fired or cured at elevated temperature, producing compact networks of resistive and capacitive elements. The process is a practical one, in being simple, low cost, quite flexible, and highly reliable.

One of the principal difficulties associated with this type of circuit, however, was the comparatively inferior quality of the printed resistor. These elements usually consisted of resin-based inks which consisted of carbon black dispersed in a resin, printed and cured at only moderately high temperatures. Such films displayed serious instability under operating conditions of high moisture and temperature.

Attempts to devise more stable compositions based on the use of inorganic materials were largely unsuccessful until the development of the palladium-silver glazes.[1] These latter consist of fine metal and metal oxide particles mixed with glass. When fired at about 750°C, they form an electroconductive glaze. The stability of these elements is excellent. The utilization of these materials has created renewed interest in the process of screen-printing for hybrid microcircuit preparation.

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[1]Dumesnil, M. E., U. S. Patent 3,052,573, E. I. du Pont de Nemours and Co. (1962)

The resistance of the glaze compositions are generally adjusted by varying the proportions of conductive material and glass in the mixture. The palladium-silver compositions can be varied from values which are quite low up to about 20,000 ohms per unit area (sheet resistance in ohms per square), without serious loss of quality. To achieve values above the 20 kilohm level, however, it is necessary to lower the concentration of metal particles to such a degree that the resulting resistors become erratic, nonreproducible, nonlinear, noisy and unstable. This behavior is basic to all composition systems, and is caused by the diminution of the particle density to a point where quantum mechanical tunneling between particles becomes significant. It is especially difficult to reproduce a given resistance value of dilute electroconductive compositions.

To determine ways in which this high-resistance limitation could be overcome, a research and development contract entitled "Development of a High Resistivity Paste for the Screened Circuit Process," was authorized by N. A. S. A. and awarded to Speer Carbon Company.

In recognition of the advantages to be gained from inorganic forms of composition resistors, Speer Carbon Company had, prior to the contract, supported an active program of research in this area. Certain mixtures of the thallium oxide and glass previously conceived and reduced to practice and covered by pending U. S. patent application were known to be particularly applicable to the high resistance range. Sufficient data had been acquired with this system in the midresistance range to indicate that these compositions might well be capable of very high values. The approach taken in this program, therefore, was to prepare mixtures with gradually reduced thallium oxide contents and to determine the characteristics of resistors made therefrom. Appropriate adjustment of processing techniques, glass composition, etc., was also necessary to effect desired improvements.

This report constitutes a record of those efforts, difficulties encountered, and achievements.

CONTRACT SPECIFICATIONS

The guidelines set forth in the contract as target objectives are summarized below:

Resistance Range: 300 kilohms to one megohm per square

Temperature Coefficient of Resistance: $\pm$350 ppm/C° (-55° to 125°)

Compatibility: the pastes developed are to be chemically and physically compatible with "fired-on" precious metal-based conductive pastes

Reproducibility: deposition accuracy of $\pm$15% from mean

Rating: 10 watts per square inch at 80°C

Reliability: less than $\pm$10% change per 5000 hours at 90% RH and 150°F

Substrate Compatibility: the paste shall be suitable for deposition on glasses and various other electroceramics, including high alumina

EXPERIMENTAL PROCEDURES

The general procedures followed in the preparation of sample resistors are described below. Deviations from these techniques, where applicable, are noted in connection with individual experiments. In all cases maximum care was exercised in control and repeatability of the process, to permit meaningful interpretation of the results.

Raw Materials

For the most part the thallium oxide was purchased in 5 kilogram quantities from the Varlacoid Company. Although limited quantities were also obtained from other sources, identical performance was achieved as far as could be detected. Spectrographic analysis revealed the following levels of impurities in the Varlacoid material.

Spectrographic Analysis of Thallium III Oxide

Varlacoid Company

Element	Concentration, ppm
Tl	major
Fe	200
Si	800
Mg	50
Ca	600
Sn	500
Pb	500
In	700

As purchased, the material had an average particle size of about 1 micron. Although a variety of methods for grinding the powder to a still smaller size were evaluated, most samples were prepared with powder which had been milled in a Model #04503 unit produced by the Jet Pulverizer Company of Palmyra, New Jersey. The average particle size of this material was estimated to be 0.2 microns.

Several glass frits were purchased or prepared in the laboratory during the contract. However, most samples were made with Grade Q-12 frit marketed by the Harshaw Company. This is basically a lead borosilicate glass frit having an average particle size of 1.5 microns and a softening point of 460°C. A large quantity of this glass was purchased to suffice for the entire contract.

The substrates employed were of two types. One was essentially a magnesium titanate ceramic prepared in-house, with a coefficient of expansion of $9.3 \times 10^{-6}/C°$ at room temperature. The second substrate material used was Grade 614 alumina, available from the American Lava Company. The coefficient of expansion of this material is approximately $6.25 \times 10^{-6}/C°$ at room temperature.

Conducting pastes of different types were tested for termination, but most samples were made with du Pont Grade 7553 platinum-gold paste, fired at 930°C.

Paste Preparation

Weighed quantities of thallium oxide powder and glass frit were placed in an automatic mortar and pestle together with a fixed amount of temporary binder. The latter consisted of a mixture of butyl carbitol-ethyl cellulose-ethyl alcohol. Subsequent adjustments in viscosity, as judged necessary for proper screening consistency, were made by addition of butyl carbitol. These ingredients were mixed (and ground) for a period of one hour.

In a typical case, actual quantities used were as follows:

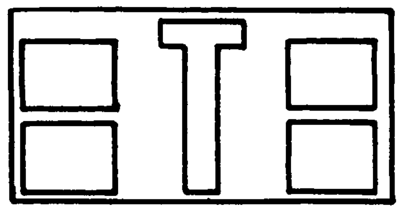
9.30 gms	thallium oxide	21.60 wt. %
20.70 gms	Q-12 glass	48.20 wt. %
0.46 gms	ethyl cellulose	1.06 wt. %
10.47 gms	butyl carbitol	23.87 wt. %
2.27 gms	ethyl alcohol	5.27 wt. %

Resistor Deposition

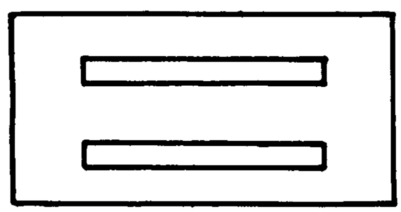
Substrates were first printed with conductive paste in the termination pattern shown in Figure 1, and then fired. Resistive paste was then printed in the pattern also shown in Figure 1. This arrangement provides four individual 4/64" x 11/64" elements per substrate wafer. The printing apparatus which utilizes an oscillatory motion of the squeegee mounted in a rolling carriage is shown in Figure 2. The printing screens employed were 165 mesh stainless steel.

The resistors were air-dried prior to firing, and were approximately one mil in thickness.

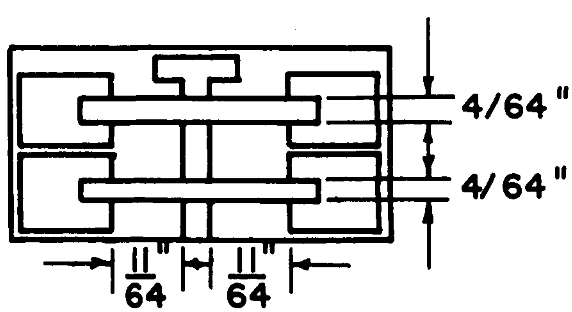
FIGURE I
PRINTING PATTERNS



Conductive Terminations



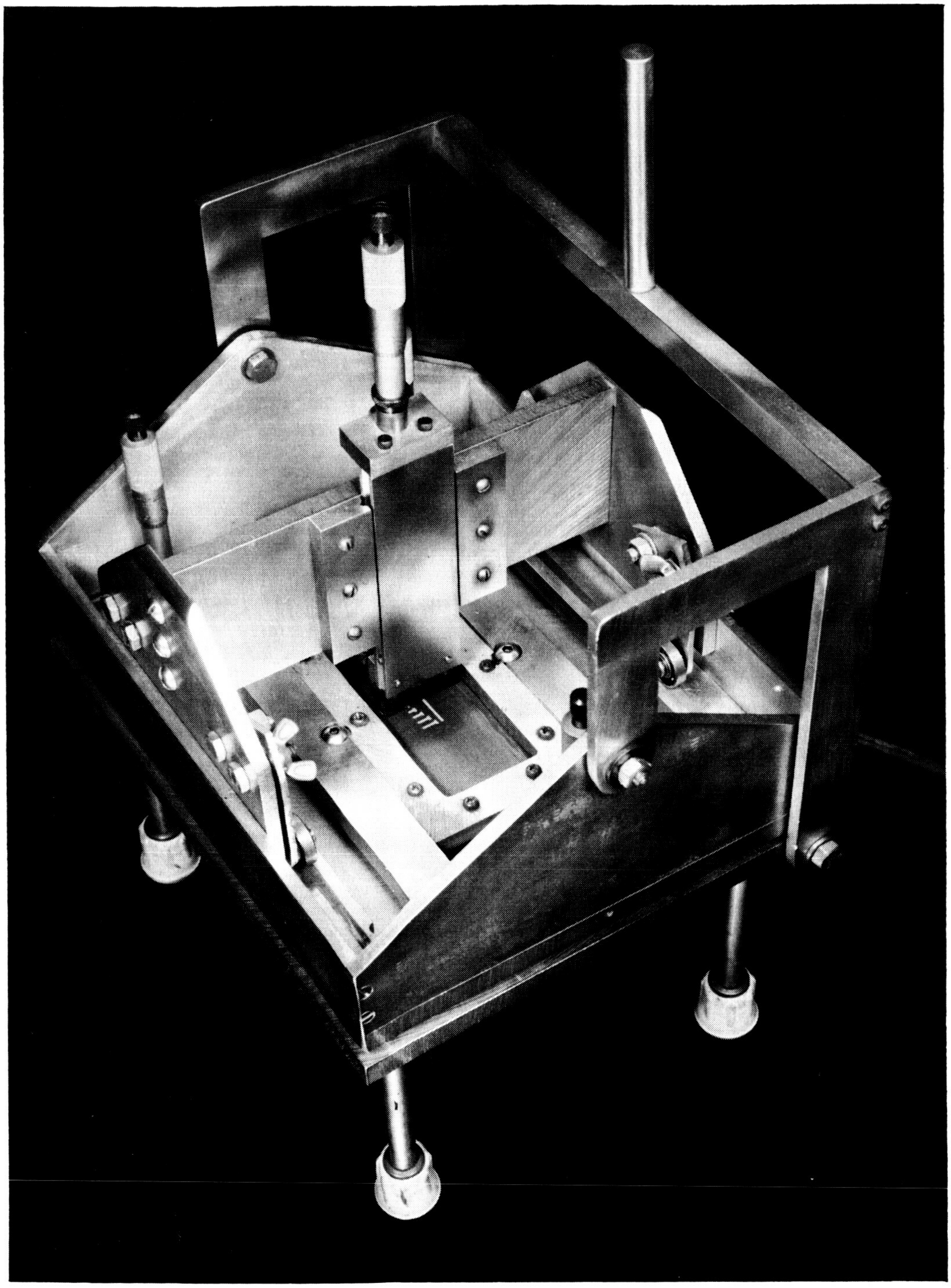
Resistor Elements



Terminated Resistors

FIGURE 2

SCREEN PRINTER



Firing

Resistors were fired in an electric tube furnace constructed with nine heating zones independently controlled by saturable reactor. The substrates are placed on a continuous belt conveyor made from a thin strip of stainless steel. The belt is driven by a variable speed gear motor which allows the complete firing operation to be conducted in periods ranging from a few minutes to several hours.

Control thermocouples were located at the inside wall of the furnace tube. Accurate data on the temperature profile experienced by a substrate was obtained by recording from a thermocouple attached to a substrate plate as it traveled through the furnace. A typical profile is shown in Figure 3.

The peak temperature during firing was set for 520°C, unless otherwise indicated.

Testing

For testing, wire leads were soldered onto the platinum-gold terminating areas. The plates were then cleaned of possible resin or other contamination by gentle scrubbing in ethyl alcohol. In some cases the plates were then oven annealed.

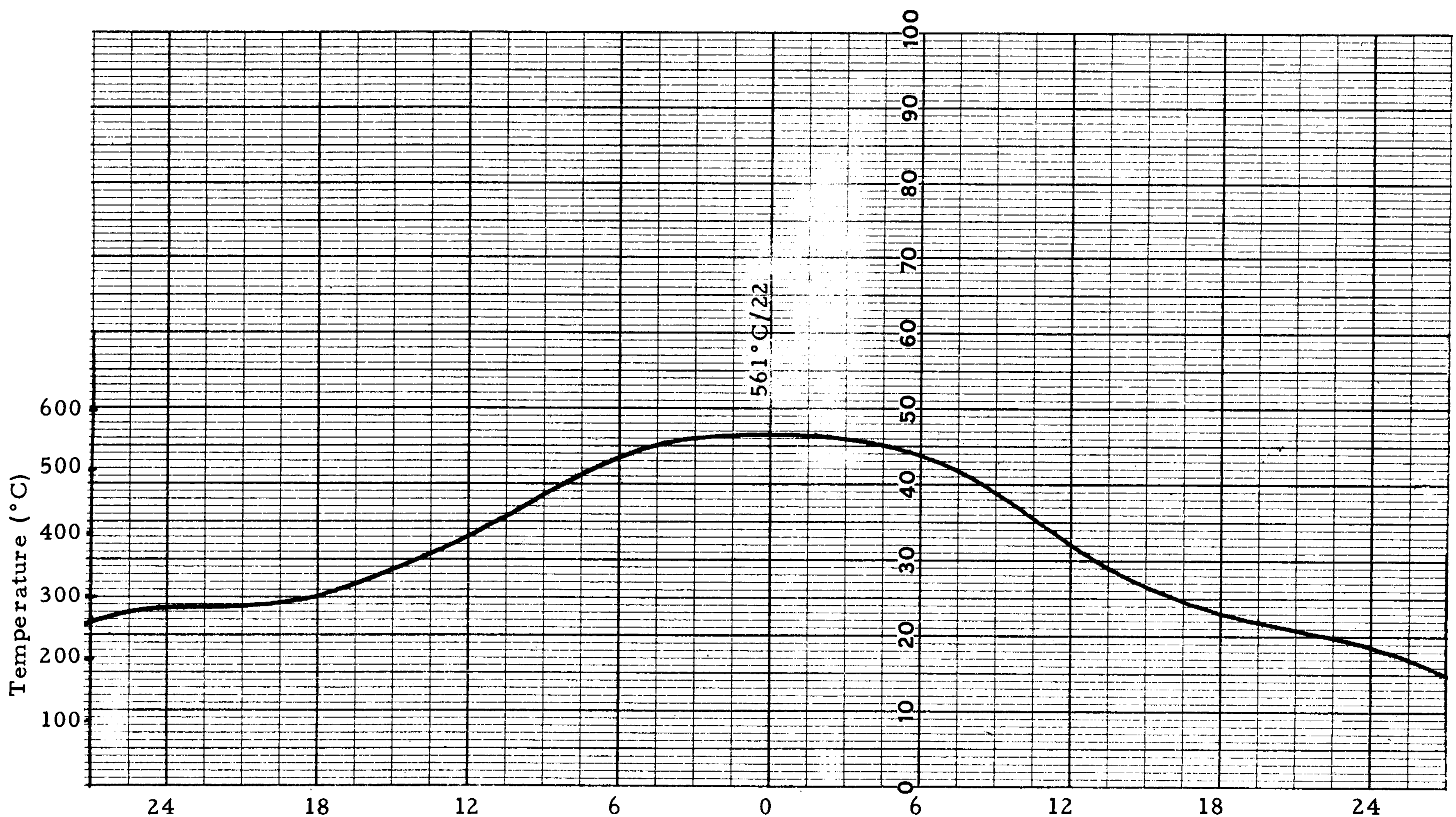
Some of the tests performed were of a preliminary nature for screening purposes. Others were made according to contract requirements or by recognized procedures as outlined in MIL-R-11E and MIL Standard 202. Brief descriptions of the tests and appropriate references are listed in Appendix I.

For testing purposes the resistors were rated at one-tenth watt power, or a dissipation rate of ten watts per square inch of actual resistive element.

FIGURE 3

FIRING TEMPERATURE PROFILE

Recorded With a Thermocouple Attached to Substrate Moving Through Furnace



EXPERIMENTAL RESULTS

Composition

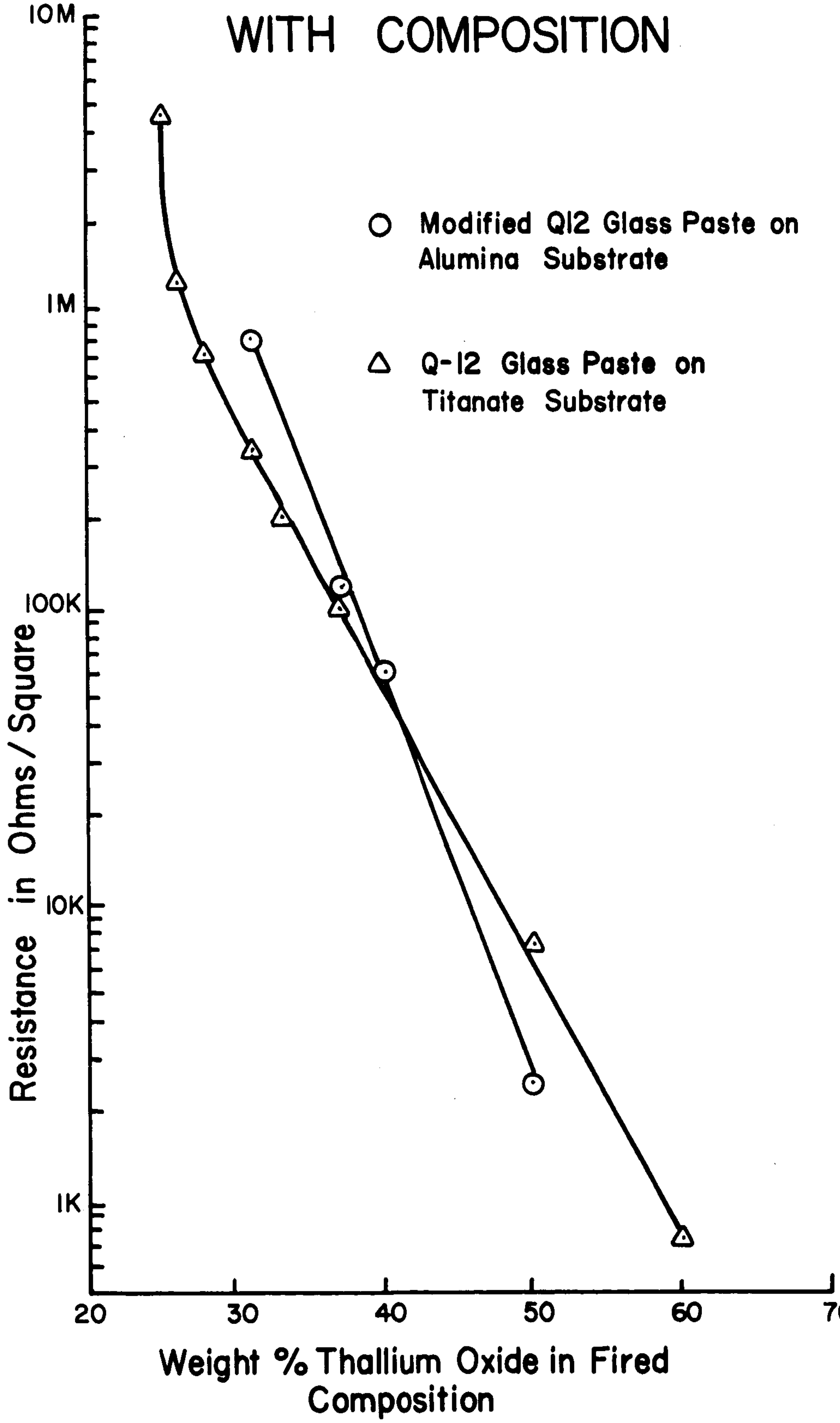
One of the principal aims of the contract was to determine the maximum limit of resistance which could be obtained in a reproducible and controllable manner. An obvious and direct approach to this problem was taken. The proportion of thallium oxide to glass was successively reduced. A series of pastes of different compositions was therefore prepared, starting with the raw materials in each case. The results are shown in Figure 4, where the resistance per square is plotted versus the weight ratio of thallium oxide to glass in the paste. Curves are shown for a paste based on Q-12 glass printed on the titanate substrate, and for paste made with a modified Q-12 glass deposited on an alumina substrate.

It can be seen that no difficulty is experienced in achieving values of up to approximately one megohm per square, in a reproducible fashion. Above one megohm per square, the change of resistance with further dilution becomes much more rapid, indicating a loss of continuity between conductive particles. The resistors then become erratic.

Termination

To study termination effects, different precious-metal pastes were applied in terminal patterns to alumina substrates. These were fired so that resistors could be prepared over them. For this particular study a special pattern was used in which resistors with "form factors" of 1/3, 2, and 10

FIGURE 4
VARIATION OF SHEET RESISTANCE WITH COMPOSITION



squares were printed simultaneously. By this means it was hoped that effects at the resistor-termination interface and those occurring within the resistor element itself could be distinguished. This experiment was conducted with resistor pastes of two different values. The results are shown in Table I.

The resistance level varies with form factor to a significant degree in the case of the silver termination. This is ascribed to substantial migration of the silver into the resistance element during firing.

The temperature coefficient did not exhibit significant variation with either termination material or form factor. It was somewhat lower for low value pastes, on the average.

The noise index, on the other hand, was greatly dependent on form factor, ranging from about +16 db for one-third square elements to about zero for 10 square elements, with the higher value paste. It must be concluded that the resistor-terminal interface contributes substantially to the total current noise of these elements. The noise for the low value pastes was again less than for the high value pastes.

On the basis of the data shown in Table I. together with results on firing and soldering characteristics, platinum-gold paste No. 7553 was designated as the best presently available termination material.

Additional electrical measurements were made on the nature of the resistor-terminal interface. A traveling probe device was constructed so that the potential distribution across a current-carrying resistor could be recorded.

TABLE I

EFFECT OF TERMINATING MATERIAL ON RESISTOR CHARACTERISTICS

Termination Material	Resistance (KΩ/□) 1/3□	2□	10□	T. C. R. (ppm/C°) 1/3□	2□	10□	Noise (db/dec.) 1/3□	2□	10□
High Value Paste									
Silver du Pont #6320	470	740	914	-380	-375	-348	+16	+12	+0.3
Gold du Pont #6976	761	771	808	-388	-322	-305	+14	+8.5	-0.8
Plat. Gold du Pont #7553	954	952	953	-232	-346	-341	+16	+11	+1.2
Low Value Paste									
Silver du Pont #6320	114	203	248	-246	-272	-275	+6.2	+2.6	-4.6
Gold du Pont #6976	217	217	226	-314	-268	-296	+7.8	+2.5	-5.2
Plat. Gold du Pont #7553	172	187	199	-452	-326	-262	+22	+10	-2.5

A schematic drawing of this apparatus is shown in Figure 5 and a photograph is shown, Figure 6. The phonograph needle traverses the specimen at a slow speed, and the changing potential is displayed on a strip-chart recorder. The surface of the specimen is polished to provide more continuous electrical contact.

Results are shown for the three different terminal materials in Figure 5. With gold and platinum-gold terminations, the potential increased sharply at the interface and thereafter exhibited a linear change of potential with distance of probe travel. However, with silver terminals, the potential change at the interface was gradual, indicative of a diffuse boundary such as could be produced by migration of silver across the interface during firing.

Most important, the results shown in Figure 5 were identical regardless of current direction in the resistor, demonstrating a lack of rectification at the boundary.

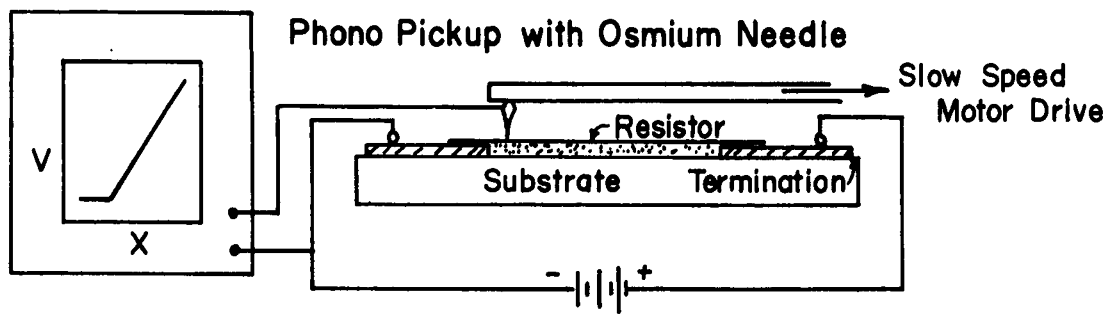
Particle Size and Dispersion

The effect of conductive particle size and distribution on the uniformity and reproducibility of the pastes, and on various resistor characteristics, is very significant in composition resistors. To obtain a measure of these effects, pastes of fixed composition were prepared with thallium oxide treated in several different ways, as identified below:

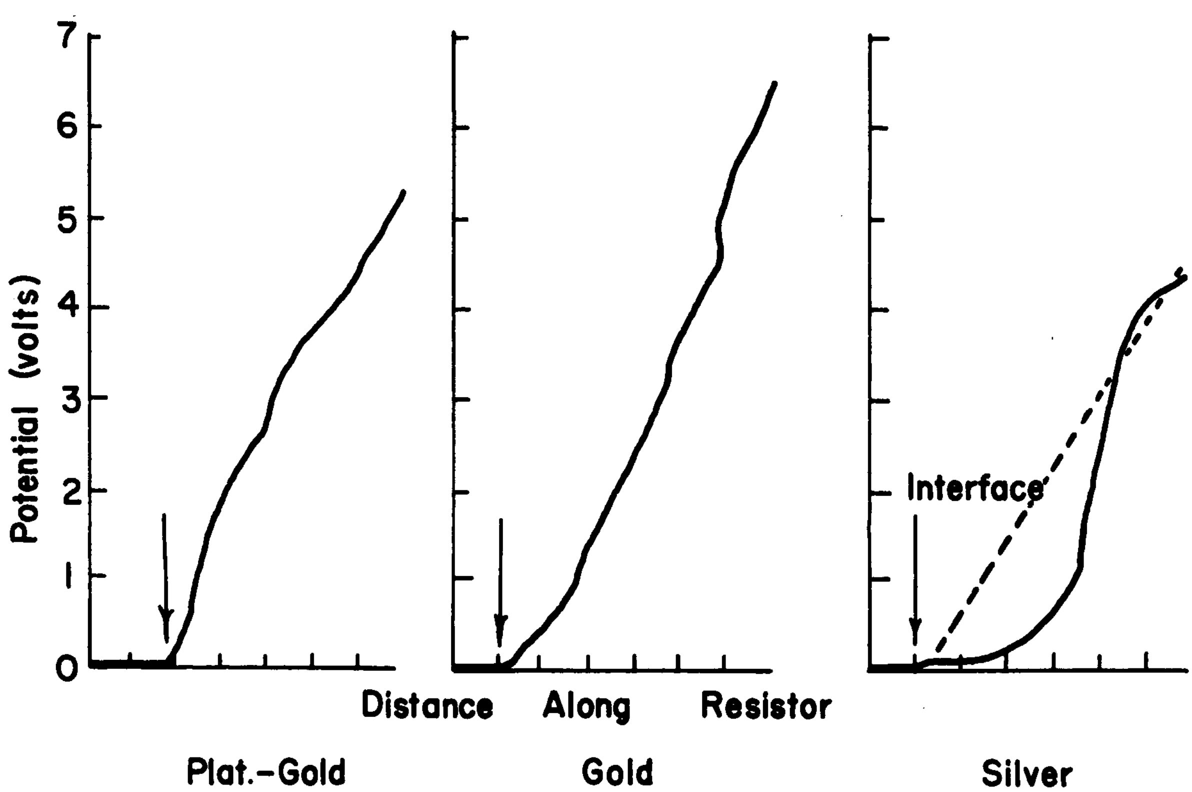
1. As received — no further treatment
2. Ball Milling — with ceramic balls for various periods of time, in alcohol, followed by decantation and oven drying

FIGURE 5

PROBE APPARATUS FOR POTENTIAL DISTRIBUTION MEASUREMENTS



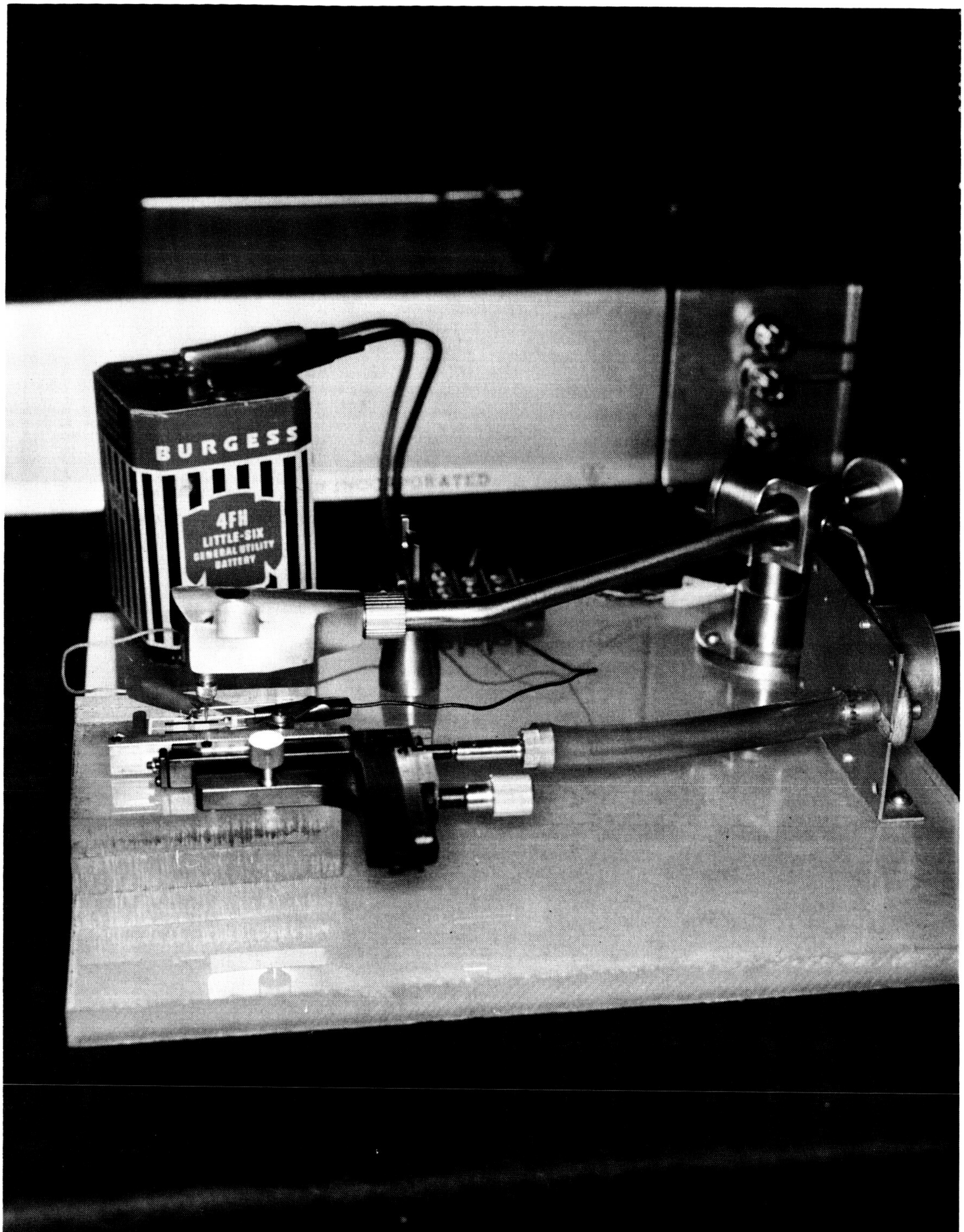
Potential Distribution Across Resistor Terminal Boundary



TERMINATION MATERIAL

FIGURE 6

ELECTRICAL PROFILE APPARATUS



3. Fluid Energy Milling — performed by the Fluid Energy Processing Company, on a Model 0202 size reduction unit
4. Jet Milling — similar in action to that of the Fluid Energy Mill. The original sample of this material was prepared by the manufacturer on a 4" unit.

From these materials, resistor pastes were prepared using Q-12 glass which had been ball milled for 110 hours resulting in a particle reduction to approximately 0.2 microns.

Several of the pastes prepared were split into two portions, one of which was used directly, and the other subjected to further dispersion by ultrasonic action. A gun-type ultrasonic unit was used with the paste being circulated by stirring.

From all these pastes, resistors were prepared and certain characteristics determined. The data shown in Table II include particle size, average resistance value, standard deviation of resistance, noise index and voltage coefficient.

Since the particle size of the original thallium oxide was quite small, (1 - 1.5 micron), the amount of reduction possible by physical techniques was rather limited. However, the resistance values obtained definitely were higher for the ground material in approximately inverse proportion to the particle size.

Ultrasonic dispersion failed to produce much improvement in the characteristics, with the notable exception of the jet-milled material. In this one case the uniformity of resistance, noise, and voltage coefficient all seemed improved to a remarkable degree.

The resistance distribution (indicated by standard deviation), noise index, and voltage coefficient were not entirely dependable as indicators of paste homogeneity, since, with pastes of fixed composition, the varying resistance value itself probably has a significant influence on these characteristics. To permit a comparison of pastes prepared with different thallium oxides, with the same final resistance, resistors were made from as-received and jet-milled thallium oxide in which the composition was adjusted to arrive at the same final resistance. The data obtained are shown in the lower part of Table II and demonstrate a substantial lowering of the resistance distribution and noise index for the paste made with ultrasonically dispersed jet milled thallium oxide. Surprisingly, no difference was found in the voltage coefficient.

Firing Schedule

Throughout the program, as major changes were made in the paste composition, a redetermination of the optimum firing schedule was required. This was especially necessary with different glass compositions. Firing was conducted at a series of different peak temperatures, and occasionally for different periods of time. The results for different pastes were not always similar in detail but usually exhibited certain common features.

The variation in resistance with peak firing temperature is shown for two representative systems in Figure 7. One curve is for a paste made with Q-12 glass and deposited on the titanate substrate; the other is for a paste

TABLE II

EFFECT OF PARTICLE SIZE REDUCTION AND DISPERSION

Thallium Oxide Preparation	Ultrasonic Dispersion	Tl_2O_3/Q-12 Wt. %	Particle Size (μ)	Av. Res. KΩ/□	σ_R%*	Noise db			V.C.R. ppm/V
						1/3□	2□	10□	
			Fixed Composition						
As Received	No	33/67	0.8	159	9.1		+19		- 97
							+		
Ball Milled 48 hrs.	No	"	0.5	204	12.1		+11		- 90
Ball Milled 110 hrs.	No	"	0.3	256	13.7		+13		- 75
"	Yes	"	0.4	185	16.9		+14		-221
Jet Milled	No	"	0.2	945	15.7		++		- 87
"	Yes	"	0.2	874	2.3		+ 8		- 43
Fluid Energy	No	"	0.3	362	15.7		+14		-111
"	Yes	"	0.3	397	11.7		++		-152
			Fixed Resistance Value						
As Received	No	33/67	0.8	159		+21	+19	+1	- 97
Jet Milled	Yes	40/60	0.3	134		+13	+ 6	-7	- 98

*Calculated for 10 resistor elements

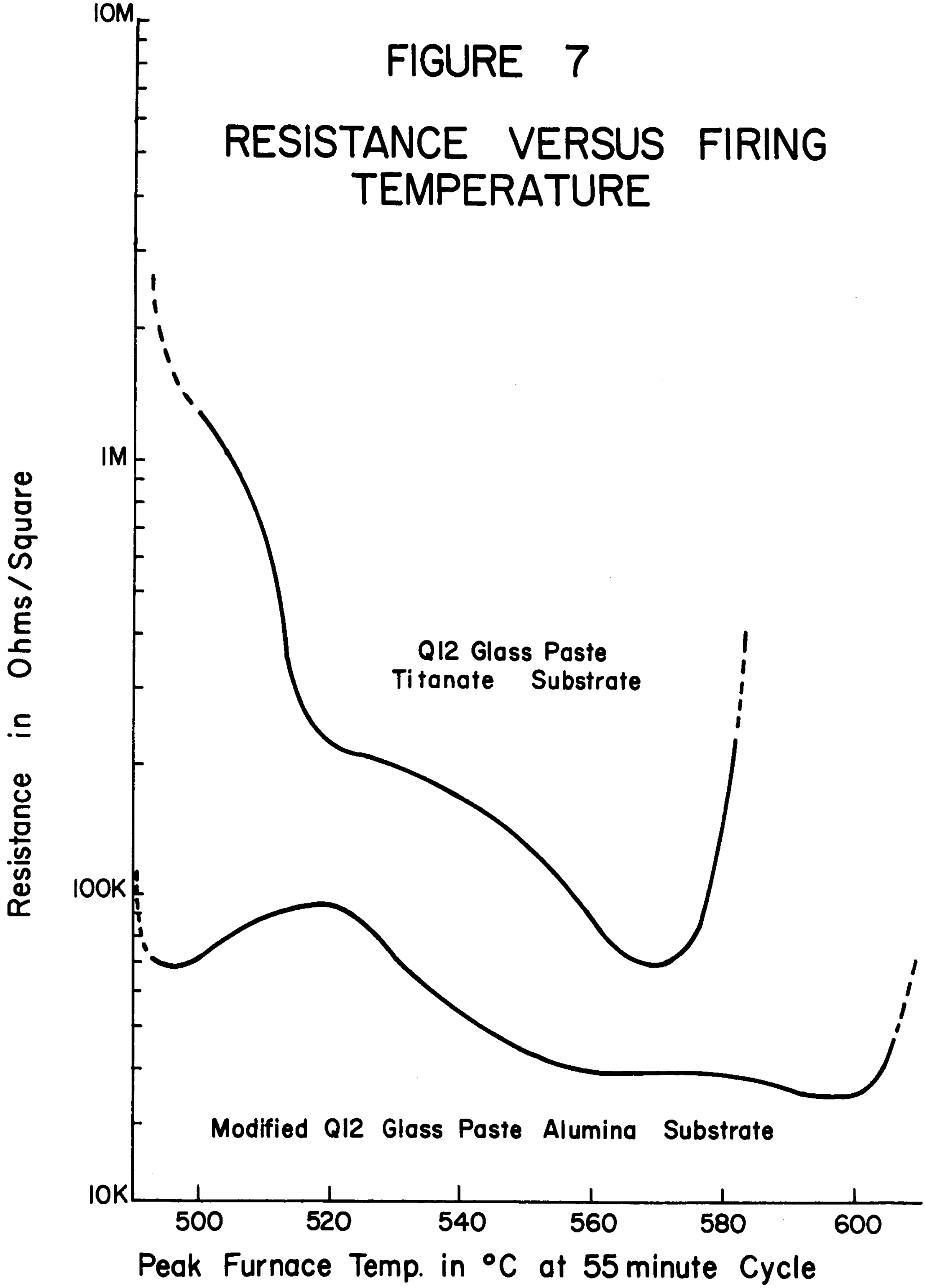


FIGURE 7
RESISTANCE VERSUS FIRING TEMPERATURE
10M
1M
100K
10K
Resistance in Ohms/Square
Q12 Glass Paste
Titanate Substrate
Modified Q12 Glass Paste Alumina Substrate
500
520
540
560
580
600
Peak Furnace Temp. in °C at 55 minute Cycle

made from a modified Q-12 glass deposited on alumina. In both cases, as with most others, the resistance drops abruptly once a temperature in the neighborhood of 500° or 520°C is reached. A region then exists up to about 600°C in which rather irregular but less rapid changes in resistance occur. With higher firing temperatures the resistance rises abruptly.

The variation of certain other characteristics with peak firing temperature are shown in Table III, for the Q-12 glass paste on titanate. The T. C. R. and noise are minimal for firing at about 510°- 520°C. The resistors fired in the range of 500° - 600°C exhibit a more glassy appearance, however. The "drift" stability shown are the permanent changes in resistance which occurred during a brief thermal annealing cycle. These are shown here to illustrate the relative decrease in thermal stability with higher firing temperatures.

Glass Composition

The composition of the glass used in the paste unquestionably influences the temperature coefficient of resistance (T. C. R.) and stability of the glaze resistor. This influence is at least partly a function of the differential coefficient of expansion between glaze and substrate. It was the purpose of this phase of the work to secure a glass whose properties would provide maximum compatibility with those of the substrate. A variety of glasses were evaluated during the program, a few of which were obtained commercially, but most of which were synthesized in the laboratory. Identification of the glasses is given in Table IV, along with their coefficient of expansion (C. T. E.) and softening point as determined by standard techniques.

TABLE III

VARIATION OF RESISTOR CHARACTERISTICS WITH FIRING TEMPERATURE

Q-12 Glass Paste on Titanate Substrate
55 Minute Schedule

Peak Firing Temp. (°C)	Av. Res. KΩ/□	T. C. R. ppm/C °	Noise Index db/dec.	V. C. R. ppm/V	"Drift" Stability (%)
500	1280	-268	+ 2.2	- 17	- .54
510	707	-272	+ 0.1	- 27	- .46
520	221	-184	+ 1.2	- 19	- .52
530	207	-245	+ 3.7	- 46	- .53
540	169	-238	+ 6.4	- 68	- .56
550	136	-225	+ 7.8	- 73	- .62
560	90	-242	+11.5	-116	- .66
570	70	-266	+13.7	-208	- .74
580	155	-403	off scale +	-182	- 1.6

TABLE IV
VARIATION IN GLASS BINDER COMPOSITION

(Firing Temperature 550°C)

Glass Index No.	Composition (%)	C.T.E. (10^{-6}/C°)	Softening Pt. (°C)	Av. Res. KΩ/□)	T.C.R. (ppm/C°)
	Commercial Glasses				
Harshaw Q-12		8.2	460	50.4	-220
Harshaw N-862		--	530	753	-348
	Modified Commercial Glasses				
623-28-2	Q-12 99.0 B_2O_3 0.4 SiO_2 0.6	8.1	480	90.5	-238
623-29-1	Q-12 97.0 B_2O_3 1.2 SiO_2 1.8	8.6	490	60.2	-231
623-29-2	Q-12 95.0 B_2O_3 2.0 SiO_2 3.0	7.8	510	282.0	-288
623-29-3	Corning 7050* 95.0 B_2O_3 5.0	4.7	780	high melting point	
623-29-4	Corning 7052 95.0 B_2O_3 5.0	4.4	770	high melting point	
623-29-5	Corning 7570 95.0 B_2O_3 5.0	6.5	570	860	-294
708-41-4	Q-12 90.0 ZnO 10.0	7.7	520	44	--

*Corning 7050 is a borosilicate glass of high softening point and low C.T.E.

TABLE IV (CONTINUED)

Glass Index No.	Composition (%)		C. T. E. (10^{-6}/°C)	Softening Pt. (°C)	Av. Res. (Ω/□)	T. C. R. (ppm/C°)
			Synthesized Glasses			
623-43-1	PbO	60	6.6	540	727	-351
	B_2O_3	10				
	SiO_2	30				
623-43-2	PbO	65	6.7	550	798	-330
	B_2O_3	10				
	SiO_2	25				
623-30-1	PbO_2	66.6	--	490	211	-304
	B_2O_3	18.6				
	SiO_2	14.8				
623-43-3	PbO	70	7.2	520	207	-282
	B_2O_3	10				
	SiO_2	20				
623-30-2	PbO_2	70.6	6.9	470	105	-272
	B_2O_3	19.6				
	SiO_2	14.8				
623-29-6	PbO_2	74.6	7.2	470	64.9	-268
	B_2O_3	10.6				
	SiO_2	14.8				
623-42-1	PbO	75	7.6	510	92.6	-274
	B_2O_3	5				
	SiO_2	20				
623-42-2	PbO	80	8.1	520	42.2	-202
	B_2O_3	5				
	SiO_2	15				

Glass frits were prepared by melting the weighed ingredients in kyanite crucibles for about one hour in a muffle furnace, at 1000° - 1100°C in most cases, and then pouring into water. The resultant frit was ball milled in alcohol for a minimum of 16 hours, and dried in an oven.

Using the same proportion of thallium oxide with each glass, pastes were made for evaluation of the corresponding resistor on alumina substrates. A series of firing temperatures was investigated for each paste to insure characterization under optimum conditions of use. Measurements of T. C. R. and noise index were made on several samples in each series. The lowest T. C. R. found for each glass is that included in Table IV. In addition, a crude measure of moisture stability was obtained on several groups by means of a 24 hour humidity test.

A ternary diagram illustrating the range of lead borosilicate compositions explored, the softening point and C. T. E. of the glass, and resistance and T. C. R. of the resistor is shown in Figure 8. Gradual variations in the properties of both glass and resistor with composition can be observed. The approximate composition for Q-12 is shown also.

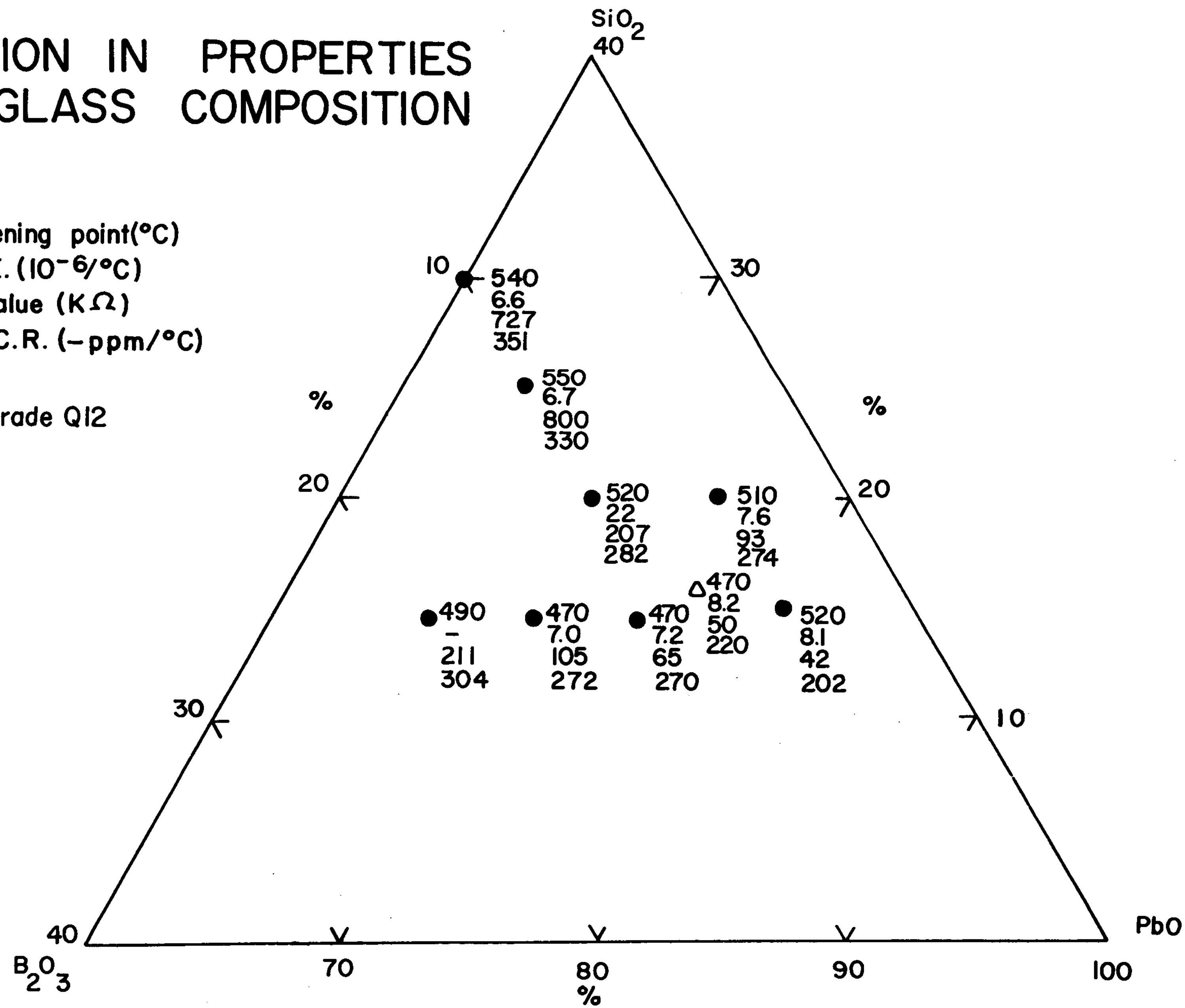
Three significant results were obtained from the glass composition phase of the program. Of the synthesized glasses, that which was closest in composition to the commercial Q-12 glass (No. 623-42-2) was apparently the best overall. Secondly, the range of T. C. R. values obtained from all the glasses was not large, ranging from -202 ppm to -350 ppm/C°. The lowest value was obtained with the Q-12 composition which, surprisingly, had a significantly

FIGURE 8

VARIATION IN PROPERTIES WITH GLASS COMPOSITION

● Glass softening point(°C)
Glass C.T.E. (10^{-6}/°C)
Resistor value (KΩ)
Resistor T.C.R. (−ppm/°C)

△ Harshaw grade Q12



higher C. T. E. than most of the other glasses. Third, the preliminary moisture stability screening of these resistors revealed that only the zinc oxide-modified Q-12 composition (No. 708-41-4) appeared at all satisfactory in this respect. Other observations related to this stability are discussed below.

Substrate Material

Both titanate and alumina substrates were used throughout the program in various phases. No large differences in resistance, noise index, T. C. R., and voltage coefficient were observed in early tests. Quick investigation of the different glasses for their relative stability in a condition of high humidity and high temperature revealed sizeable variations, however. Subsequently, this was found to correlate with the presence of microcracks in the resistor, which were, in turn, attributed to a mismatch between the C. T. E. of resistive composition and substrate.

The difference between resistors prepared from a given paste (made from Q-12 glass) on dissimilar substrates is demonstrated by the data shown in Table V. Resistors were prepared with a high and low value paste on alumina and titanate substrate in identical fashion. For each paste, the resistance, noise index and T. C. R. were higher on alumina. In addition, the change in resistance of these elements, when subjected to postsoldering cleaning involving both aqueous and nonaqueous solvents, was essentially zero on the titanate substrate, but very large on alumina.

TABLE V

EFFECT OF SUBSTRATE MATERIAL ON RESISTOR CHARACTERISTICS

Substrate Material	Av. Resist. (KΩ/□)	Resistance Change During Cleaning (%)	Noise (db)	T. C. R. (ppm/C°)
614 Alumina	37	+17	>>+20	-800
	134	+19	>+20	-800
Titanate	20	+ 0.1	>+20	-150
	115	$\pm$ 0.0	+3.8	-150

Coefficient of Thermal Expansion

(25 - 300°C)

Thallium Oxide	11.1×10^{-6}/C°
614 Alumina	6.3
Titanate Ceramic	9.3
Q-12 Glass	8.2
Modified Q-12 (No. 708-41-4)	7.7

The surface of resistors fired on alumina and titanate, described above were examined by microscope, as shown by the micrographs in Figure 9. The resistors on alumina displayed fine microcracks. The data given in Table IV indicates that the differential C. T. E. between glaze and substrate should be substantially greater for alumina than for titanate substrates, therefore accounting for the crazing.

As mentioned previously, a thorough screening of resistors made from the different glass compositions was undertaken* concerning their compatibility with alumina, using various criteria such as microscopic examination. The net result was that only glass No. 708-41-4, Q-12 to which 10% zinc oxide had been added (subsequently referred to as "modified Q-12"), appeared capable of providing the necessary stability. The variation of resistance with peak firing temperature for this glass is shown in Figure 7.

Resistor Stability

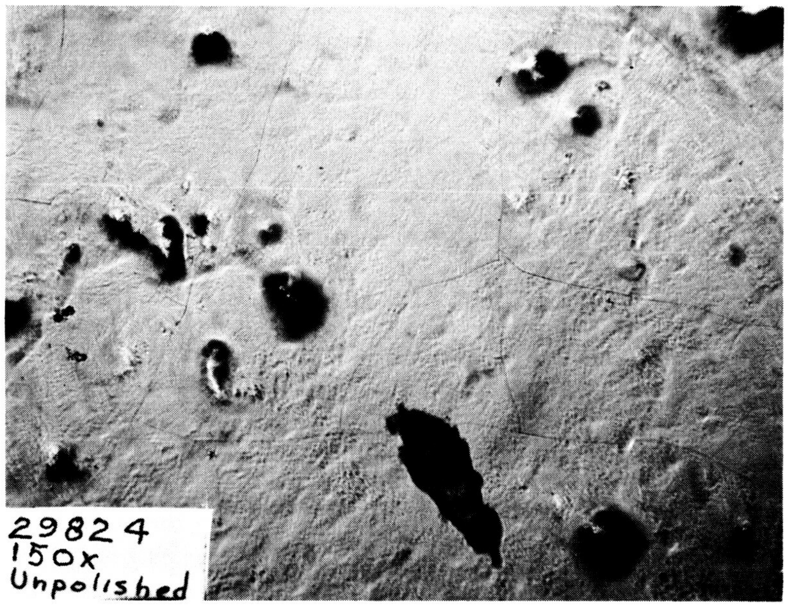
To obtain a more complete characterization of the better glaze compositions prepared during this program, a large number of resistors in several different values were prepared and subjected to a wide variety of tests. Three types of samples were included.

*Along with a variety of other measures; for instance, fairly complex firing schedules were found to reduce the cracking somewhat (and improve the stability) but failed to eliminate it completely.

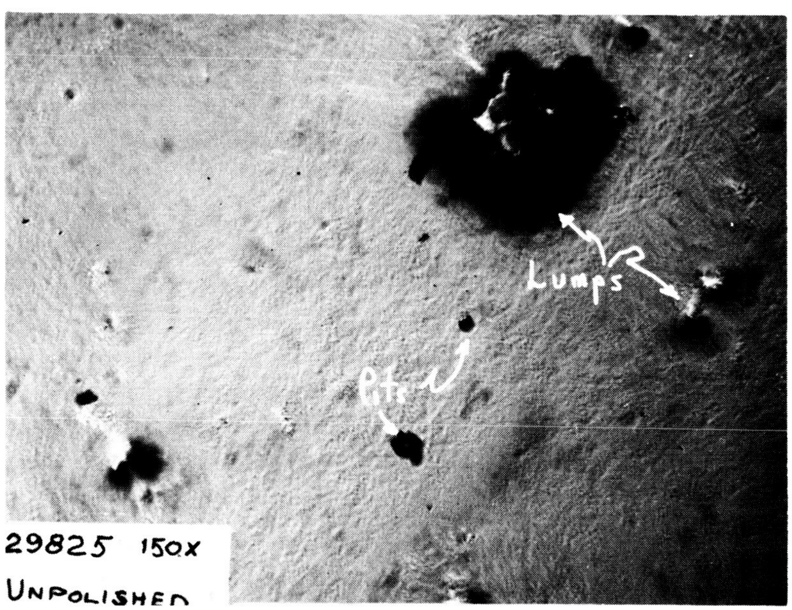
FIGURE 9

MICROGRAPHS OF FIRED RESISTOR SURFACE UNPOLISHED

Paste Made With Q-12 Glass



On Alumina Substrate



On Titanate Substrate

1. a paste made with Q-12 glass, printed on titanate substrates
2. the same paste, printed on alumina substrates
3. a paste made from the zinc oxide-modified Q-12 printed on alumina

Several hundred pieces of each type were made, using techniques described previously. Platinum-gold terminations were employed, and four resistors were printed per plate, as shown in Figure 1. The firing was conducted using the furnace profile shown in Figure 3, at a peak temperature of 520°C. The resistors were annealed at 200°C for 20 hours. Leads were soldered to the conductive areas and the plates were cleaned in ethyl alcohol. The shift in resistance which occurred during these processes was recorded.

The resistors were tested without trimming and without encapsulation. The tests were conducted according to procedures described in Appendix I. The individual elements, 4/64" x 11/64" in dimensions, were rated at one-tenth watt each.

A summary of all test results, based on average values, is given in Table VI, a, b, and c. The data in Table VI. a, for the Q-12 glass paste on titanate, are evidence of very satisfactory stability. Changes observed in the 10-day moisture cycle, short time overload, temperature cycling, and load life tests were well under 1.0%. The temperature coefficient, ranging from -247 to -338 ppm/C°, is within the contract objective of 350 ppm. The voltage coefficient, (30 ppm/volt at 730 kilohms per square) is remarkably

TABLE VI. a
RESISTOR CHARACTERISTICS

Q-12 Glass on Titanate Substrate

Test		Resistor Properties				Stand. Dev.*	Test Elements Per Value
Sheet Resistance (KΩ/□)		100	350	730	1310		
Std. Dev. of Res. (%)		8.4	11.5	19.5	23.0	15.58	60
Process Shift							
Annealing (%)		-1.2	-1.2	-1.1	-1.1		20
Cleaning (%)		<1	<1	<1	<1		
T.C.R. (ppm/C°)		-271	-247	-278	-338	45	20
V.C.R. (ppm/V)		- 64	- 46	- 30	-174		
Noise Index (db)		+6.7	+7.2	+5.8	>+12		2
90% RH/65°C							
94 hrs. (%)		-.29	-.31	-.25	-1.32		
164 hrs. (%)		-.38	-.42	-.39	-1.21		8
10 Day Moisture Cycle							
No Load (%)		-.02	-.04	±.02	+ .67		8
Rated Load (%)		-.26	+.13	∓.48	±1.51		8
Temp. Cycling (%)		+.03	+.03	+.04	+ .04		16
Low Temp. Operation (%)		-.04	-.04	-.04	- .05		16
Short Time Overload (%)		+.01	+.03	+.01	+ .03		16
Load Life (%)	75 hrs.	-.19	-.15	-.09	- .26	.0763	20
	100	-.19	-.06	±.05	- .28		20
1/10 Watt	250	-.44	-.38	∓.27	- .64		20
	500	-.75	-.73	-.64	-1.10	.1063	20
	750	-.67	-.68	-.62	-1.16		20
	1000	-.93	-.91	-.80	-1.36	.1303	20
	1750	-1.07	-.96	-.92	-1.61		20
	2000	-1.07	-.96	-.93	-1.47		20
	3000	-1.13			-1.77	.1548	
Paste No.		708-30-2	708-30-1	708-29-1	708-30-3		

*The standard deviation shown is the average of the σ's for each value.

TABLE VI. b
RESISTOR CHARACTERISTICS

Q-12 Glass on Alumina Substrate

Test		Resistor Properties			Stand. Dev. *	Test Elements Per Value
Sheet Resistance (KΩ/□)		121	369	836		100
Std. Dev. of Res. (%)		8.3	9.5	12.8	10.20	
Process Shift						
Annealing (%)		+ 1.0	+ 2.4	+ 1.1		20
Cleaning (%)		+11.3	+16.6	+14.2		4
T.C.R. (ppm/C°)		-706	-912	-820	220	20
V.C.R. (ppm/V)		- 40	-590	-630		20
Noise Index (db)		+ 14	>+14	>+12		2
90% RH 65°C						
94 hrs. (%)		+ 38	+65	+38		8
164 hrs. (%)		+143	--	--		
10 Day Moisture Cycle						
Rated Load (%)		+37.5	+28.2	+22.6		20
Temp. Cycling (%)		+ 5.5	+ 5.1	+ 4.7		20
Low Temp. Operation (%)		+ 5.1	+ 5.3	+ 4.9		20
Short Time Overload (%)		± 3.8	± .9	± 1.1		20
Load Life (%)	50 hrs.	±1.35	-1.24	± .82		20
	100	∓1.62	-1.47	±1.18		20
1/10 Watt	250	-2.47	-2.25	∓1.94		20
	500	-3.13	-2.98	-2.61		20
	750	-3.09	-2.90	-2.58		20
	1000	-3.67	-3.41	-3.06	1.20	20
Paste No.		308-30-2	708-30-1	708-29-1		

*The standard deviation shown is the average of the σ 's for each value.

TABLE VI. c
RESISTOR CHARACTERISTICS

Modified Q-12 Glass on Alumina Substrate

Test	Resistor Properties			Stand. Dev. *	Test Elements Per Value
Sheet Resistance (KΩ/□)	60. 9	120. 9	823. 6		
Std. Dev. of Res. (%)	9. 5	8. 1	7. 7	9. 39	
Process Shift	-. 6	-. 6	-. 6		20
Annealing (%)	-. 6	-. 6	-. 6		20
Cleaning (%)	+. 7	+. 5	+. 3		4
T. C. R. (ppm/C°)	-375	-368	-371	22	8
V. C. R. (ppm/V)	-24	-30	-40		8
Noise Index (db)	+2. 6	-. 3	+9. 6		2
90% RH 65°C					~ 8
96 hrs. (%)	+3. 2	-1. 4	-3. 5		
10 Day Moisture Cycle					
Rated Load (%)	±1. 23	±. 33	±. 24		8
Temp. Cycling (%)	±. 17	±. 08	-. 13		8
Low Temp. Operation (%)	+. 27	-. 11	-. 18		8
Short Time Overload (%)	±. 03	±0	±. 03		8
Load Life (%) 50 hrs.	- . 55	- . 34	- . 33		8
150	- . 77	-1. 07	-1. 02		8
1/10 Watt 250	-1. 24	-1. 05	-1. 05		8
500	-1. 19	-1. 17	-1. 20		8
750	-1. 29	-1. 52	-1. 60		8
1000	-1. 50	-1. 51	-1. 63	. 08	8
1500	-1. 53				8
Paste No.	708-42-4	708-47-1	708-47-2		

*The standard deviation shown is the average of the σ 's for each value.

low for such high-resistivity materials, but the current noise index (+5 to +7) is believed higher than might be tolerated in many applications. The lower value elements are observed to be somewhat more stable than the 1310 kilohms per square samples.

In Table VI. b, data on the same pastes fired on alumina substrates reveal a higher T. C. R., higher voltage coefficient, higher noise index, and greatly inferior stability, than the foregoing data on titanate substrates.

The data in Table VI, c, indicate that the modified-Q-12 compositions, fired on alumina, possess generally acceptable characteristics. While exhibiting slightly greater changes in some of the tests than the Q-12-on-titanate resistors, i. e. most properties, with the possible exception of the long-term humidity test, generally compare favorably.

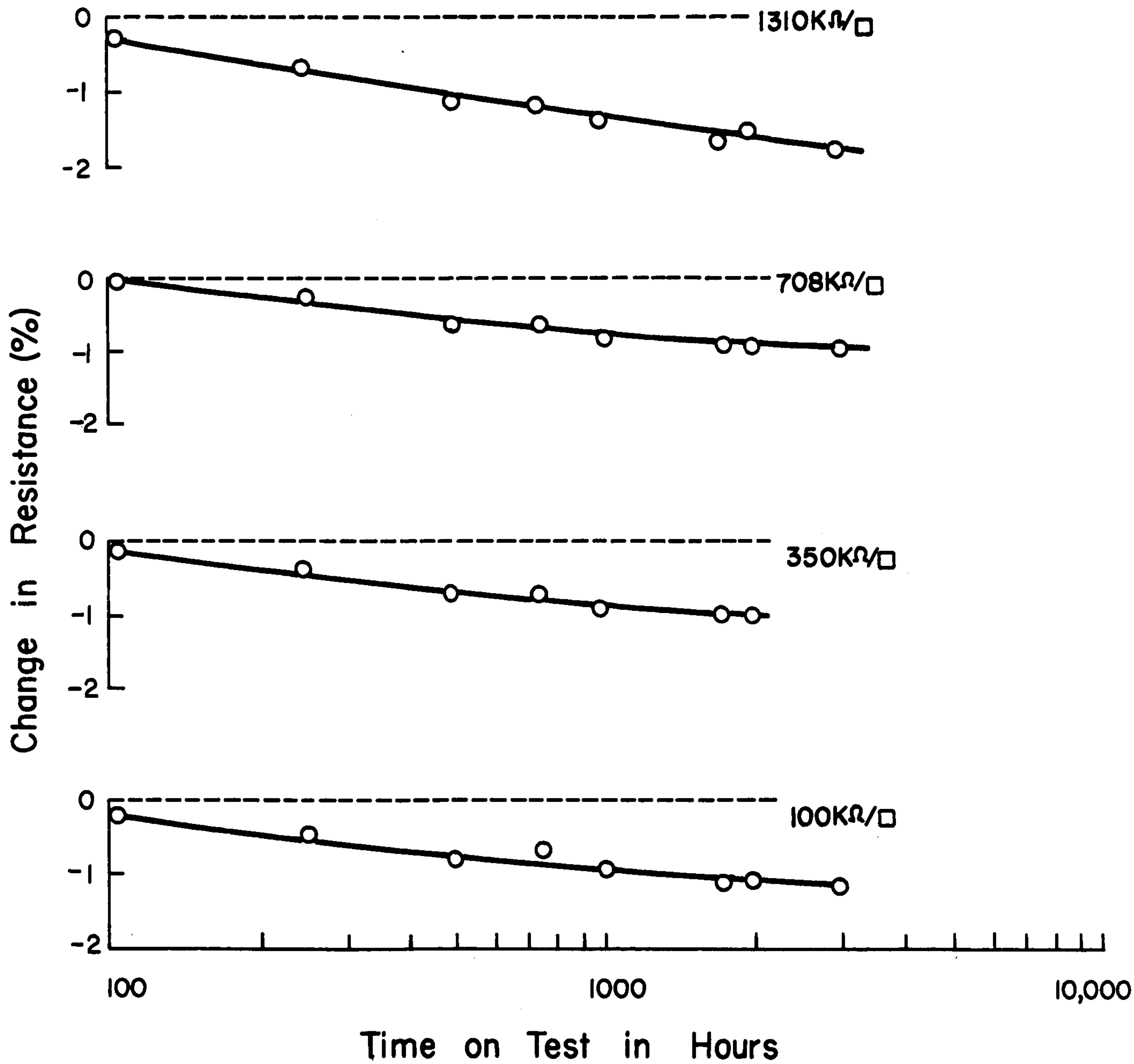
Failure Rate

The load-life data for the Q-12 glass paste on titanate substrates are plotted in Figure 10, for the period up to 3000 hours. The rate of change of resistance is observed to be such that the average change at 10,000 hours is predicted to be 2% or less for all four values tested. The distributions, as represented by the standard deviations in Table VI. a, are extremely narrow, to the degree that an anticipated failure rate at 1000 hours, based on a normal distribution, is vanishingly small.

Paste Reproducibility

Ability to reproduce these compositions from a given set of raw materials and in practical quantities would be essential for their successful

FIGURE 10
CHANGE OF RESISTANCE ON LOAD-
-LIFE TEST



utilization in circuit production. A high degree of confidence in this respect was gained during the life of this project. To demonstrate this confidence, however, three presumably identical one-quart batches of paste were prepared separately according to a prescribed recipe, and without adjustment of any type. Many resistors from each lot were printed and fired. The results are shown in Table VII, and verify that a given resistance value can be reproduced, from lot-to-lot, within quite satisfactory limits. In actual practice, substantially closer agreement could be reached by adjustment of the different pastes through blending with small quantities of a higher or lower value paste.

TABLE VII
VARIANCE IN PASTE FROM LOT TO LOT

Q-12 Glass Paste Fired on Titanate Substrates
One-Quart Quantities

Batch	Average Resistance $K\Omega/\square$	Std. Deviation (%)
708-30-1	249	6
708-46-2	295	6
708-46-4	289	10

Standard Deviation based on 20 elements per lot

CONCLUSIONS

Printed glaze resistors composed of thallium oxide and certain lead borosilicate glasses have proved capable of much higher resistance values than have previously been available. This is accomplished <u>without</u> appreciable loss of quality or control. By varying the proportion of ingredients sheet resistance values up to one megohm per square can be obtained, with a temperature coefficient less than 350 ppm/C°. The moisture, thermal, and electrical stability of these pastes applied and fired on ceramic substrates such as steatite and titanate bodies is excellent, as evidenced by the complete set of test results in Table VI. a.

The same pastes have not been found compatible with alumina, due, presumably, to a mismatch between the coefficients of expansion of the glaze and alumina. However, it has been found possible to modify the glass used in the paste to a degree which appears to provide an acceptable degree of compatibility with alumina. The characteristics of this modified-glass resistor on alumina appear, on the basis of limited tests and with very little refinement, to be only slightly inferior to those of the titanate.

A comparison of the data and specifications is made in Table VIII. The test data show that these pastes have met or exceeded the original contract specifications. However, these pastes cannot yet be considered optimum for the preparation of resistors on alumina substrates. Additional refinement of the glass composition is believed both desirable and possible. It is considered highly probable that the stability, T. C. R., and noise index of the

TABLE VIII

COMPARISON OF RESULTS WITH CONTRACT SPECIFICATIONS

Contract Requirement	Q-12 Glass Paste	Modified Q-12 Glass Plate
substrate compatibility	higher-C. T. E. ceramics	alumina
firing schedule: 600 - 1000°C	520°C	520°C
terminal compatibility	satisfactory	satisfactory
90% RH/150°C : 100 hours	<0.5% change	< 4% change
5000 hours; ± 10%	not determined	not determined
deposition reproducibility ± 15%	satisfactory	satisfactory
resistivity range: 300 kilohms-one megohm/□	satisfactory	satisfactory
power dissipation: 10 w/in.^{2}/80°C	<1% change/1000 hours	<1.7% change/1000 hours
T. C. R.: ± 350 ppm/C°	satisfactory	slightly higher than
adherence to substrate	satisfactory	satisfactory

compositions can be improved. Moreover, further tests, greatre in both number and severity, are required of these pastes to insure their reliability before actual use. Testing should also be performed on trimmed and encapsulated units.

The thallium oxide-glass system is a highly unique one, possessing many remarkable properties. Development of this system to its full potential should result in a printed resistor which is ideal for processing, high in quality, and very wide in range. It should contribute significantly to more widespread use of the printed microcircuit.

APPENDIX I

DESCRIPTION OF TESTS UTILIZED

Resistance-Temperature Coefficient:

Samples are subjected to and measured at each of the following temperatures; 25, -15, -55, 25, 65, 105, and 150°C. The value of T. C. R. reported is the greatest among those calculated between all temperature intervals.

Reference MIL-R-11E 4.6.3

Voltage Coefficient:

Samples are measured at rated continuous working voltage and at one-tenth of same. Reported as ppm change per volt.

Reference MIL-R-11E 4.6.4

Noise Index:

Samples are measured on a Quan-Tech Laboratory Resistor. Noise Test Set Model 2136 according to manufacturer's specifications and at the 1/10 watt rating.

Humidity Test (90% RH/65°C):

Samples are subjected to 65°C in a dry state and measured, then put in a sealed test container with distilled water and a small amount of $CaSo_4$ in the bottom of the container not in contact with the samples and at 65°C. Measurements are taken at various intervals during the test under test conditions and compared to the

65°C dry reading for a determination of relative change.

N. A. S. A. requirements.

Moisture:

Samples are subjected to ten consecutive one day cycles. Each one day cycle includes an increase from RT to 65°C, a drop to RT, an increase to 65°C, and a drop to RT, all at 90 - 98% RH. The samples are given an initial conditioning cycle prior to the start and certain special subcycles during some of the main cycles. The subcycles drop the temperature to -10°C and involve vibration for a period of time. During this entire test half of the samples are subjected to full working wattage.

Reference MIL-R-11E 4. 6. 9, MIL Standard 202B Method 106A.

Temperature Cycling:

Samples are subjected to five identical temperature cycles, each involving the sequence of -55, 25, 85 and 25°C for short periods of time. The total change is reported.

Reference MIL-R-11E 4. 6. 8, MIL Standard 202B Method 102A.

Low Temperature Operation:

Samples are subjected to -65°C, allowed to stabilize, and full rated working voltage applied for 45 minutes. The load is removed and the sample returned to RT. The change after 24 hours at room temperature is then reported.

Reference MIL-R-11E 4. 6. 7

Short Time Overload:

Samples are subjected to 2-1/2 times rated working voltage for 5 seconds, and allowed to stand for 30 minutes. The total change is then reported.

Reference MIL-R-11E 4.6.10

Load Life:

Samples are subjected to 70°C for a period of not less than 1000 hours. During this time the rated continuous working voltage is applied intermittently 1-1/2 hours on and 1/2 hour off. Samples are measured during the "off" period after 50, 150, 250, 500, 750, 1000, 1500, 2000 and each successive 1000 hours to the end of test. These changes are calculated based on initial value at 70°C.

Reference MIL-R-11E 4.6.11, MIL Standard 202B Method 108