FINAL REPORT Covering the Period June 1, 1970 to March 31, 1976

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MICROELECTRONIC COMPONENTS AND METALLIC OXIDE STUDIES AND APPLICATIONS

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ABSTRACT

This report covers research activities under NASA Grant No. NGR 34 - 012 - 004, Microelectronic Components and Metallic Oxide Studies and Applications, covering the period from June 1, 1970 to March 31, 1976. The project involved work in two basic areas: (1) Evaluation of commercial screen printable thick film conductors, resistors, thermistors, and dielectrics as well as alumina substrates used in hybrid microelectronics industries. Development of a microelectronics laboratory with the capability of processing these materials which were of interest to the Flight Instrumentation Division of NASA LRC, was desirable since their laboratories involved in this effort were being phased out in 1970. Results of tests made on materials produced by seven companies are presented. (2) Experimental studies on metallic oxides of copper and vanadium, in an effort to determine their electrochemical properties in crystalline, powder mixtures and as screen printable thick films constituted the second phase of this research effort. Oxide investigations were aimed at finding possible applications of these materials as switching devices, memory elements and sensors. The project was interdisciplinary and involved faculty members as well as undergraduate and graduate students in Electrical and Mechanical Engineering and Physics.

INTRODUCTION

In June of 1970 evaluation tests on Dupont 7828 thick film resistor ink samples which had been processed five years previously, were begun. Since that time screen printable thick film conductors, resistors, thermistors, and dielectrics, manufactured by Dupont, Electro-Science Laboratories, (ESL), Electro Materials Corporation of America (EMCA), Thick Film Systems (TFS), and Sel Rex (SX) have been processed and evaluated in a laboratory developed at N. C. A & T State University during the period of research reported on herein. The reliability and effectiveness of these materials have been of especial interest to NASA and those engaged in manufacturing hybrid microelectronic circuits, an industry which has undergone great expansion in recent years. Results of the various tests performed on representative products of the referenced manufacturers are reported on in the first part of this report.

The second phase of this research effort involved contemporary experimental studies on metallic oxides of copper, and vanadium mixed with other chemicals which have exhibited semiconductor as well as metal-resistor-semiconductor - transitions under the influence of thermal and electrical fields. Efforts were made to gain insight into the electrochemical properties of these oxides in crystalline, powder, and screen printable thick film form. The oxides were processed via heat treatment in air, vacuum, inert and gaseous atmospheres to produce samples which underwent static and dynamic volt-ampere, and temperature-resistance tests with the aim of finding possible applications of these as switching devices, memory elements and sensors since related phenomena were observed in the various samples fabricated. Some X-ray diffraction studies were employed in both phases of the project in an effort to determine structural and/or chemical changes in the oxides and in the thick film resistors as a result of the firing process. Experimental results of the oxide studies are reported on in the second part of this report.

I. MICROELECTRONIC COMPONENT TESTS AND EVALUATION

Evaluation of Dupont No. 7828 Resistor Ink (A3, B8)

Two hundred alumina substrates containing five thick film resistors per substrate were processed, using Dupont No. 7828 resistive ink, by the Flight Instrumentation Division of NASA Langley Research Center in 1965. These screened resistors fell into four basic types relative to encapsulation: Type A was encapsulated; type B, C and D were encapsulated with G. E. RTV, 3M Scotchcast and Wornow Processing Co., Blue Resist respectively. Half of the resistors were trimmed and half were untrimmed. The five nominal resistance values were 10 K ohms to 50 K ohm in 10 K ohm steps. Initial load tests, resistance vs. temperature, and TCR measurements from -25 to 150 degrees C were made at NASA - LRC and the samples were stored "on shelf" for a period of five years. Thereafter, temperature - resistance tests from -50 to 150 degrees C and above, load tests, noise measurements, relative humidity, and water immersion tests were made on the resistors during the sixth year after fabrication at N. C. A. & T. State University. Relative resistance, TCR, drift over the six year period and an evaluation of the effectiveness of encapsulation was made. Table 1 gives a summary of the type and number of the tests performed and the alphabetically designated groups (A, B, ..Z) involved in each test. Each alphabetical group contained ten substrates (a total of 50 individual resistors per group), however not all of the substrates in a group underwent a test designated for it. For example only two substrates of the same group may have undergone the relative hymidity test, etc.

Over a five year period the average drift for untrimmed resistors was well below 1%, while that for types A and C was 7% and type B 12 to 14% for trimmed resistors. Drift was negative for untrimmed resistors and positive for trimmed resistors in most cases. Drift was greater in trimmed resistors.

Maximum temperature coefficient of resistance (TCR) was 325 ppm for trimmed type D samples. Average TCR for types A, B, and D was in the range of 200 ppm, in the 25 to 150 degrees C temperature range. Between -50 and zero degrees C TCR was negative and generally less than 100 ppm.

In type A resistors, resistance decreased with increasing humidity averaging about -4% between 71% and 94% R.H. This decrease in resistance was greater in higher resistors varying from -1% for R-1's to about -6.2% in R-5's. At higher temperatures the change in resistance decreased with increasing R.H., e.g. at 50 degrees the change in R-5's was -5.6%. Generally,

TABLE 2. EVALUATION TESTS ON NASA THICK FILM RESISTORS:

	TEMPERATURE VS. RESISTANCE °C -50 to 25	TEMPERATURE VS. RESISTANCE °C 25 to 150	LOAD (watts/in²) ΔR AFTER __ HRS.	SUBSTRATE TEMPERATURE f(LOADING)	RELATIVE HUMIDITY	WATER IMMERSION ΔR AFTER __ HRS.	NOISE QUAN-TECH
NO. OF TESTS	1	2	3	2	4	2	3
DATE / SUBSTRATES	6-23-70 All A,C,N,H,R,P O,T,U,Y W,S,Z,B E,K,J	12-2-69 All 10-27-70 All	3-23-71 A,N,J 11-27-71 C,J,P,Z 2-16-72 A's 50 to 400 watts/in²	3-29-71 A,N,J 2-21-72 A's (special)	6-18-71 N,E,J 7-9-71 N,E,J 10-30-71 C,O,J,H,P,S,Z 11-13-71 P,C,O,J,H,S + Z	11-16-71 C,J,P,+Z (49 hrs) 3-29-72 E,B,J,H,N,S,+Y (213.5 hrs.)	6-15-71 E's 7-19-71 J,N 11-26-71 C,P

RESISTIVE INK-DUPONT 7828 (1965)
CONDUCTIVE INK-DUPONT 7553 (1965) PLATINUM GOLD

SUBSTRATES TYPES (1 sq.in. 96 % ALUMINA, 50 mil.)

A - unencapsulated
B - encapsulated GE RTV-602 (cured @ 150°F for 2 hrs.)
C - encapsulated 3M SCOTCHCAST XR-5088 (cured @ 150°F for 2 hrs.)
D - encapsulated WARROW BLUEPRINT 181-11-Y BLUE RESIST
(cured @ 150°F for 0.25 hrs.)

NOMINAL VALUES OF RESISTORS PRINTED ON EACH SUBSTRATE:

R1 - 10 KΩ   R3 - 30 KΩ
R2 - 20 KΩ   R4 - 40 KΩ
R5 - 50 KΩ

5

most resistors were not affected by relative humidity (at constant temperature) up to 71%. The effect of increasing R. H. was to decrease resistance in all type resistors and this effect dwindled with increasing temperature. It would therefore seem that there is a resistance compensating effect produced by increasing temperature and relative humidity contemporaneously.

Water immersion tests were run in which substrates of all four types were completely immersed in distilled water for a specified time. These tests indicate evident absorption of moisture and seems to correlate with the relative humidity tests results. Type B seems to have been most affected by water immersion and showed no change after "drying". The encapsulation on most of these substrates had cracked in varying degrees over a period of time and evidence of moisture was noticed which apparently was not expelled by the drying process, in fact the drying seems to have made matters worse. The data seems to argue for type D as being the best water proofing encapsulant at least over short periods of immersion. However, over long periods of immersion it appears that the unencapsulated resistor holds its own.

Load tests were performed by applying the same voltage to all resistors on a substrate (differential loading) and by applying different voltages to all resistors such that the same loading in watts/sq. inch resulted for all resistors. Loading was obtained by dividing the power dissipated in the resistor by its effective area (excluding the area of the resistor overlapping the conductor area). Differential loads as high as 400 w/sq. in. on R-1 and 15.4 w/sq. in on R-5 were applied with corresponding intermediate loads on the other resistors.

In a 63 hour test trimmed resistors exhibited greater resistance stability than non trimmed resistors during loading by not deviating over +2.51% (this minimum deviation being found in type D resistors). Maximum deviation, not more than +5.5% change in resistance occurred in untrimmed resistors type B. Other tests not reported tend to support this same conclusion.

For constant loading the following data gives some idea of temperatures as well as temperature gradients on loaded substrates: after thermal equilibrium had been established for 20 hours or more:

Total Watts on Substrate	Maximum Temp-C	Minimum Temp-C
3.56	128	103
3.11	145.5	123.5
2.53	105	94
2.51	112	100
2.15	106	86
1.32	45	44

Data seems to imply that greater stability was obtained for this resistive ink by preloading at higher power densities than the resistor was designed for and stability is also better for trimmed resistors.

Some samples were tested at temperatures above 200 degrees C and it was noted that substrate cracking occured in some of the encapsulated substrates, while there was no substrate cracking in unencapsulated samples. Some resistors came aloose from the substrate bodily but those resistors which were undammaged showed no appreciable changes in resistance values.

Evaluation of Current Microelectronic Materials (A5, B10-B13)

Thick film products manufactured by five different companies in more recent years (1973 - 1975) were processed and tested in a laboratory at North Carolina A & T State University. In addition to the tests previously described resistor and substrate profile studies were also conducted on the samples made. Table 2 lists manufacturers' specifications for the products tested.

Evaluation tests were made on Electro Science Laboratories (ESL) 2800 series, Electro Materials Corporation of America (EMCA) 5000 series, Thick Film Systems (TFS) 780 and 850 series, Dupont (DP) 1000 and 1400 Birox series and Sel-Rex (SX) 6000 series thick film resistor inks and compositions. Data on a total of 23 different types of resistor ink ranging from 10 ohms/square to a megohm/square from the five companies was obtained. Resistor samples were printed, dried and fired according to manufacturers' specifications on 96% and 99.5% alumina substrates manufactured by American Lava Corporation (3M Company) and Cours Porcelain Company. The printing was done on a manual Weltek 400 screen printer using monotex polyester and stainless steel masks. Conductive patterns were prefired in most cases although some cofiring was also attempted, using Dupont type 8227 Pd/Au, and Thick Film Systems 3412 ConductroX Pd/Ag conductive inks. Each substrate contained ten resistor samples varying from 1 to 5 squares. Room temperature resistance measurements were made and recorded on all samples processed. One or more substrates of each type was selected to undergo temperature resistance tests from -40 degrees C to 150

Table No. 2 Manufacturers' Specifications for Thick Film Resistor Inks

Manufacturer	Type	Code	ohms/sq.	TCR ppm/°C	Peak Firing Temp. °C
Electro-Science Laboratories, Inc. (ESL)	2813-B	ES-13	1.K ± 25%	± 150	780-850
	2815-B	ES-15	100 K ± 25%	± 200	for 10-15 min. 1 hour cycle
	2816-B	ES-16	1 Meg. ± 30%	- 300	
Electro Materials Corp. of America (EMCA) 5000 series	5013	EM-13	1 K	± 200	750-1000
	5015	EM-15	100 K	± 200	10 min.
	5016	EM-16	1 Meg.		30 min cycle
Thick film Systems, Inc. (TFS), 780 series	780-500	TF-00	50 ±20%	± 200	
	780-102	TF-02	1 K ± 20%	± 200	
	780-104	TF-04	100K ± 20%	± 200	850
	850-102	TF-2	1 K	± 100	10-12 min.
	850-103	TF-3	10 K ± 10%	± 100	25 min cycle
	850-104	TF-4	100 K	± 100	
	850-105	TF-5	1 Meg.	± 200	
Dupont Birox 1000 series (DP)	1021	NB-21	99 10%	± 100	760-860
	1041	NB-41	9.05 K 10%	± 100	9-10 min.
	1053	NB-53	316 K 10%	± 100	40-80 min.
	1421	DB-21	97	+ 52(-63)	cycle
	1431	DB-31	1 Kr	+68(-28)	850
	1441	DB-41	10.3 K	+35(-52)	10 min.
	1451	DB-51	101 K	+51(-27)	60 min. cycle
Sel Rex	60320	SX0	10		
	60322	SX2	1 Kr	± 100	825-875
	60323	SX3	10 Kr		9-11 min.
	60324	SX4	100 K		30 min cycle

degrees C, power loading, relative humidity tests, water immersion in tap and distilled water, and untested samples were stored on shelf for percentage drift determinations.

Cold and hot TCR results for selected samples tested are shown in tables 3 and 4. The hot TCR data shows that all Birox and Thick Film Systems samples were consistently lower in TCR than the nominal specified values. Only the 100 K ohm/square ink of the ESL series was well within specifications and the one megohm/square ink is not listed since most of these samples showed open circuit. Only the lowest resistivity ink of the EMCA samples were within specifications while TCR for the higher resistivity types generally increased proportionately with resistivity. In all cases the performance of the TFS samples were superior for the cold TCR tests and the table reflects the fact that substrates which had been previously subjected to temperature tests had higher TCR values than those substrates which had not undergone previous temperature tests.

A plot of normalized resistance versus temperature is given in Fig. 1 to give some idea of relative variation of resistance with temperature. The slope of these curves is proportional to TCR.

Table No. 5 reflects TCR test results for samples printed on substrates supplied by two different manufacturers. The Selrex and Birox 1400 series were expected to represent the latest advancement in technology since they were among the latest resistor compositions placed on the market at this writing. Average values of TCR are indeed within manufacturers' specifications and in some cases considerably lower.

Substrate Profile Studies

Surface roughness and camber of the substrates on which the inks were printed as well as the resulting profiles of the inks themselves influence the resulting resistance, TCR, as well as some of the other tests to be discussed. Repeatability in the printing process as well as the resulting ohms per square could be adversely affected by these factors. Results of repeata-

Table No. 3

RESULTS OF COLD TCR TESTS
ON THICK FILM RESISTORS

Manufacturer and Ink Type	Substrate #	TCR - ppm/°C from 0.6 °C to -24 °C Maximum	Minimum	Average
Birox # 1021	61	-318	-223	-270
	70	-265	-176	-218
EMCA # 5013	61	-141	-118	-128
	70	-137	-100	-121
EMCA # 5015	61	-481	-362	-427
	70	-447	-367	-418
EMCA # 5016	61	-821	-745	-793
	70	-781	-718	-762
ESL # 2813B	61	-364	-348	-355
	70	-342	-320	-330
ESL # 2815B	61	-347	-211	-242
	70	-282	-146	-202
Thick Film # 780-102	61	-168	+ 29	-121
	70	-152	-109	-134
Thick Film # 780-104	61	-124	- 19	- 30
	70	+ 93	+ 14	+ 25

All substrates # 61 were previously tested from - 40 °C to 150 °C. No previous tests were ran on # 70 substrates.

Table No. 4

TEMPERATURE COEFFICIENT OF RESISTANCE FOR THICK FILM RESISTORS, FROM 25 DEGREES C TO 125 DEGREES C.

SUBSTRATE NUMBER	TCR in PPM/°C MINIMUM	MAXIMUM	AVERAGE
NB 21-61	- 42	- 83	- 63
NB 41-61	60	95	84
NB 53-51	- 18	- 44	- 32
ES 13-61	-204	-216	-210
* ES 15-61	-115	-154	-139
EM 13-61	- 18	- 44	- 32
EM 15-61	-249	-275	-263
EM 16-61	-598	-622	-612
TF 00-61	128	185	159
TF 02-61	- 68	- 88	- 82
TF 04-61	68	100	88

* Most of the ES-16 samples showed opened circuit and great instability.

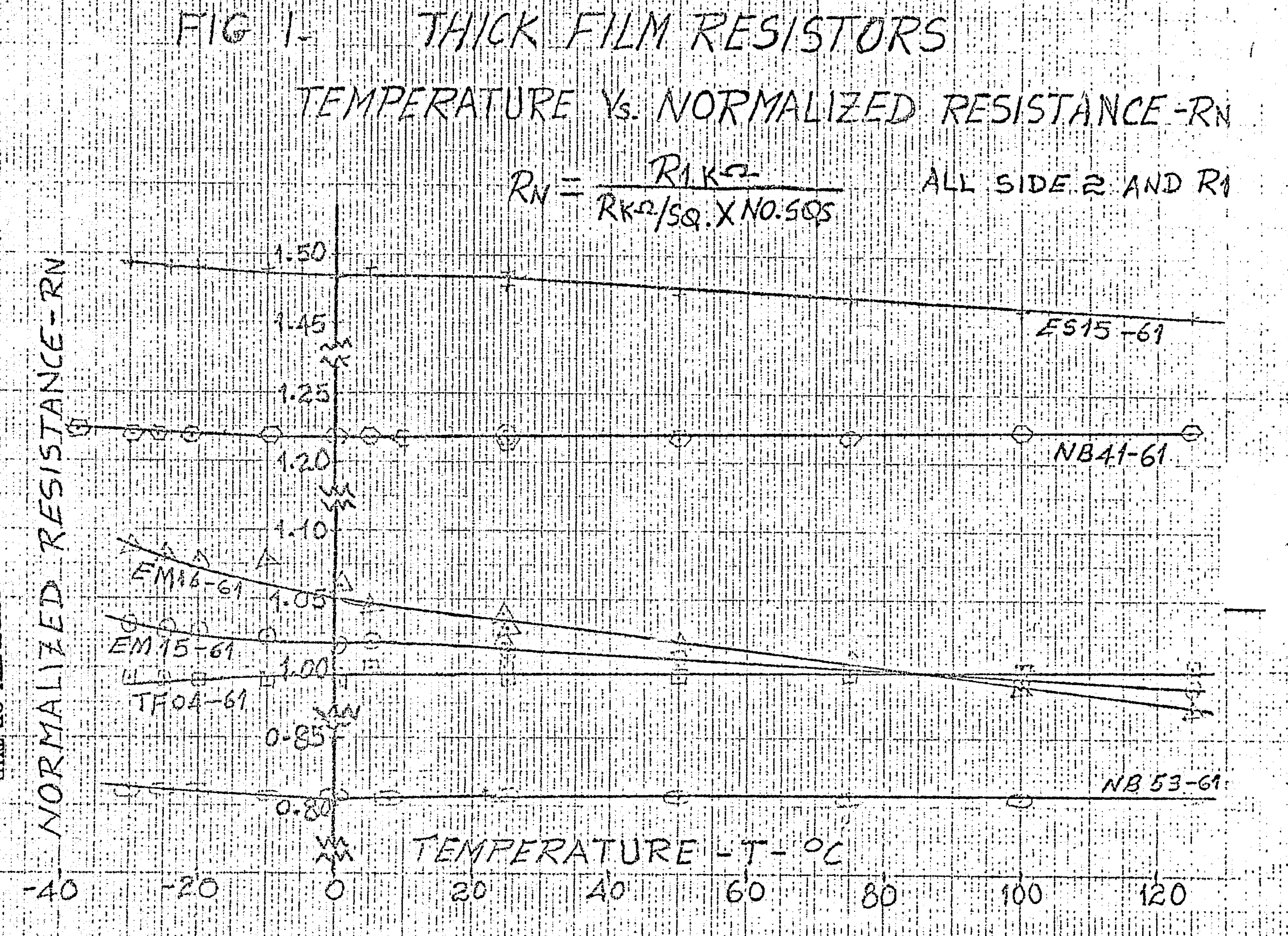


FIG 1- THICK FILM RESISTORS
TEMPERATURE Vs. NORMALIZED RESISTANCE-RN
$R_N = \frac{R_{1K\Omega}}{R_{K\Omega/SQ.} \times NO.SQS}$
ALL SIDE 2 AND R1
NORMALIZED RESISTANCE-RN
1.50
1.45
1.25
1.20
1.10
1.05
1.00
0.85
0.80
ES15-61
NB41-61
EM16-61
EM15-61
TF04-61
NB53-61
TEMPERATURE -T- °C
-40
-20
0
20
40
60
80
100
120

19

Table No. 5 Temperature Coefficient of Resistance for Thick Film Resistor Inks On 3M & Cours Substrates

Substrate and ink type	TCR 25°C to 125°C Minimum	Average	Maximum	TCR 0.6°C to -30°C Minimum	Average	Maximum
M-SX0	-115.00	-11.64	+309.38	-73.60	-59.55	-46.68
M-SX2	-172.66	-146.43	-95.52	-236.18	-226.48	-217.25
M-SX3	-662.23	+117.10	+522.51	+7.44	+30.18	+67.48
M-SX4	-92.35	+100.94	+459.50	+32.03	+64.66	+99.63
C-SX0	-294.12	-76.06	+156.25	-439.34	-46.01	+637.96
C-SX2	-291.15	-154.53	-22.75	-366.71	-291.94	-194.18
C-SX3	-126.08	+118.22	+211.02	-4.30	+63.33	+179.52
C-SX4	+42.63	+157.57	+461.37	0	+66.86	+186.68
M-DB21	-44.46	+28.84	+73.26	-135.85	-54.91	0
M-DB31	+12.24	+63.14	+124.52	-105.27	-20.77	+188.67
M-DB41	-453.76	-14.83	+83.05	-292.90	-88.65	+59.86
M-DB51	-22.09	+16.49	+53.57	-179.59	-56.24	+156.73
C-DB21	-196.08	+38.59	+89.00	-109.31	-90.76	-64.47
C-DB31	+12.38	+31.55	+43.46	-95.61	-72.75	-54.65
C-DB41	-354.72	-64.87	+50.32	-144.64	-82.36	0
C-DB51	-128.69	+38.23	+374.93	-160.16	-131.03	-106.67

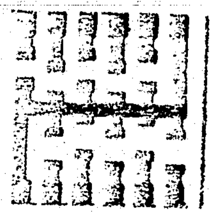
(B12)

bility studies outlined in our status report dated April, 1974 indicated repeatable values of resistance for corresponding resistors on consecutively printed substrates and variations in values of resistors designed to be equal on the same substrate were adversely affected by substrates which were warped or had surface irregularities as well as non uniformly deposited ink thickness. Efforts were therefore made to measure profiles of substrate surfaces and cross-sections of the processed thick film resistors. A system consisting of microprobe Model 118-A cerama probe, dial indicators and a microscope was devised to obtain cross-sectional profiles of the processed resistors and the alumina substrates. While this system was somewhat laborious since it was essentially a point-by-point method, it nevertheless proved to be quite accurate when compared to the results obtained using a continuous profile measuring recording system at NASA LRC's FID.

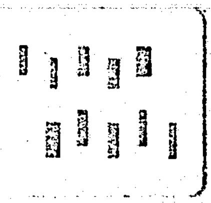
Earlier resistor samples were printed on 1 inch square, 96% alumina substrates furnished by Magneco Electronics with a specified surface finish of 20-30 micro-inches. The newer samples (substrate numbers 60 to 70) were printed on American Lava Corporation, Alsimag 614 substrates, also 96% alumina, specified to have a 25 micro-inch AA surface and a camber of 4 mils per inch. Samples of the resistor and substrate profiles obtained after firing are presented in the following pages. These profiles were obtained using a Sloan Dektak Model 138 profile meter. Actual room temperature resistance values and number of squares for each resistor is also included on the plots to allow comparisons of actual ohms per square obtained to the nominal ohms per square designated by the manufacturer. Ink manufacturers differ in their designations of ohms/sq - some specify ohms per square for a specified given thickness of dried or fired ink, usually in the order of 1 mil. EMCA for example specifies that resistor values are reported in ohms/sq/mil of <u>dried paste</u> and that after firing this translates into ohms/sq/$\frac{1}{2}$ mil of <u>fired film</u>.

A consideration of the profiles shown indicates that most of the fired thicknesses are less than 0.5 mil with variations from about 0.25 to 0.5 mil. It is also evident that variations of the contour of the substrate caused differences in thickness for the various resistors on the same substrate. The resistivities of the inks were shown to be constant and adhered very closely to the $R = rL/A$ relationship where r, L, and A are the resistivity, length and cross sectional area of the resistor respectively. This fact was verified by using a microprobe and dial gages to plot resistor profiles on graph paper and measuring the cross-sectional areas using a planimeter and by counting squares. The re-

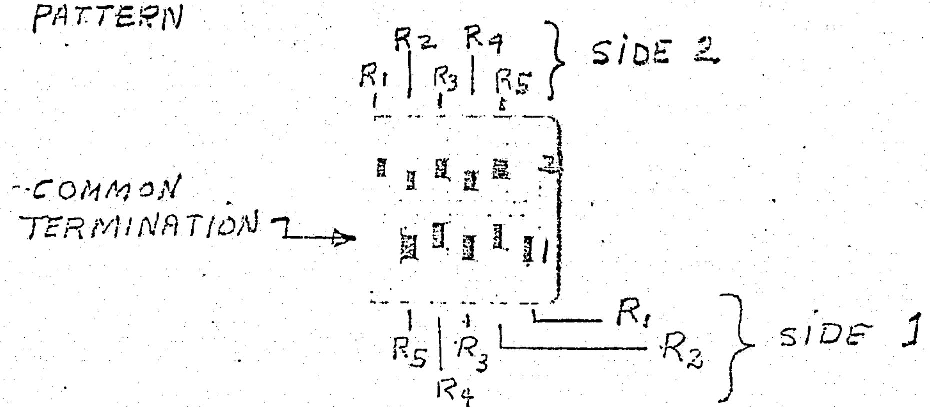
THICK FILM RESISTOR GEOMETRY & DESIGNATIONS



CONDUCTOR PATTERN



RESISTOR PATTERN



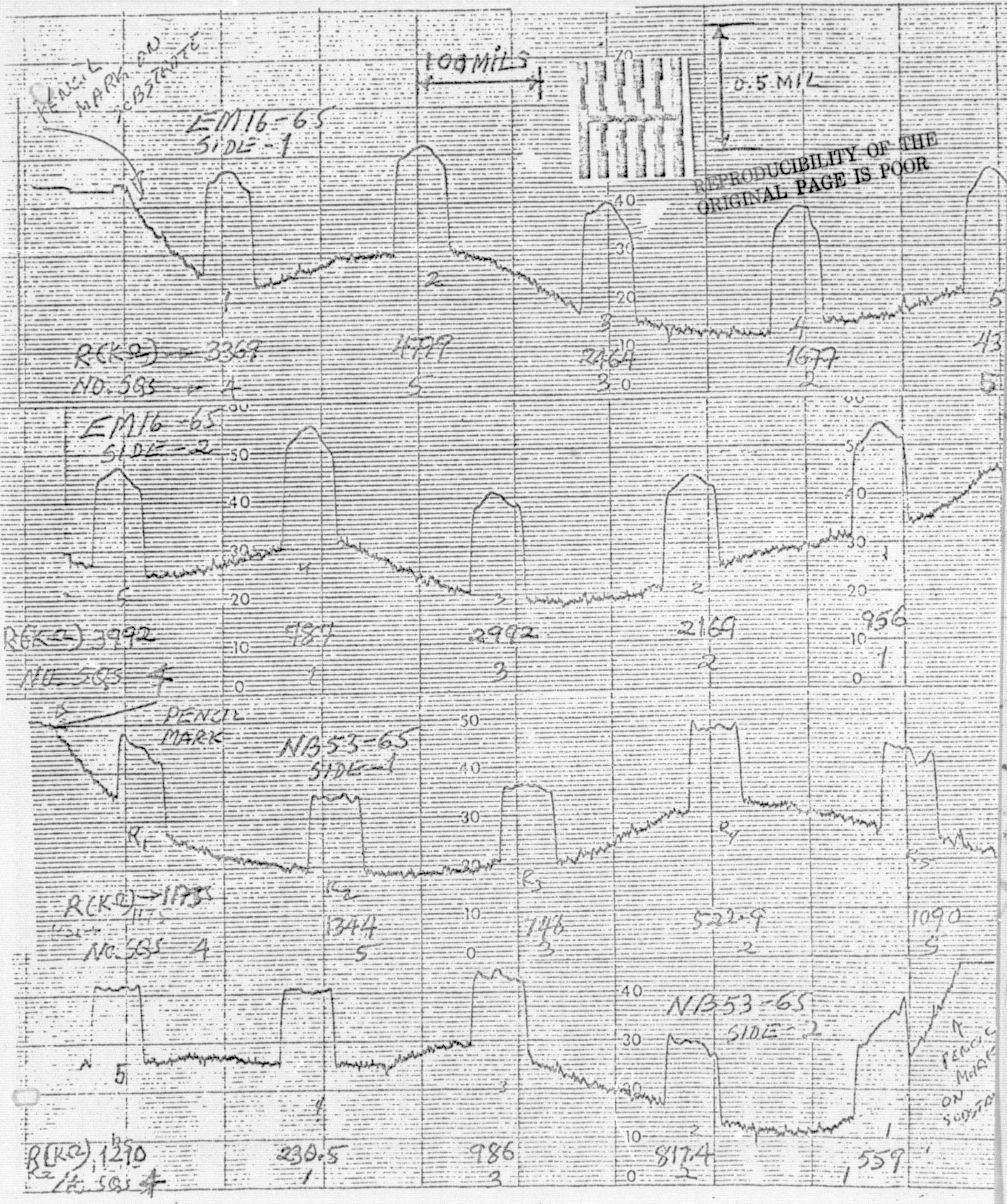
FIRED RESISTOR - CONDUCTOR PATTERN ON 1 IN. SQ. ALUMINA SUBSTRATE

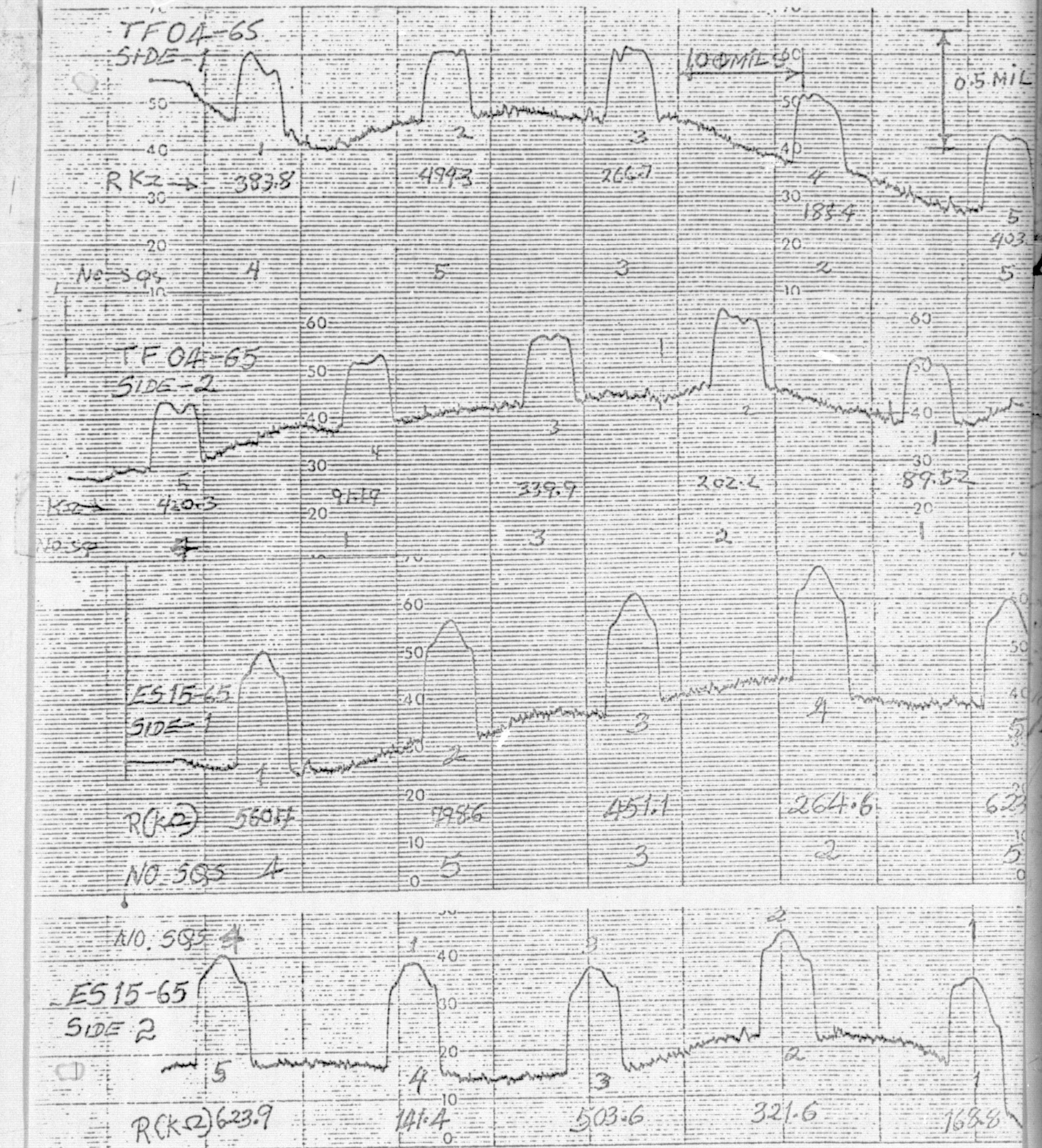
<u>SIDE 1</u>

$R_1 = 3\,1/3$ SQUARES
$R_2 = 3\,1/3$ "
$R_3 = 2\,2/9$ "
$R_4 = 2\,2/9$ "
$R_5 = 1\,2/5$ "

<u>SIDE 2</u>

$R_1 = 2\,1/2$ SQUARES
$R_2 = 2\,1/2$ "
$R_3 = 1\,2/3$ "
$R_4 = 1\,2/3$ "
$R_5 = 1\,1/4$ "


PENCIL MARK ON SUBSTRATE
100 MILS
0.5 MIL
EM16-65
SIDE-1
REPRODUCIBILITY OF THE ORIGINAL PAGE IS POOR
R(KΩ) 3369
NO. SQS 4
EM16-65
SIDE-2
R(KΩ) 3992
NO. SQS 4
PENCIL MARK
NB53-65
SIDE-1
R(KΩ) 1175
NO. SQS 4
NB53-65
SIDE-2
PENCIL MARK ON SUBSTRATE
R(KΩ) 1210
NO. SQS 4


TF04-65
SIDE-1
100 MILS
0.5 MIL
RKΩ
383.8
499.3
266.7
185.4
No. SQS
4
5
3
2
5
TF04-65
SIDE-2
KΩ
420.3
91.19
339.9
202.2
89.52
No. SQ
4
1
3
2
1
ES15-65
SIDE-1
R(KΩ)
560.7
798.6
451.1
264.6
NO. SQS
4
5
3
2
5
NO. SQS
4
ES15-65
SIDE 2
R(KΩ)
623.9
141.4
503.6
321.6
168.8

sulting ratio of the cross sectional areas for two resistors compared to the inverse ratio of their measured resistances were in agreement to within tenths of a percent.

Profiles shown on page 19 gives some idea of cross-sectional reduction due to the firing process. The figure shows a sample fired and dried only by the manufacturer. The profile resulting after firing of sample SX4D-R-1 in our laboratories is presented for comparison.

Drift Test

Resistance values were measured for six substrates of 11 types of ink (a total of 660 resistor values) and the substrates were then stored on shelf for 28 days. After this period the resistance was measured again and the percent change was recorded as percent drift. Substrate EM16 showed the highest average percent drift (0.74% for Side 1) and had the largest variation (from -13.7 to ±18.2%).

Substrate EM15 had one point well outside of the range for the remaining change and was omitted from the computation of the sample mean. Similarly substrate NB21 had one point which was omitted from the computation of the sample mean.

Table 6 shows the sample mean and the 95% confidence interval on the variance for the drift test. Based on this approach to analyzing the data, ink type ES13 was the most consistent, as reflected by the low variance (between 0.0006 and 0.0017). The substrate with ink type NB41 had the lowest average drift and had the third smallest variance.

Load Test and Relative Humidity Tests

Load tests were conducted on side 2 of substrate No. 60 for NB41, EM15, ES15, and TF04. Each of the 5 resistors on each substrate was loaded at 30, 40, and 60 watt/sq. inch for 96 hours at each load. Resistance measurements were made at room temperature prior to loading and at the end of the load period after the substrate had been allowed to cool to room temperature. From these resistance measurements the percent change in resistance was computed. Thermocouples were placed at various locations on the substrate during the loading period to determine the maximum temperature attained on the substrate. Similar load tests had previously been performed on the old substrates (bearing substrate numbers 1 to 10). Table No. 7 shows a comparison of the average percent change in resistance and the maximum temperatures reached on the substrates for the old and new substrates.

SEL REX RESISTOR PROFILES

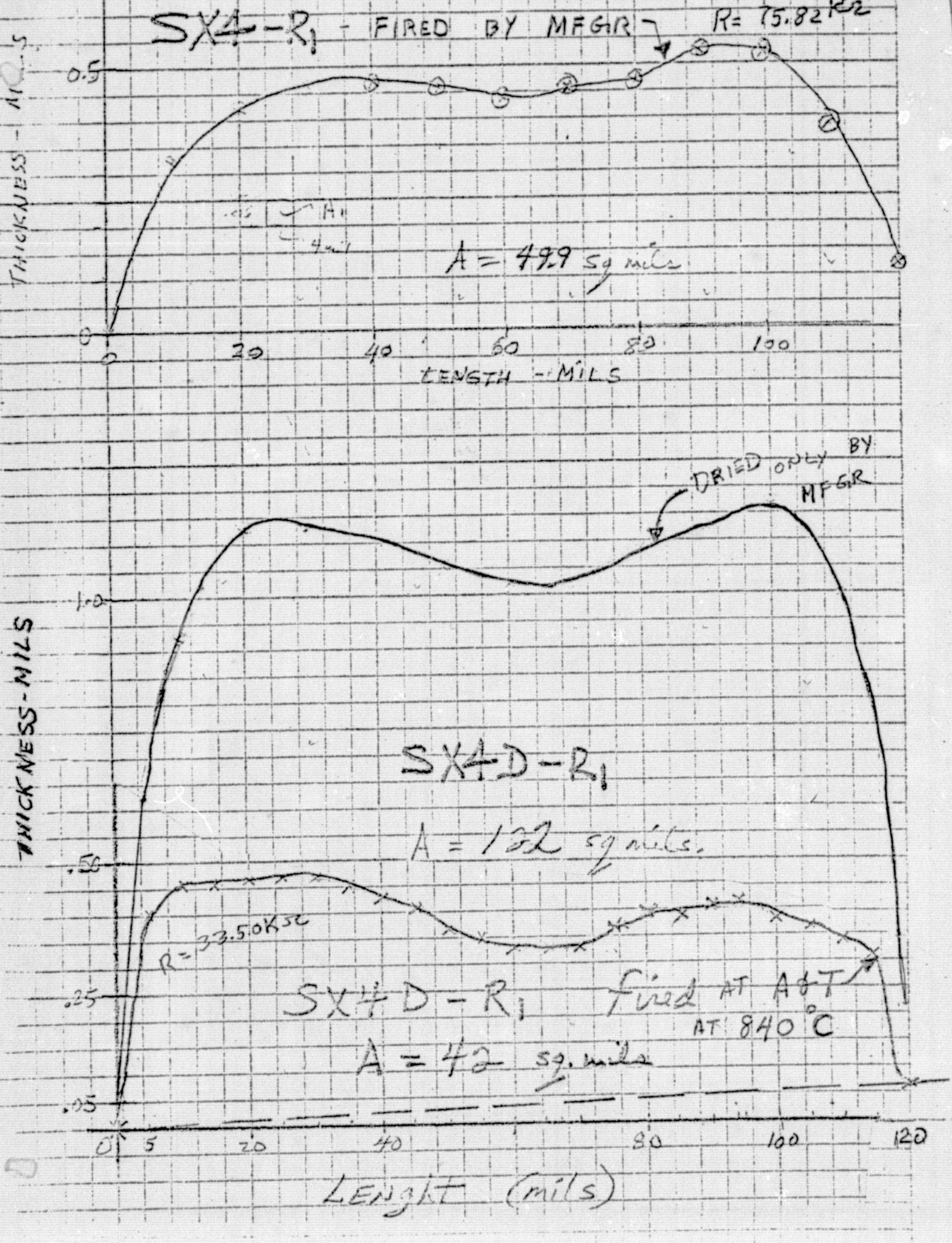


Table No. 6

PERCENTAGE DRIFT FOR SIDE 1 OVER THE 28 DAYS
(5/17/74 to 6/14/74)

SUBSTRATE	MEAN	95% CONFIDENCE INTERVAL
NB21	-0.141	$0.021 \leq s^2 \leq 0.059$
NB41	-0.0067	$0.002 \leq s^2 \leq 0.006$
NB53	-0.043	$0.004 \leq s^2 \leq 0.011$
EM13	-0.093	$0.006 \leq s^2 \leq 0.017$
EM15	-0.015	$0.019 \leq s^2 \leq 0.055$
EM16	0.747	$40.05 = s^2 = 114.4$
ES13	-0.188	$0.0006 = s^2 = 0.0017$
ES15	-0.143	$0.007 = s^2 = 0.020$
TF00	-0.079	$0.139 = s^2 = 0.397$
TF02	-0.053	$0.002 = s^2 = 0.005$
TF04	0.063	$0.027 = s^2 = 0.078$

s^2 = population variance
σ^2

Table No. 7

COMPARISON OF PERCENT CHANGE IN RESISTANCE
DUE TO LOADING BETWEEN OLD AND NEW SUBSTRATES

SUBSTRATE	LOAD WATTS/SQ.IN.	OLD $\bar{X}$	OLD MAX.TEMP. °C	NEW $\bar{Y}$	NEW MAX.TEMP. °C
NB41	30	N/A	N/A	-5.3	32
EM15	30	-1.85	46	-0.64	45
ES15	30	-1.78	54	-4.44	40
TF04	30	-0.94	54	-14.82	41
NB41	40	N/A	N/A	-2.23	39
EM15	40	-2.78	53	-0.28	43
ES15	40	-2.74	60	-5.54	41
TF04	40	-5.74	56	-10.16	41
NB41	60	N/A	N/A	-0.20	54
EM15	60	-4.14	62	-0.18	52
ES15	60	-4.73	61	-2.16	45
TF04	60	-6.36	72	-3.70	51

Relative humidity tests were conducted on substrate No. 62 for 12 types of ink listed in Table 2 at relative humidities of 56% to 94% at constant temperatures of 40 degrees C and 50 degrees C. The tests were run in a Blue M Relative Humidity Chamber. Table No. 8 gives results of the maximum, minimum, and average percentage change in resistance over a 57% to 88% humidity range. The greatest resistance changes occurred at the lower temperature for inks having resistivities below 100 K ohms/sq. with just the opposite taking place for inks of resistivities higher than 100 K ohms/sq.

Table No. 8 PERCENTAGE CHANGE IN RESISTANCE DUE TO RELATIVE HUMIDITY

Relative humidity range from 57% to 88%
* Actual humidity range was 61% to 82%
** Actual humidity range was 65% to 84%

SUBSTRATE	MINIMUM CHANGE		MAXIMUM CHANGE		AVERAGE CHANGE	
	40°C	50°C	40°C	50°C	40°C	50°C
NB21-62	-0-	-0-	- 0.55	- 0.02	- 0.14	-0-
NB41-62	-0-	-0-	+0.09	- 0.05	- 0.01	-0.02
NB53-62	-0.14	-0.07	-0.30	- 0.66	- 0.22	-0.19
EM13-62	-0-	-0-	- 0.01	0.01	- 0-	-0-
EM15-62	-0.40	-0-	- 3.34	- 0.47	- 1.49	-0.21
EM16-62	-1.02	-0.70	-47.17	-13.25	-16.33	-5.29
ES13-62	-0-	-0-	- 0.02	- 0.09	- 0-	-0.01
ES15-62	-0.07	-0.07	- 0.65	- 0.49	- 0.21	-0.17
ES16-62	-0.78*	1.35**	- 0.78*	1.35**	- 0.78*	1.35**
TF00-62	0.07*	-0-**	0.50*	0.17**	0.20*	0.03**
TF02-62	-0-*	-0-**	- 0.30*	0.08**	- 0.01*	0.02**
TF04-62	0.46*	-0.92**	10.06*	- 5.71**	3.74*	-3.06**

A water immersion test was performed for a period of eight days in tap and distilled water on 11 ink types. The results of this test are given in table 9. The column heading labeled "wet" refers to the change in resistance based on measurements recorded immediately after removal of the substrate from the water and drying it thoroughly in soft absorbent tissue. The "dry" change in resistance is based upon measurements made after the substrate had been exposed to 125 degrees C for 30 minutes. Ink type EM16 had the maximum average change in resistance after soaking and NB41 had the smallest. Except for types NB53 and EM16 there was little difference between the change in resistance for tap water and distilled water in the "dry" condition.

Table 9

8 DAY WATER IMMERSION TEST

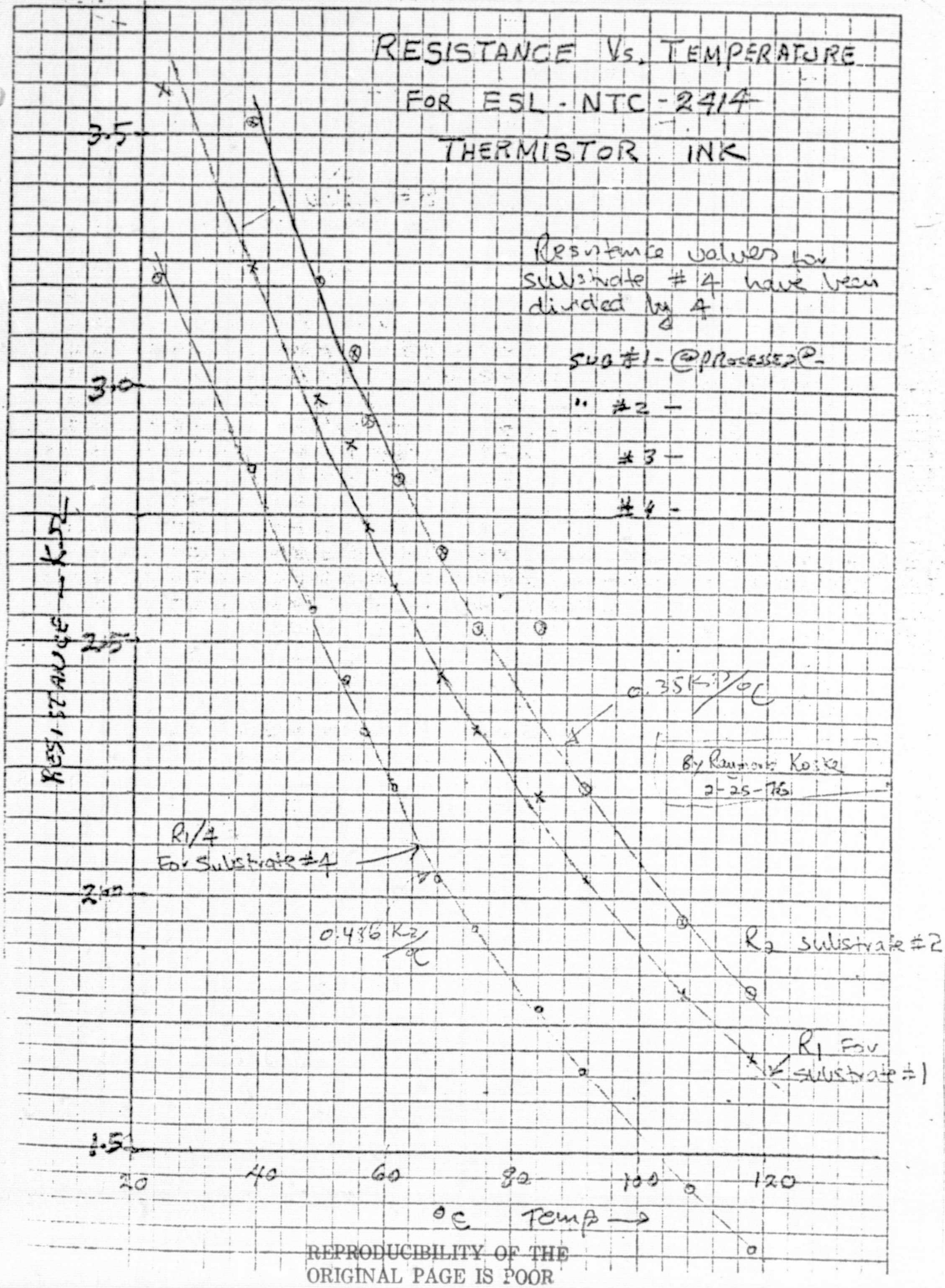
PERCENTAGE CHANGE IN RESISTANCE

Sub. 64 in distilled water
Sub. 63 in tap water

Substrate	Minimum Change		Maximum Change		Average Change	
	Wet	Dry	Wet	Dry	Wet	Dry
NB21-63	0.07	0.03	0.24	0.14	0.15	0.10
NB21-64	0.07	0.02	0.24	0.24	0.17	0.10
NB41-63	-0-	0.02	-0.3	-0.35	0.04	0.04
NB41-64	0.1	0.06	0.2	0.25	0.16	0.16
NB53-63	-0-	-0.08	-20.7	-20.71	-4.2	-4.24
NB53-64	0.1	0.09	0.2	1.02	0.1	0.33
EM13-63	0.2	0.18	0.3	0.32	0.24	0.23
EM13-64	0.2	0.20	0.3	0.29	0.24	0.23
EM15-63	-0-	-0.02	-20.6	-20.62	-4.1	-4.18
EM15-64	-0-	2.67	-0.2	5.78	-0-	4.54
EM16-63		0.06	-48.5	-48.48	-9.72	-9.24
EM16-64	0.2	1.78	-71.6	-71.62	-30.7	-29.66
ES13-63	-0.6	0.18	18.0	0.24	2.6	0.20
ES13-64	0.2	0.18	0.5	0.51	0.16	0.25
ES15-63	-0-	-0.02	0.3	0.52	0.12	0.10
ES15-64	-0-	0.06	0.2	0.33	0.10	0.20
TF00-63	-0-	-0-	0.1	-0.08	0.06	-0.03
TF00-64	0.1	-0-	0.3	-0.16	0.2	-0.05
TF02-63	-0-	-0.07	0.2	1.09	0.16	0.32
TF02-64	0.2	0.18	0.2	0.24	0.2	0.20
TF04-63	-0-	-0.02	0.2	+0.62	0.08	0.13
TF04-64	-0-	-0.25	0.1	-0.47	0.02	-0.37

Electro - Science Laboratories NTC - 2414 Thermistor Glaze Composition

This thick film screen printable ink was designed for making thermistor films on ceramic substrates and firing in air in a tunnel kilm at 900 to 1000 C. Its nominal sheet resistivity is 10 K ohms/sq.; batch variation of ±20% and a TCR of -7000 ppm/degree C between 25 and 125 degrees C. Samples were screen printed, dried and fired using the resistor-conductor pattern on page 15. Results of a temperature - resistance test are shown on the following page. The samples turned out to be fairly linear and repeatable as shown by the almost parallel plots made for resistors of varying nominal values and taken from different substrates. Samples were found to have resistance stability (relative to drift) comparable to that of economical thick film resistors.


RESISTANCE Vs. TEMPERATURE
FOR ESL-NTC-2414
THERMISTOR INK
Resistance values for substrate #4 have been divided by 4
SUB #1 - @processed@ -
" #2 -
#3 -
#4 -
0.35 KΩ/°C
By Raymond Koike
2-25-76
R1/4
For Substrate #4
0.486 KΩ/°C
R2 substrate #2
R1 For substrate #1
RESISTANCE - KΩ
3.5
3.0
2.5
2.0
1.5
20
40
60
80
100
120
°C Temp

II. METALLIC OXIDE STUDIES AND TESTS

Experimental studies on the electrochemical properties of copper and vanadium oxides in powder, crystalline and in thick film screen printable form were conducted.

Commercial grades of CuO, Cu_2O and V_2O_5 (Fisher Scientific Company) in anhydrous powder form were used in these studies. A hydraulic press was employed in pressure tests and to make compressed disc samples some of which were subsequently sintered. These samples were tested in both sintered and unsintered form, unencapsulated and encapsulated in commercial encapsulants.

Special plexiglass and bakelite sample holders were constructed to facilitate studies of the oxides at low pressures. The V-5, vanadic acid technical grade and V-7, certified V_2O_5 were heat treated to form vanadium oxide polycrystals which had well defined geometrical configurations as revealed by microscopic and micrographic study. Sintered and crystalline samples were mounted on alumina substrates and thick film conductive inks were used to make terminal connections for obtaining electrical characteristics. Resistance dependence on pressure, temperature and moisture as well as static and dynamic volt-ampere characteristics were determined for the various samples.

Charge storage and internal voltages up to 0.3 v were observed in wet oxide samples, [B8] some supplied over 50 microamperes to external loads. Electrolysis test demonstrated that thin films of copper oxides could be deposited on copper electrodes at low temperatures.

Vanadium pentoxide and copper oxides were mixed with other chemicals, glass frit, etc., and heat processed in inert and reducing atmospheres to produce screen printable thick films and devices on which resistance-temperature, dynamic and static volt-ampere, and pulse tests were performed. X-ray diffraction data was complied on major constituents used, in an effort to identify internal changes which might be responsible for the switching characteristics observed.

Thick films were made using various mixtures of, vanadium pentoxide cupric and cuprous oxides with barium resistive and conductive vehicles and thinners, etc. Much time was spent on running and evaluating temperature-resistance tests, static and dynamic volt-ampere and pulse tests, designing, and testing circuits using metallic oxide elements to investigate the switching, sensing and memore characteristics exhibited, with a view to applications in these areas. Extensive literature searches were made to obtain information on research results obtained by others especially at other Universitv and Industrial libraries. The International Symposium on Electronic Properties and Applications of Oxides which was held at Purdue University on May 29 - June 1, 1974 which was attended by Mr. D. N. Patel and Professor Leo Williams, Jr., proved to be a source of much pertinent information in the form of research paper presentations. (30, 31, 32)

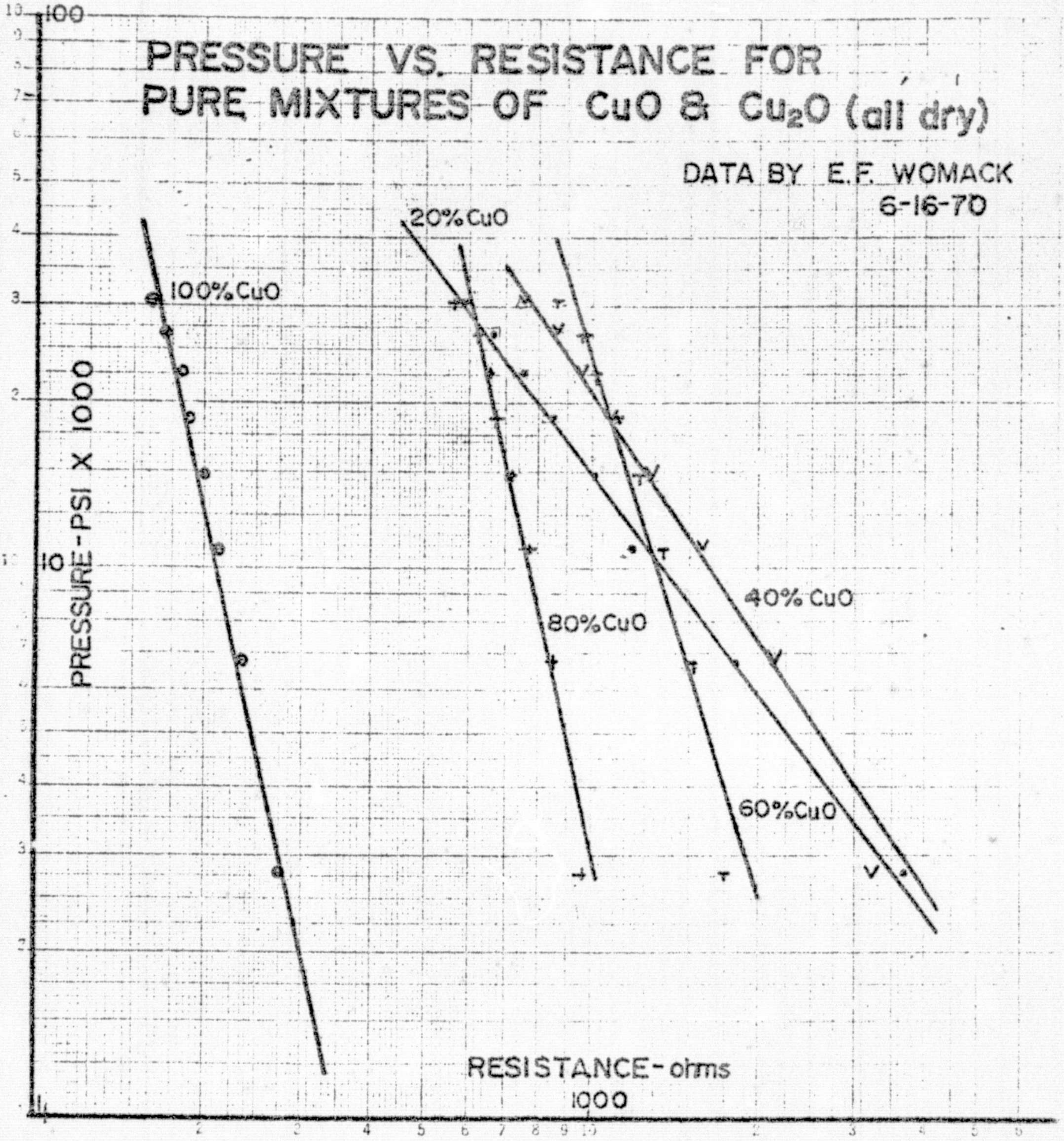
Pressure Vs. Resistance Tests on Oxides

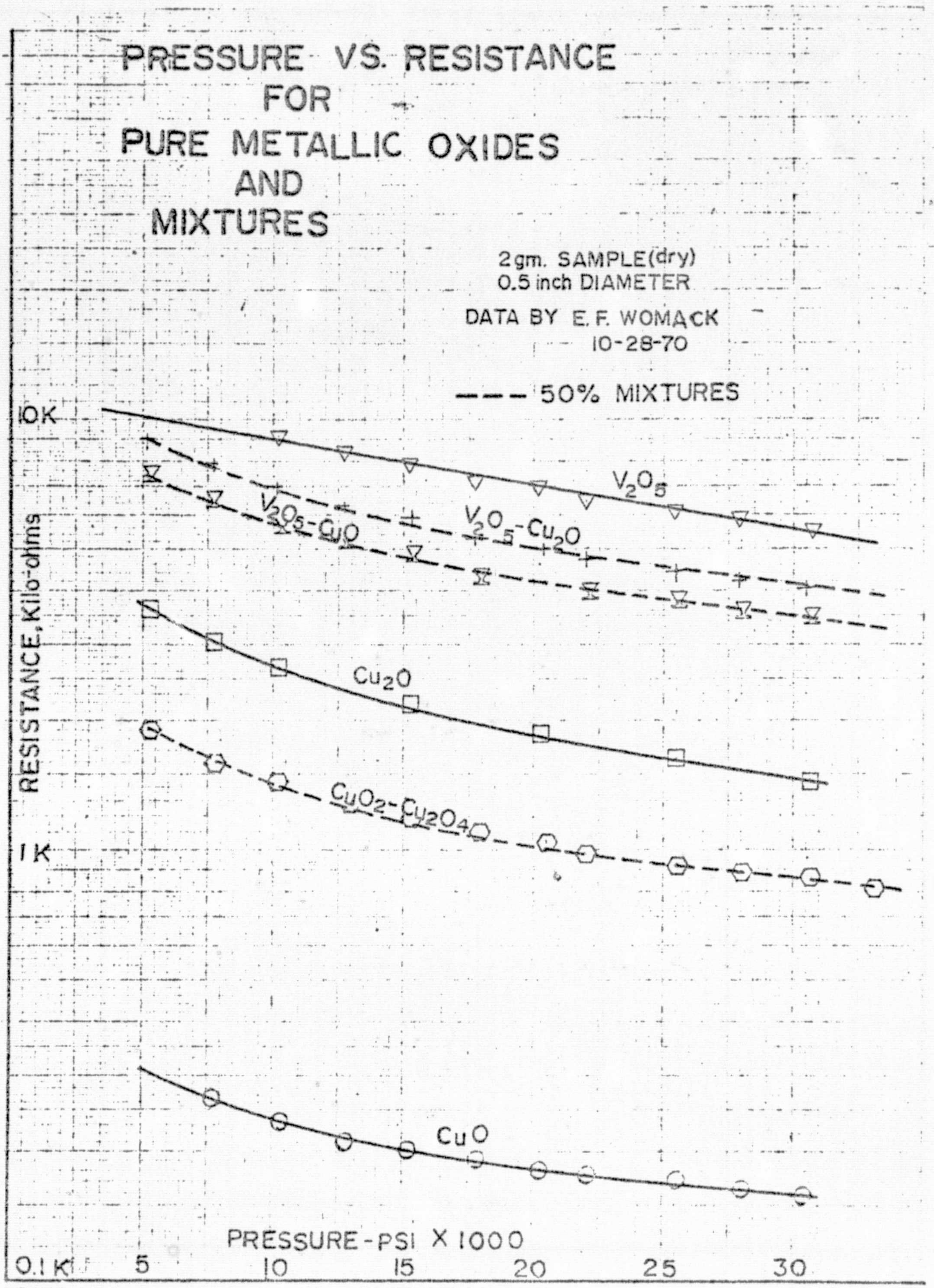
Measured weights of the untreated oxide powders were compressed in cylindrical configuration at pressures up to 30,000 psi and bulk resistivity measurements were made as the pressure was varied. For purposes of comparison, bulk resistivity is herein defined as the resistance of a given weight of oxide compressed in a specified geometry with constant cross-sectional area perpendicular to the axis of compression. For monotonic increases or decreases in pressure the curves were regular but shifted for each pressure run, the shift being an unknown function of previous pressure functitonal history. Test results are shown on the following pages.

Compressed oxide discs were encapsulated in various commercial epoxies so that more stable volt-ampere and resistance curves could be obtained. The resistance of one such sample encapsulated in Stycast 2651 was monitored as external compressive forces were applied to it. The results of applying monotonic increasing and decreasing forces on this sample are shown on page 30. Although hysteresis effects are in evidence, a large range of linearity exists. The axis of compression was known to be non perpendicular to the flat surface of the encapsulated disc, a fact which could account for some of the irregularity. These studies and tests suggest that these semiconductor materials could have possible applications in making economical pressure and/or force transducers.

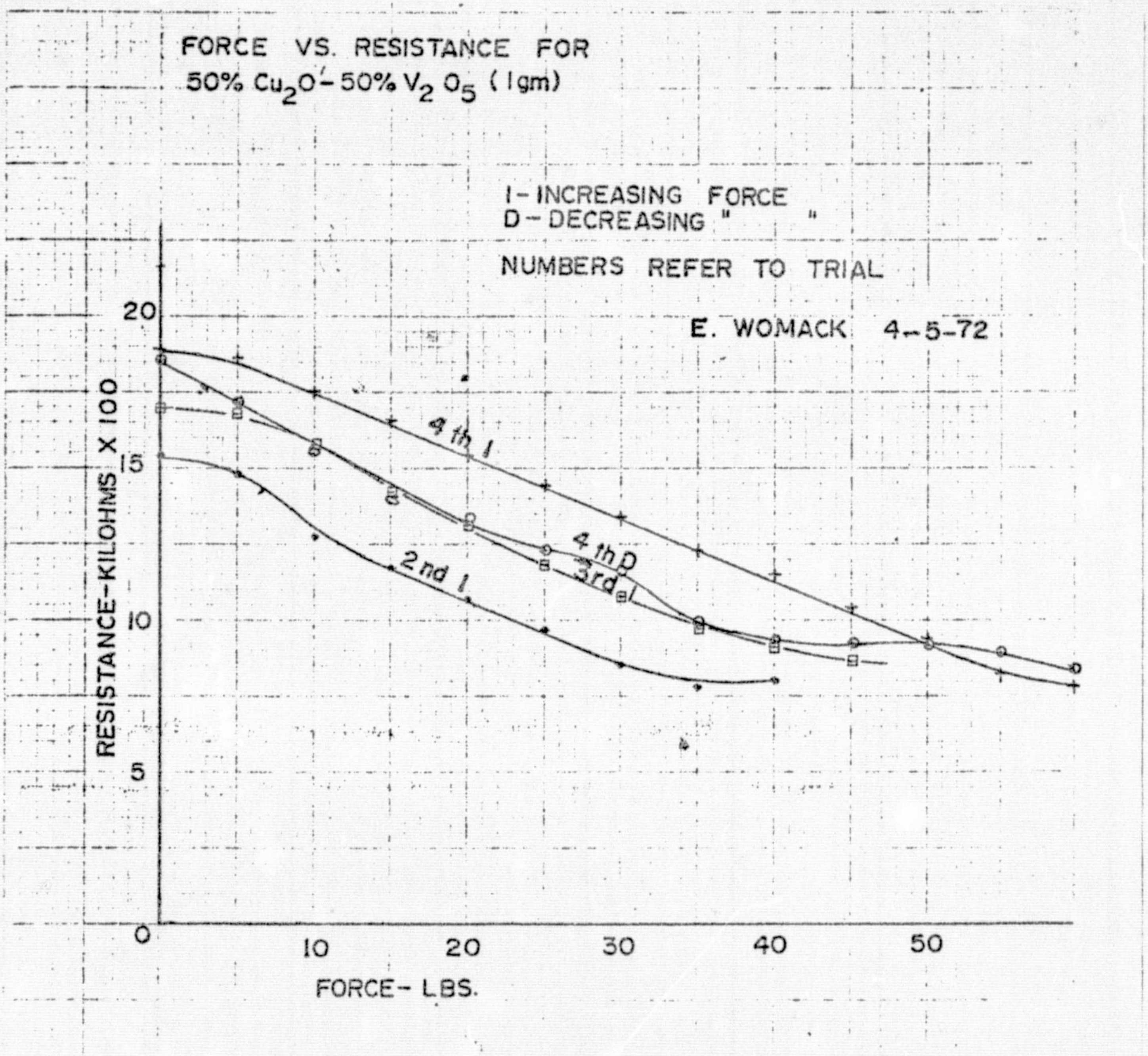
Sintered Oxide Samples

Sintered oxide samples were made by compressing the powdered oxide into the form of discs; placing the discs in a quartz tube, evacuating the air, and sealing the tube with a torch. The quartz tube was then placed in a furnace and brought up to a temperature just below the melting point of the oxide and allowed to remain at this temperature for about 72 hours or longer. The resulting samples were hard enough so that conductive paste could be applied to the flat surfaces, cured, and leads were attached by soldering. Some of these samples were sliced and cut into smaller rectangles and mounted on alumina

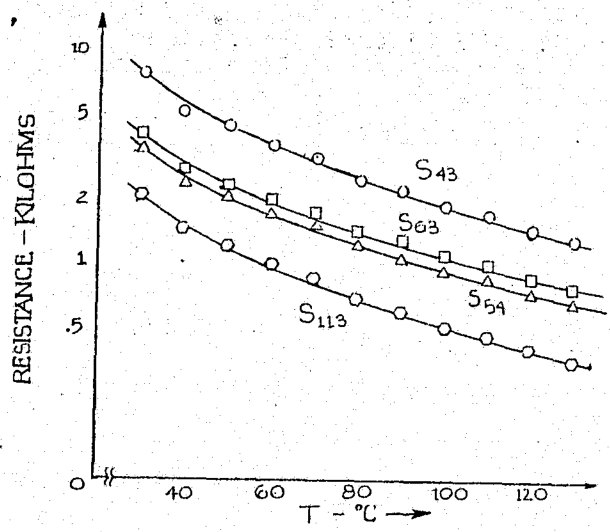

PRESSURE VS. RESISTANCE FOR
PURE MIXTURES OF CuO & Cu2O (all dry)
DATA BY E.F. WOMACK
6-16-70
20% CuO
100% CuO
40% CuO
80% CuO
60% CuO
PRESSURE - PSI X 1000
RESISTANCE - ohms
100
10
1000


PRESSURE VS. RESISTANCE
FOR
PURE METALLIC OXIDES
AND
MIXTURES
2gm. SAMPLE(dry)
0.5 inch DIAMETER
DATA BY E.F. WOMACK
10-28-70
50% MIXTURES
10K
1K
0.1K
RESISTANCE, Kilo-ohms
V2O5
V2O5-Cu2O
V2O5-CuO
Cu2O
CuO2-Cu2O4
CuO
PRESSURE-PSI X 1000
5
10
15
20
25
30

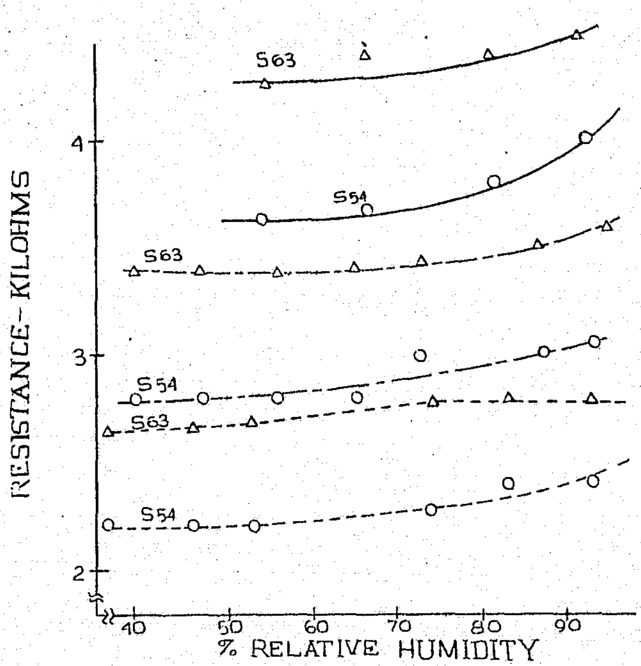
substrates on which suitable thick film conductors had been previously screened and fired to make electrical contact with the oxide samples.



Temperature Vs. resistance tests were made on various sintered oxide samples. High resistance samples showed hysteresis effects while those with lower resistance did not show this effect and the data was also repeatable. Resistance varied with temperature in much the same way as it did with pressure on the powdered samples. This variation with temperature is typical with many semiconductors. Resistance Vs. humidity tests were also run on these samples. Representative curves are shown below. From a consideration of these curves it is clear that resistive samples could be made to be temperature and/or moisture sensative or to compensate for these two variables.



-TEMPERATURE VS RESISTANCE FOR SINTERED V_2O_5 SAMPLES

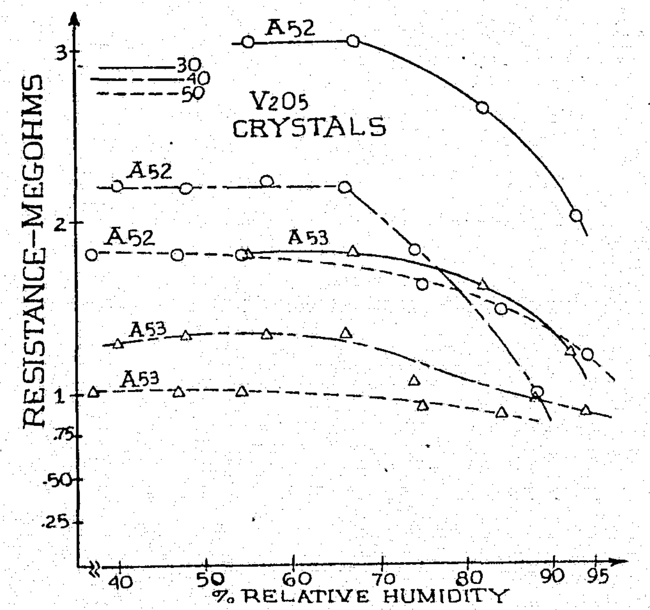


EFFECT OF HUMIDITY ON SINTERED V_2O_5

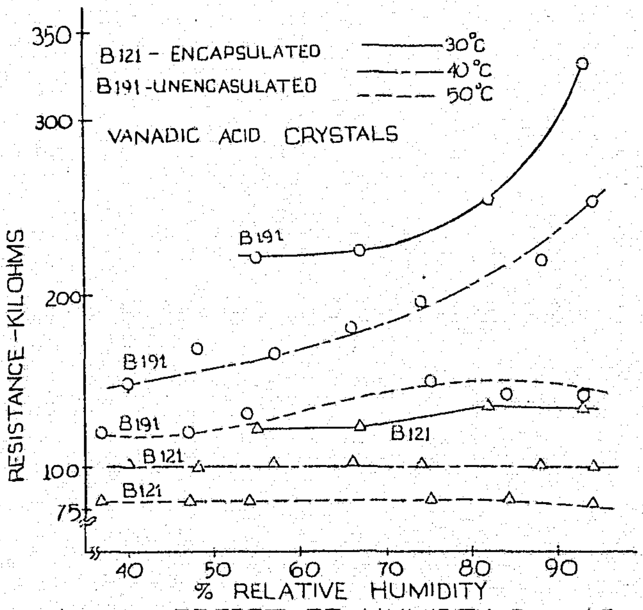
Vanadium Oxide Crystals

Vanadium oxide polycrystals were made using both V-5 and V-7 vanadium pentoxide. The V-5 crystals were darker and bluish in color while the V-7 crystals varied from brownish yellow to a burnish copper color. These crystals were produced by placing a sample of V_2O_5 powder in a covered non-porous crucible and heating a 200 degrees C/hour to 650 degrees. After maintaining the peak temperature for about five to ten minutes the furnace was turned off and the sample allowed to cool slowly to a room temperature (over a period of 17 to 19 hours.) The resulting crystals were needle shaped, some were flat, extremely thin rectangles, others were laminated, etc. A desired crystal configuration could easily be "mined" from the conglomerate with the aid of a microscope. Test samples were made by selecting the desired crystal shape and size, placing them on alumina substrates between pre fired thick film conductors and using a low temperature cure conductive ink to complete electrical connections.

The resistance of a V-7 crystal decreases with increasing relative humidity at constant temperature in contradistinction to sintered samples. The curves below reflect the combined effect on temperature and humidity on the resistance of V-7 and V-5 type crystals.



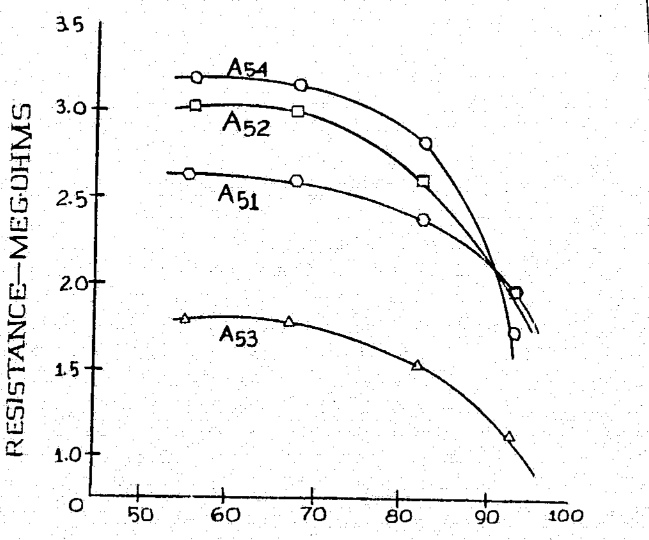
-RESISTANCE VS. RELATIVE HUMIDITY FOR V-7 CRYSTALS



-EFFECT OF HUMIDITY ON V-5 CRYSTALS

Sample B-121 was encapsulated by spraying on a thin coating of sears clear acrylic containing alkyd resin and methylene chloride, which made it essentially non responsive to humidity, especially above 40 degrees. The curves suggest that a suitable encapsulant could be used to produce a temperature sensor which would be effective in a highly humid environment without loss of sensitivity, i.e., if used as a thermistor element, this crystal would have a sensitivity of 2000 ohms per degree. Since sample B-191 is not encapsulated its resistance is responsive to moisture. Thus the two crystals could be employed in combination to sense moisture and temperature at the same time. An example of relative humidity Vs. resistance at constant temperature as well as resistance-temperature variations are depicted below.

Notable resistance transitions took place in specific temperature ranges for all of the V-5 crystals. Data taken at increasing, decreasing and random temperatures showed all of these curves to be repeatable. Most of the references listed in this report describe resistance anomalies in vanadium oxide single crystals which are insulator to metal transitions e.g., in VO_2, V_2O_3 and VO but only one such transition falls within the temperature range considered herein (this is for VO_2 with a transition temperature of about 68 degrees C the others occur at -105 and -150 degrees C respectively). Futaki[25] has described a critical temperature resistor based on sintered mixtures of V_2O_5 and other acidic or basic oxides, but here again all transitions occur within a 60 to 75 degree temperature range. Obviously these crystals could be employed in applications in critical temperature sensing and automatic control circuits.



RESPONSE OF V-7 CRYSTALS TO HUMIDITY AT CONSTANT TEMPERATURE

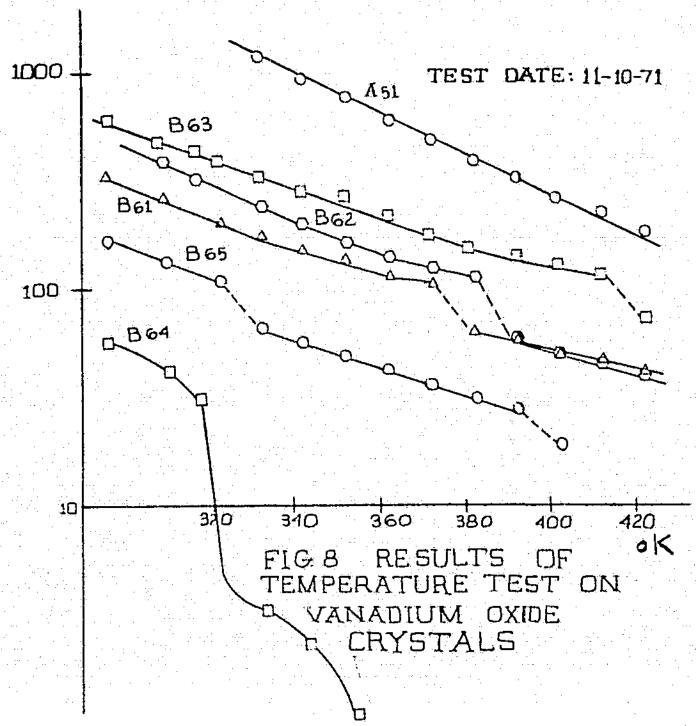
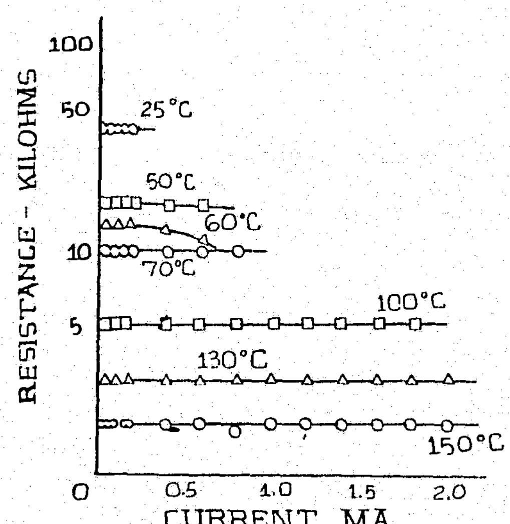


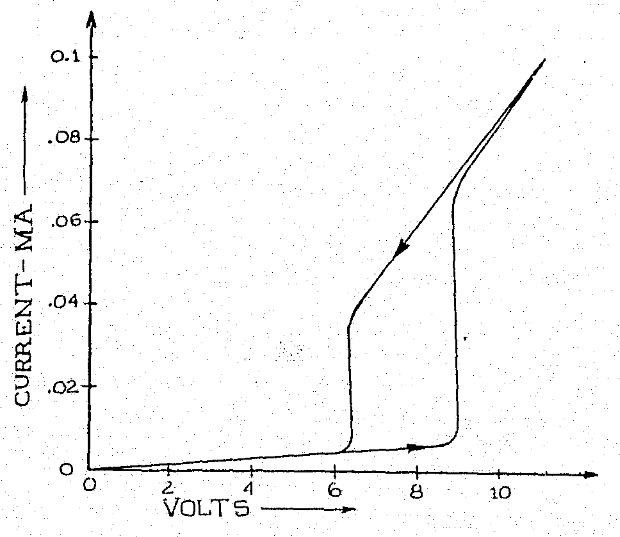
FIG 8 RESULTS OF TEMPERATURE TEST ON VANADIUM OXIDE CRYSTALS

The results of a dynamic volt-ampere test on crystal B-65 conducted at room temperature is shown below. The crystal shows a bistable switching characteristic, as could be expected in the light of the temperature - resistance data already considered, and also shows a hint of negative resistance during the switching phase. It switched from a resistance of 900 K ohms below 9 volts to about 70 K ohms above this voltage. Subsequent pulse tests showed the switching time to be in the microsecond range. Cope and Penn[26] have reported switching times as low as 0.02 microsecond in fused oxide mixtures containing vanadium pentoxide. Because of the small size and low switching power (of the order of 0.01 inch and 0.1 milliwatt) for this crystal, its use as a memory element in the computer industry is suggested.

Type V-7 crystals were pulverized, mixed with V_2O_5 and organic binders, compressed in the form of a disc, heat treated to remove the binder and leads were attached as previously outlined to form sample "I". This sample was placed in the temperature chamber to observe a current - resistance dependency using temperature as a parameter. The results of this test are presented on the left below and shows that the resistance of the sample is insensitive to current except in the vicinity of 60 degrees C. This type of element could be used as a feedback and/or input resistive element in operational amplifiers to control or vary the gain in accord with a temperature function or as a nonlinear function generator in analog computer or simulation circuits.

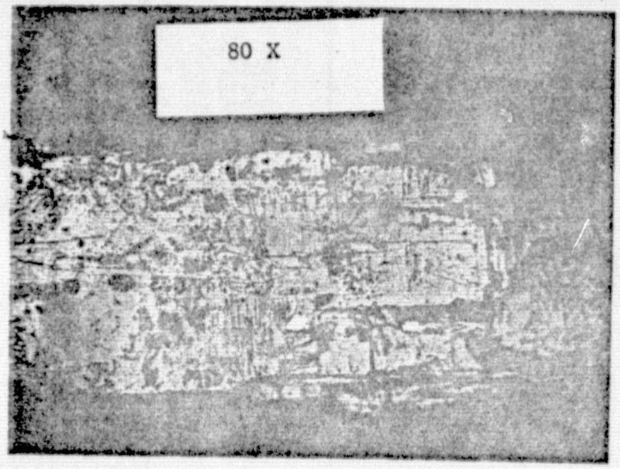


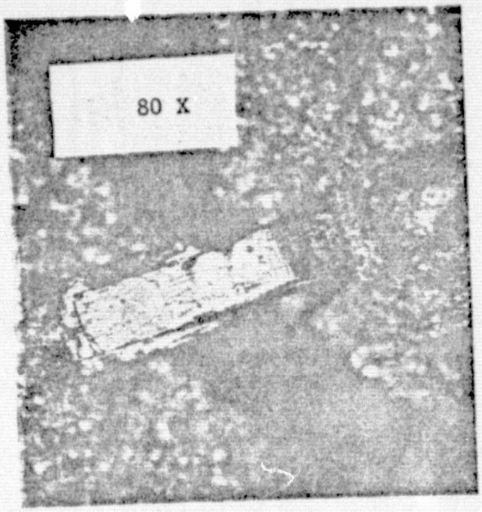
CURRENT VS. RESISTANCE
CURVES FOR V_2O_5 CRYSTAL MIXTURE

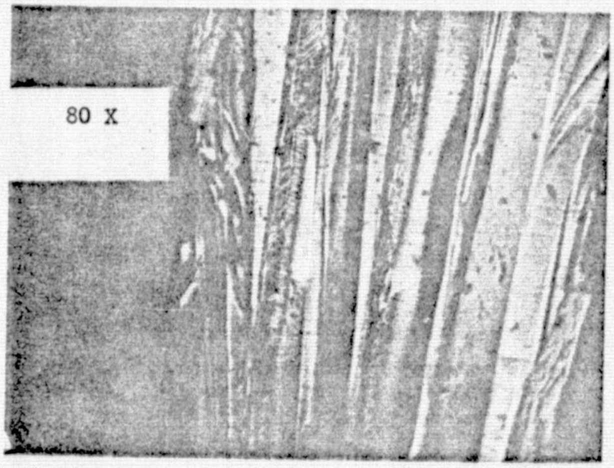


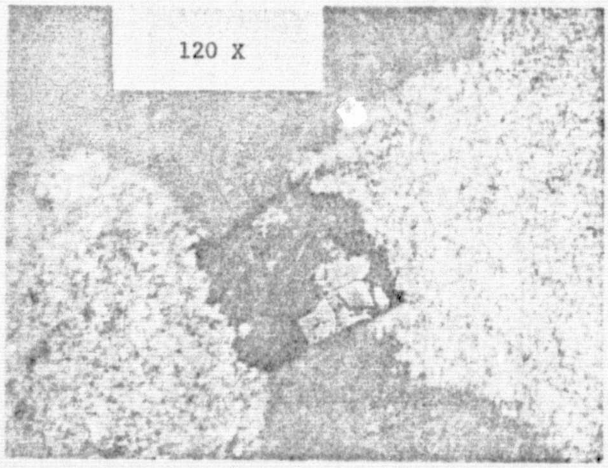
: DYNAMIC VOLT - AMPERE CURVE
FOR VANADIUM OXIDE CRYSTAL B-65

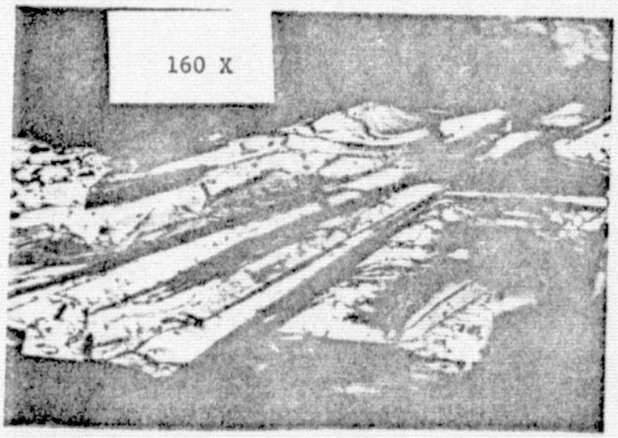
Micrographs showing the various crystal geometries, and thick film terminations on alumina substrates are presented below.

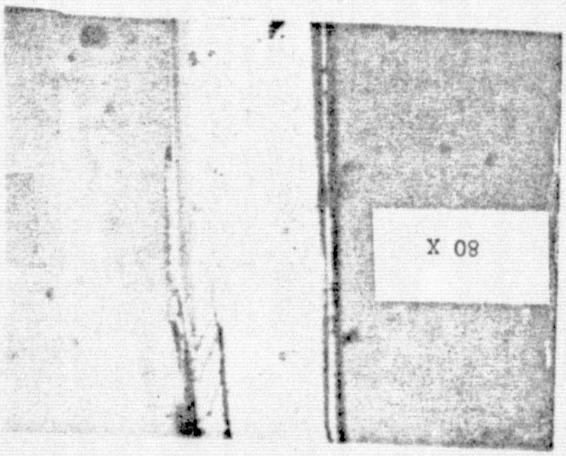




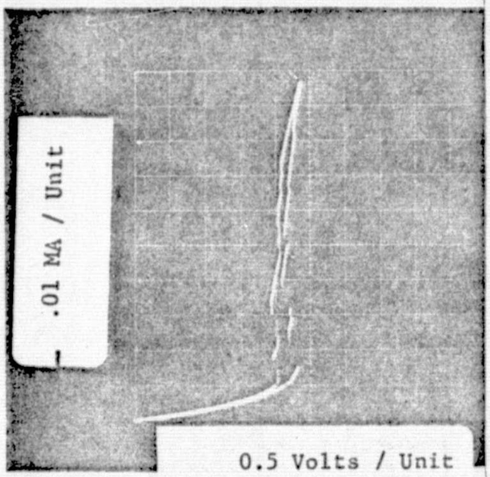


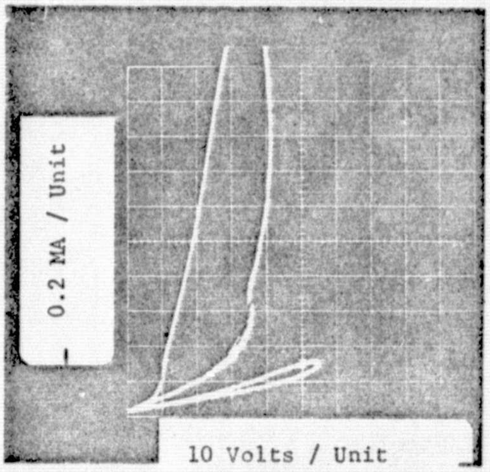


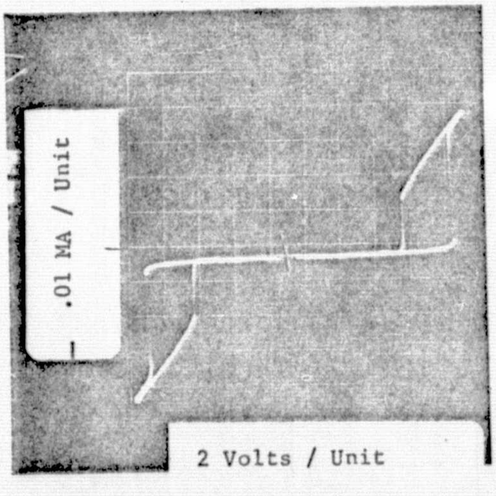


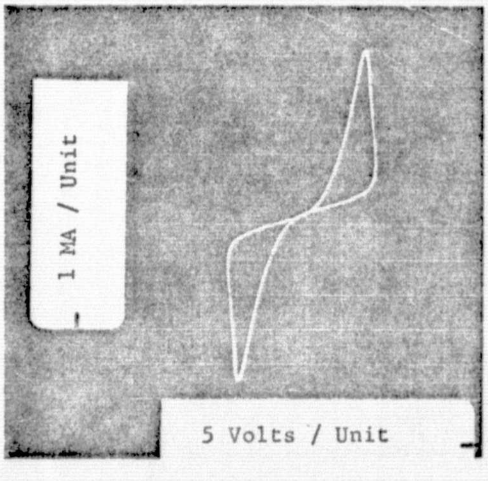


The following oscillograms are representative of dynamic volt-ampere characteristics for vanadium oxide crystals.









Thick Film Metallic Oxide Switching Devices[6, 25-27, 31, 33, 34]

The crystals described did not lend themselves to practical processing of devices since much time was required in selecting, and mounting specimen with the characteristics of interest. Research efforts were therefore aimed at using thick film techniques to make repeatable switching devices for study and applications. For the most part suggested materials and methods of preparation based upon Futaki's paper[25] were used in making the devices to be described hereafter. All materials were ground in a micromill and combined with ESL type 405 conductive vehicle and suitable thinners to make a paste, or ink suitable for thick film printing and applied to 1 inch square alumina substrates. Processing involved heat treatment at varying temperatures up to 1000 degrees C in vacuum, argon, reducing atmospheres and air. A gold or silver conductive ink was screen printed and fired on the substrates to facilitate electrical termination of samples. The switching materials were applied by hand between printed conductors, between platinum wires, and by screen printing. Although a large variety of mixtures were processed and tested the three major types consisted of (1) one basic oxide, (2) two basic oxides i.e., binary mixtures and (3) ternary mixtures consisting of three basic types of materials, at least two of which were metallic oxides.

Selected resistance-temperature curves for the various samples are designated as figures 2 through 5 on the following page. Fig. 6 shows similar test results on a new vanadium oxide - based thick film switching ink, Tyox 9253 which is also screen printable and recently placed on the market E. I. Dupont De Nemours & Co. It is included here for comparative purposes.

Resistance anamolies occurred at various temperatures between 50 and 100 degrees C depending upon composition and processing conditions and both positive and negative transitions occurred as evidenced by these curves.

Static and dynamic volt-ampere characteristics were obtained for the various samples and are indicated in Figs. 7 to 10. The static voltages required to switch these devices varied from about 6 to 30 volts, but the dynamic voltages ranged from two to about five times the corresponding static voltage. All samples were bilaterial and all tests were performed at room temperature.

The power required for switching these devices can be approximated from the V-I curves to be in the order of milli-

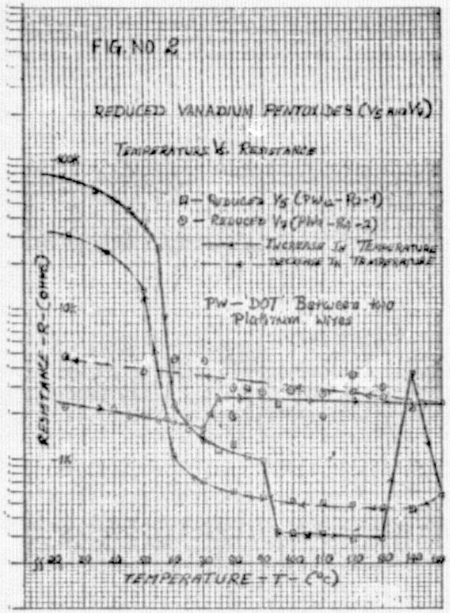


Fig. 2 Resistance-Temperature curves for V-5 and V-7 type vanadium pentoxide "PW" samples which were processed in a reducing atmosphere.

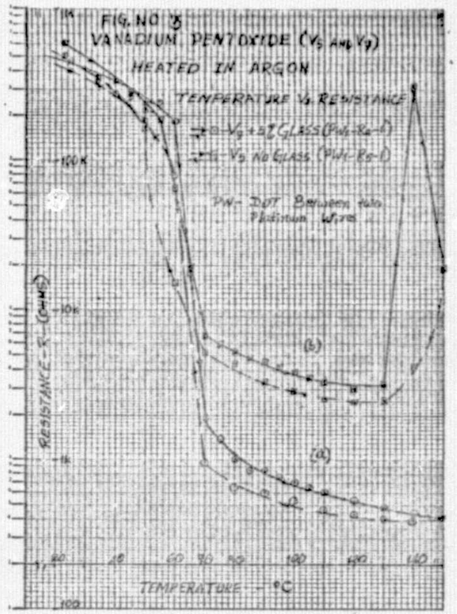


Fig. 3 Resistance-Temperature curves for "PW" vanadium pentoxide samples processed in an argon atmosphere. (a) V-7 mixed with 5% borosilicate glass (b) V-5 without glass.

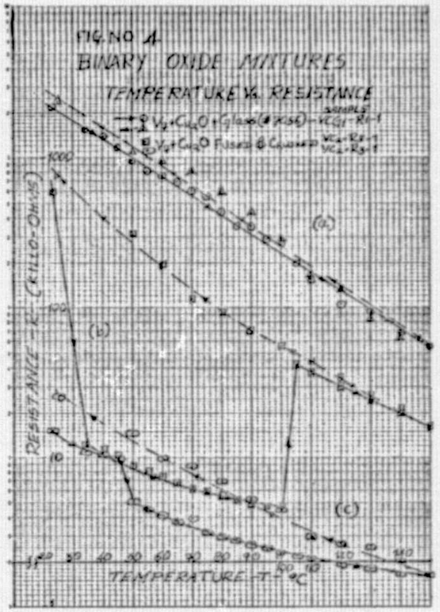


Fig. 4 Temperature-Resistance curves for mixtures of type V-7 vanadium pentoxide and cuprous oxide (a) with glass, (b) and (c) without glass

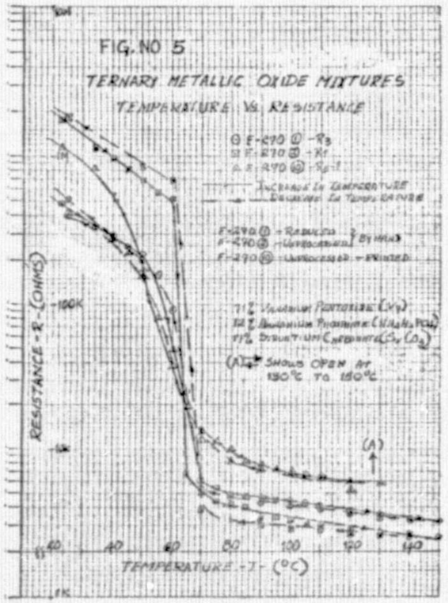


Fig. 5 Temperature charateristics of ternary mixtures (vanadium pentoxide, strontium carbonate and ammonium phosphate). Materials were applied to the substrate by hand and by screen printing.

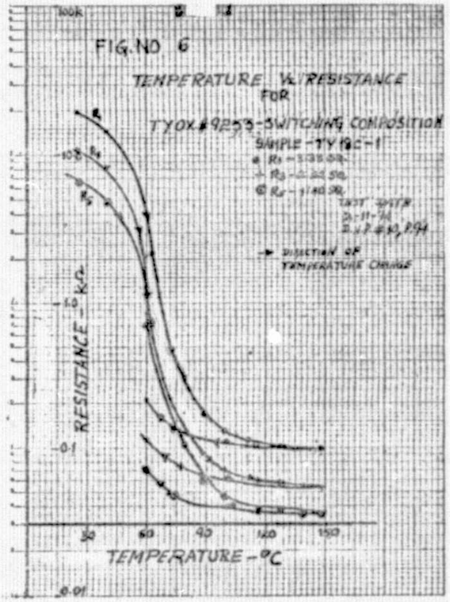
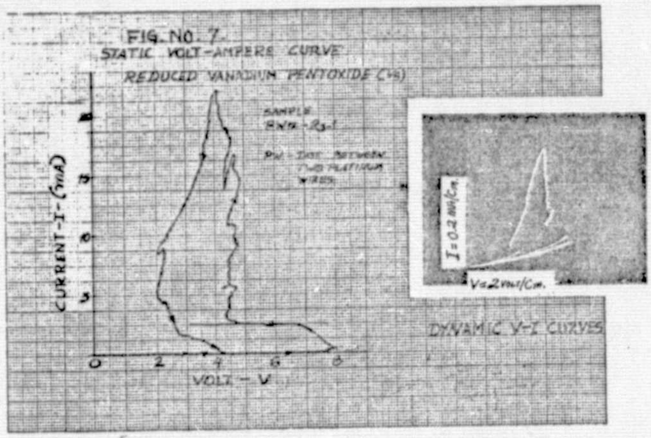
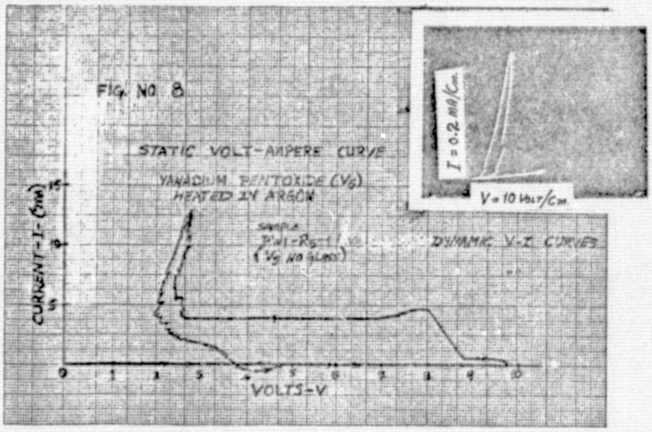
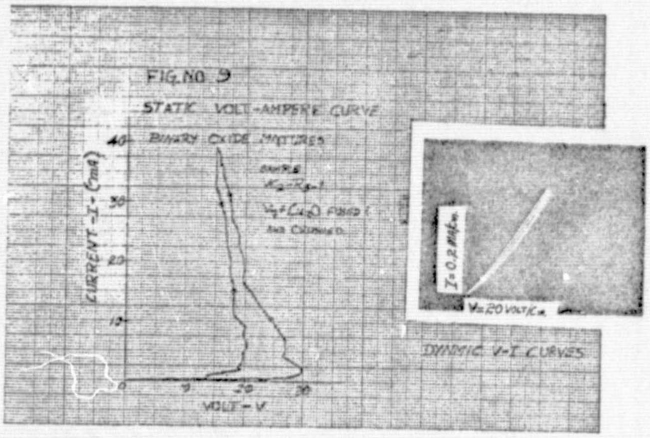


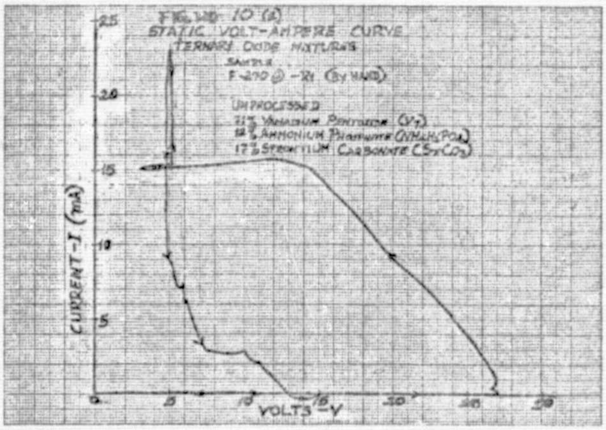
Fig. 6 Temperature - Resistance characteristics for three samples of Tyox 9253 switching composition screen printed and fired on a 96% alumina substrate.

watts and is a function of thermal conductivities of the oxide materials, terminals, the substrate and the immediate environment, etc. Switching power can be reduced by incorporating thermal bias circuits as well as decreasing the size of the devices. Switching time varied from a millisecond or less for the single oxide system to a microsecond or less for the ternary samples as indicated in the pulse tests.

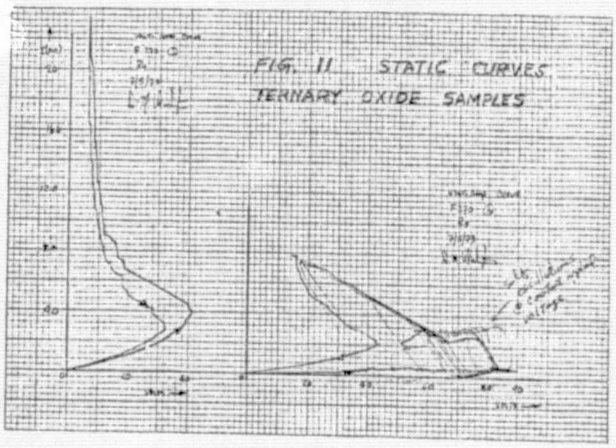








The self oscillatory nature of some of the devices is indicated in Fig.11. This was a type "F270" ternary device which spontaneously went into self oscillation while its static curve was being recorded on an X-Y plotter as shown on the right side of the figure. This phenomenon suggests the use of these devices in oscillator circuits as will be shown later.



Pulse test wave forms for the "F270" device whose thermal characteristic is given in Fig. 5 is also indicated in Fig. 12 on the right. The test was performed at room temperature without thermal bias and indicates a switching time of 3 microseconds. The minimum energy required for switching was calculated to be in the order of 10^{-7} joule. Switching times and energies in these ranges suggest that the switching mechanism could be induced by strong electric field strengths coupled with thermal effects. Other researchers[5] who observed comparable switching times using similar materials, have advanced a theoretical explanation based on thermal considerations.

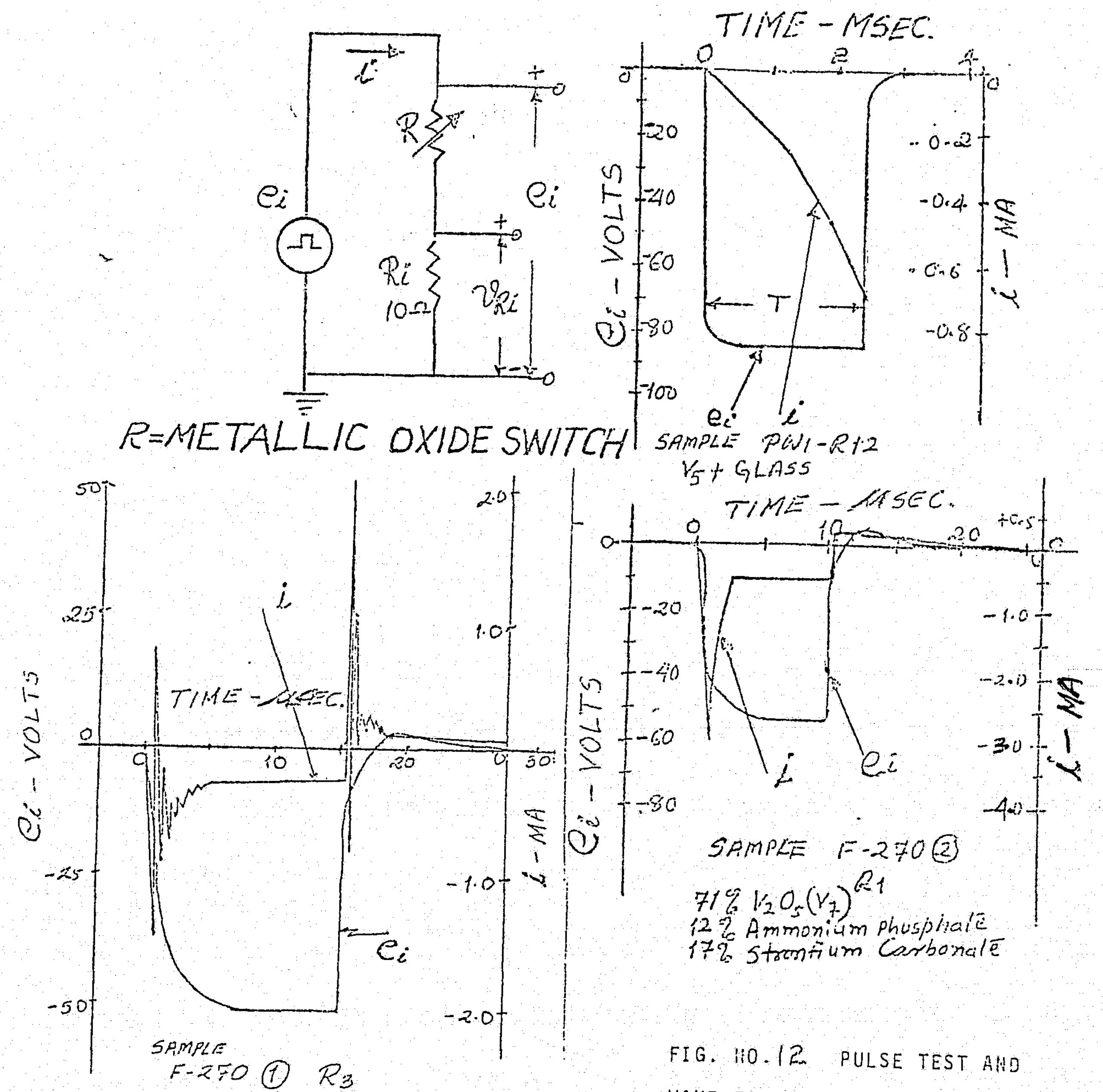
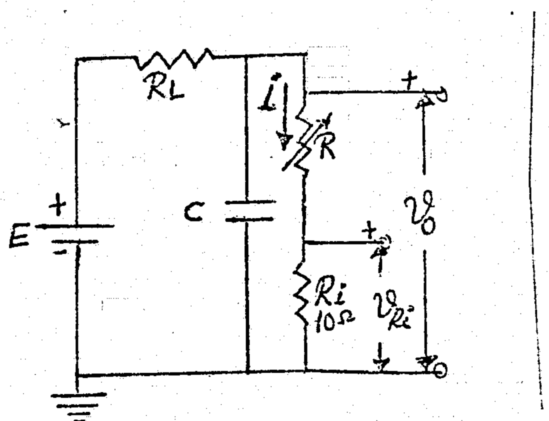


FIG. NO. 12 PULSE TEST AND WAVE FORMS FOR METALLIC OXIDE SWITCHES

Oscillator Applications

Both high and low frequency oscillator applications of these devices are possible as indicated by the negative resistance type self oscillations presented in Fig. 11 and the high frequency "ringing" indicated by sample F270-1-R3 in Fig. 12. This sample is equivalent to a high frequency "tank" circuit. Although the oscillations were not sustained in these cases there is evidence that the necessary conditions for sustained oscillations could be met by proper circuit design and more accurate ambient temperature control. The experimental relaxation oscillator circuit shown in Fig. 13 was set up using a single oxide system device which gave reliable sustained oscillations at frequencies ranging from 2.0 Hz. to 100 Hz. by varying the value of the capacitor.



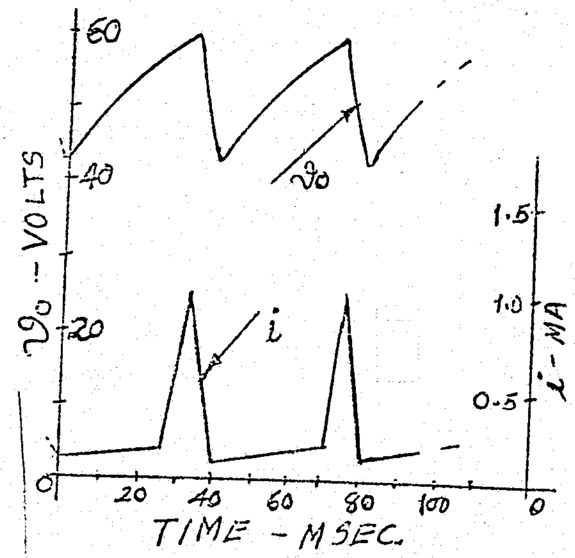


Fig.13 Relaxation oscillator circuit and wave forms. R is the metallic oxide switch, sample PW1-R51 consisting of V-5 processed in an argon atmosphere.

This Research effort has proven that pratical metallic oxide switches may be processed using thick film technology. Critical switching temperatures from 30 to 130 degrees C were observed. Applications of these devices in logic and switching circuits, memory elements and oscillators are apparent. Because these devices can be made extremely small, require milliwatt to microwatt switching power with switching times in the order of a microsecond or less at voltages from 10 to 150 volts, they could be readily used in the hybrid microelectronics industry.

III. X - RAY DIFFRACTION STUDIES[B11, 13]

X-Ray diffraction studies were made on thick film resistor samples and metallic oxide materials to ascertain structure and possible chemical transitions which might account for some of the phenomena observed. Drs. Donald A. Edwards and Jason Gilchrist of the Physics Department assisted by students laboratory assistants majoring in physics and electrical engineering did the bulk of the work in this area.

Apparatus and General Procedure

Tracings were made using the logarithmic scale of a General Electric XRD-5 Diffractometer. Traces were run at 2 degrees per minute using filtered copper radiation. The powder method was used exclusively, since single crystal equipment was not available.

Some samples were placed in a thermal vacuum chamber, which provided for heating the sample in vacuo up to about 250 degrees C and cooling to liquid nitrogen temperature. Temperature was measured by an iron-constantan thermocouple which was inserted into the rear of the sample holder to a point near the sample. A portable Rubicon precision potentiometer was used to measure the EMF of the thermocouple. Temperature changes were produced by an electrical heater immersed in a silicon oil bath, or by liquid nitrogen when heater and silicone oil were removed. Heat transfer was provided by a copper cylinder to which the sample is attached. At fixed temperatures regulation was provided by a fine-wire copper coil immersed in the oil, the coil being one arm of a bridge circuit which activates an On-Off heater switch.

Some samples were in powder form and placed in bakelite holders. Other samples, with preferred orientation were on Al_2O_3 substrates (99% and 96%).

In general the preparation and heat treatment of samples was done by Mr. Patel, a graduate laboratory assistant involved in resistance measurements under the direction of Professor Williams. This was done so that x-ray samples would be prepared under the same conditions as samples used for resistance measurements. After heat treatment the samples were cooled to room temperature before diffraction patterns were made.

Thick Films At Temperatures Up To 1100 Degrees C

Thick films of Birox (1021, 1031, 1041, 1051, 1053) were screen-printed on substrate. X-ray traces were made at room temperature of the samples, some of which had been dried at 150 degrees C and others which had been fired to peak temperatures of 750, 775, 800, 825, 850 degrees C. X-ray traces were made at room temperature of another group of Birox films which were dried and fired at 1100 degrees C in the Thermolyne box furnace.

Since the samples were on substrate, preferred orientation was present. As a result of heating, changes occurred in line positions and in intensities. A major change in structures was indicated when heated to 1100 degrees C.

When diffractometer tracings were arranged in order of increasing resistance (1021, 1031, 1041, 1051, 1053) comparison of one with another showed progressive changes which might be indicative of structure changes.

When arranged as described above, before firing (after drying at 150 degrees), a visual examination showed: (1) no change in line positions for the group; (2) a progressive decrease in some line intensities; (3) the area of a broad hump underneath lines of the region 25 - 35 degrees two-theta showed a decrease. After heating to 850 degrees C a visual examination showed: (1) no change in line positions; (2) no obvious progressive change in intensities. Since line positions did not change, there was no change in unit cell dimensions or type as we go from 1021 to 1053. Intensity changes indicated a rearrangement of atoms within the unit cell. If the lines could be indexed correctly, the nature of the rearrangement might be determined.

Other comparisons were made of the traces of the same ink before and after heating. Traces made after firing at 850 degrees C were compared with traces of the same ink made after drying at 150 degrees C. Visual inspection showed no significant changes for 1021, 1031, and 1041. Traces which showed significant changes in intensities of lines, but not in line positions, were made from 1051 and 1053. Traces made of 1021 after firing at 1100 degrees C were compared with those made from the same ink after drying at 150 degrees C. For 1021 new lines appeared, intensities were altered, so that a decided change in structure was indicated. A visual examination of the other inks indicated that they too had experienced a change in structure.

After firing at 850 degrees C Birox 1041 was found to have a cubic structure with a = 10.25 kX. The data for this determination is shown in Table 1 (B11). After firing, Birox 1021 was found to have a cubic structure with a = 20.50 kX. A complete determination, with intensity calculations, was not possible, since chemical composition was not known. Attempts to determine the structure of Birox 1041 fired at 1100 degrees C were inconclusive, due perhaps to lack of time remaining.

Effects Of Orientation Of Substrate On X-Ray Pattern

The thick films were on Al_2O_3 substrates, 96% and 99%. Examination of a few initial x-ray traces seemed to indicate that the sample thickness was sufficient to prevent the showing of lines from the substrate. In later work difficulties were encountered because of lines from the substrate were mixed with those of the sample. Assignment of Miller indices was difficult. This led to a study of the substrate lines alone, in order to determine differences in pattern when substrate face was reversed and/or rotated 90, 180, 270 degrees. Also it is possible that the crystal growth of a sample on the substrate, while heating, can be affected by the crystal structure of the substrate itself or by the roughness of the surface. One side of the substrate is smoother than the other; samples are put on the smooth side.

For the smooth side a rotation of 90, 180, 270 degrees showed no clear change of line positions. Intensities of most lines are unaffected. The intensity of the line at 45.0 degrees changes by a factor of 16 when rotated 180 degrees. For the rough side, rotation produced no change in line positions nor in intensities of most lines. Rotation of 90 degrees introduced a line at 65.4 degrees, while a rotation of 180 degrees produced no change.

A comparison of the rough with the smooth side showed that the line at 45 degrees was stronger for the smooth side.

The differences in pattern mentioned above were due to a change in preferred orientation, not in crystal structure. However, indexing difficulties were encountered when substrate lines showed in addition to lines from the sample. Some lines from the sample may coincide with those from the substrate. Also a rotation of sample and substrate may produce a different pattern because of substrate differences. Thus the pattern obtained may depend upon how it was oriented in the x-ray diffractometer.

X-Ray Studies On Metallic Oxide Samples

Vanadic acid, hydride, V-7 is certified by Fisher Scientific Company as V_2O_5 and containing impurities; Fe 0.01%, chloride (Cl) 0.005%. V-5 is the technical grade of V_2O_5 vanadic acid, containing unspecified impurities.

Samples were prepared by grinding the vanadium oxide with mortar and pestle and were packed into bakelite holders.

The x-ray patterns for V-7 and V-5 were found to be different. V-5 showed a line at 7.8 degrees while V-7 did not. This difference did not suggest a doubling of one dimension of the unit cell. Rather it suggested a difference in arrangement of atoms within the unit cell such that a reflection occurs in one case and not in the other. Both showed a broad hump at about 10 - 16 degrees (see Figure 7).

Other samples were mixed with an organic vehicle, screen-printed on substrate, and were dried at 150 degrees C. Data obtained from V-7 after firing at 1360 degrees F were compared with ASTM (American Society for Testing Materials) x-ray data cards for identification purposes. Only V_2O_5 was present after firing. (see table II).

From data for V-7 (after drying at 150 degrees C the unit cell was determined to be orthorhombic with a = 11.55 kX, b = 4.373 kX, c = 3.561 kX. ASTM index values are a = 11.51, b = 3.559, c = 4.371. No calculations of intensity were made, but indices are the same as those in ASTM data.

After firing at 850 degrees C V-5 (sample by Womack) was pulverized with mortar and pestle and placed in regular bakelite holder. The unit cell was determined to be orthorhombic with a = 11.5 kX, b = 7.14 kX, c = 4.36 kX. Thus two of the parameters are essentially the same after firing, while the third parameter was doubled as result of firing. Thus the size of the unit cell has been doubled as a result of the heat treatment. Also the arrangment of atoms within the unit cell has been altered, since the intensities do not now match those of the ASTM Index data.

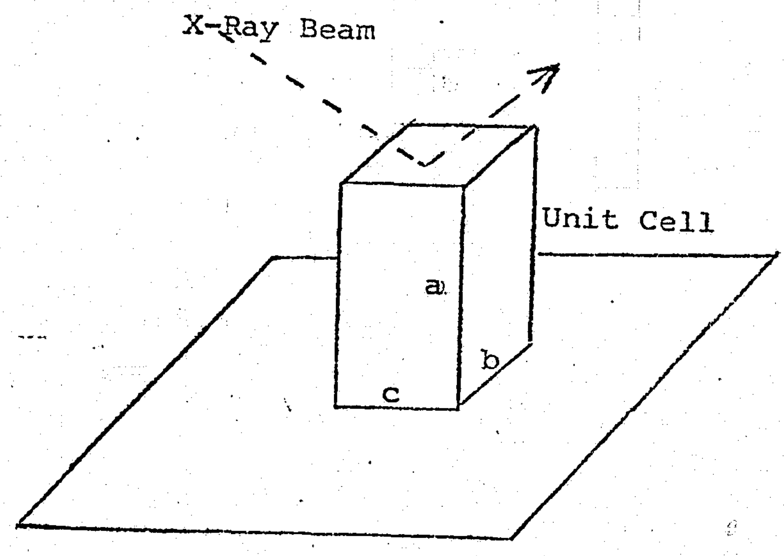
The line at 12.3 degrees, for V-5 after firing at 850 degrees C, is the evidence for the doubled parameter. Previous work by other investigators (reported in ASTM Index related the line at 51.4 degrees to one dimension of the unit cell with a value of about 3.56 kX. The appearance of a line at 12.3 degrees has the effect of doubling this value, since $\sin^2\theta 001$. Both V-7 and V-5 before heating, show a broad hump at about 12 degrees. This hump shows that the doubled parameter is present to some extent before heating, i.e., the smaller unit cells show some tendency to line up in this direction. This is a kind of partial "long range ordering". The heat treatment causes V-5 to have complete alignment or "ordering".

An attempt was made to observe structural changes in V-7 at elevated temperatures. A sample with vehicle 405 and 402 was placed in the x-ray thermal vacuum chamber. Traces of the sample were made on successive days with temperatures held constant at about 72, 114, 138, and 175 degrees C. No changes in pattern were observed. Then the sample was held at 84 degrees C for a week, with traces made every other day. No changes in pattern were observed. Other investigators have reported electrical resistance anomalies within this temperature range.

A study was made of the preferred orientation of V-7 crystals on substrate. Mr. Williams has used single, flat, needle-shaped slabs for making earlier resistance measurements. His measurements were made along the long axis of the flat crystals. Since resistance might well depend upon orientation of the crystal, an attempt was made to determine an average orientation of many flat crystals on substrate in terms of the unit cell.

Lines from V-7 powder were indexed as mentioned above. Another sample was recrystallized on substrate by heating at 1360 degrees F to form many crystals flat against the substrate. When traces of this sample were compared with those from powder, a visual observation of line intensities showed reflections from planes 200, 400, 310, 600 were enhanced, while those from 010, 101, 002, 020 were reduced (as compared with reflections from powder sample). Thus the recrystallization process increased the number of planes parallel to 200, 400, 600.

Next the sample was rotated 90 degrees about the "a" axis. No changes in intensities were observed for 200, 400, 600 reflections. A change in the reflection for 010 was observed. Thus the average orientation for the flat needles is as shown in the figure on page 47. The long axis of the flat crystal is in a plane perpendicular to the "a" axis of the unit cell.



ORIENTATION OF LARGE FLAT CRYSTALS

Actual X-Ray diffraction patterns and data for the results described above may be found in reference B11.

Chemical Analysis Of Materials Used In Oxide Switches

Chemical analyses via x-ray spectroscopy were made of 7 samples:

V_7	Certified V_2O_5
V_5	Non-certified V O
V_5R	Powder reduced by heating up to 1000 degrees F in Argon
V_7R	Compressed V and then reduced
F-270	74% V_7 + 21% $NH_4H_2P\ O_7$ + 5% BaO
F-270R	Reduced by heating
V C	50% V_7 + 50% Cu_2O

All runs were made on NASA XR_D 5 spectrometer. Filtered copper radiation was used. The samples were prepared by grinding with motar and pestle and were packed into bakelite holders. The data from the tracings were reduced by the formula:

$$d = \frac{1.542A}{2 \sin 0} .$$

Data for all of the samples understudy and also for Cu_2O and Bao, which were needed for interpretation, are listed in reference B 13.

V_7 and V_5

The d-values and the normalized intensities were calculated for each sample from the x-ray traces. Comparisons were made with (V_2O_5) 140 from the ASTM index cards and of the observed values of V_7 and V_5 .

Some low intensity lines shown in V_2O_5 ASTM were not present in the V_7 and V_5 traces. Also V_7 had some low d-value lines that are not present in the ASTM index. This indicates that there is another crystalline substance in V_7. With further study it may be possible to determine these substances.

Only the more intense lines of V_2O_5 show up in the V_5 x-ray trace and there is one line unaccounted for d = 1.290 normalized intensity 13.

The x-ray trace of V_5 has a low, relatively even background. It appears that a non-crystalline material is mixed with the V_5 sample.

V_5 R and V_7 R

Some of the more intense lines of V_7R were matched with those of V_5O_7 from the ASTM file, see Table III. Hence V_5O_7 is a component of V_7R. There are several lower d-values that are not accounted for. This may indicate a mixture of vanadium oxides.

F-270 and F-270R

F-270 sample (74% V_7 + 21% NH_4 H_2 PO_4 + 5% BaO) trace was compared to the tracing of V_7 and Bao (a BaO trace was made for this purpose). Most of V_7 lines were accounted for and some of the BaO lines showed up, There were several unmatched lines in F270, notably d = 3.535 A abd 1.565 A. These d-values are probably dut to the NH_4H_2 PO_4. The d-value 3.535 showed up as the maximum in F 270R. If this value is due to NH_4H_2 PO_4, it would mean that the NH_4 H_2 PO_4 has not been altered substantially in the heat treatment. Many of the lines in the F-270R trace are identical to the V_7R lines.

VC.

The trace of the VC sample was compared to the traces of V_7R and Cu_2O (which was made for this purpose). The prominent lines were those of Cu_2O and V_7R. Hence, the V_7 was reduced and much of the copper oxide was not.

IV. CONCLUSIONS

During the course of this research project a laboratory with the capability of evaluating microelectronic components was developed and utilized for this purpose. This lab has provided hands on experience for advanced undergraduates and graduate students in conjunction with a new course in microelectronics which was also developed during this time. Results of evaluation of industrial microelectronic products compare favorably with those obtained in industrial and established research and development centers.

The work done on metallic oxides is significant. It has been demonstrated from studies, experiments, and tests that they can be used as sensors, and as switching and memory devices. A more detailed theoretical and mathematical analysis should be undertaken in order to more fully characterize the materials to gain insight into observed phenomena and thereby establish a better foundation for their possible use in making practical and repeatable devices. A proposal has been submitted to the National Science Foundation which if supported would expand research efforts in this area. The prognosis for research support in this area seems favorable as both governmental and some industrial organizations have expressed interest.

REFERENCES

A. Research Papers and Conference Presentations

1. Experimental Studies and Applications of Copper and Vanadium Oxides, by Leo Williams, Jr., presented at the International Society for Hybrid Microelectronics (ISHM), Florida Area Chapter Technical Meeting, Walt Disney World, Florida, April 17, 18, 1972.

2. Experimental Studies and Applications of Copper and Vanadium Oxides, by Leo Williams, Jr., Paper No. 27-E-72, presented at the 74th Annual Meeting of the American Ceramic Society, Electronics Division Washington, D.C., May 9, 1972.

ABSTRACT (Published in ACS Bulletin, April, 1972, p. 358)

Electrical and electro-chemical properties of commercial grades of CuO, Cu_2O, and V_2O_5 were investigated. Effects of pressure, temperature and moisture on the bulk resistivity of the oxides in powder, sintered, and crystalline form were determined and static and dynamic volt-ampere characteristics were obtained. Sintered samples tested showed better electrical stability than the compressed powder samples. Two types of vanadium pentoxide were heat treated to obtain various crystalline oxide forms which were mounted on alumina substrates and terminated by thick film conductors for making electrical connections. Indications are that these materials could have applications as sensors, critical temperature resistors, high speed switches and temperature compensation elements in hybrid microelectronic circuits.

3. Evaluation Tests of NASA Thick Film Resistors Over a Six Year Period, by Leo Williams Jr., Paper No. 19-E-72 ibid

ABSTRACT (Published in ACS Bulletin, April, 1972, p. 359)

200 alumina substrates containing 5 thick film resistors per substrate were processed using resistive ink. These screened resistors fell into four basic types relative to encapsulation. Each type is described. Initial load tests, resistance vs temperature, and TCR measurements from -25 degrees to 150 degrees C were made and the samples were stored "on shelf" for a period of five years. Thereafter, temperature-resistance tests from -50 degrees to 150 degrees C and above, load tests, noise measurements, relative humidity and the results of complete immersion in water over long periods of time were made on the resistors during the sixth year after fabrication. Relative resistance and TCR drift over the six-year period and an evaluation of the effectiveness of encapsulation was made. This paper gives the six-year historical test program. (Supported under NASA grant NGR 34-012-004, North Carolina A&T State University and Westinghouse Educational Foundation.)

4. Experimental Studies and Applications of Vanadium Oxides, by Leo Williams, Jr., presented at the 1972 International Microelectronic Symposium, October 30-31, November 1, 1972, Washington, D.C. Published in Proceedings.

ABSTRACT

Electrical and electro-chemical properties of commercial grades of CuO, Cu_2O, and V_2O5 were investigated. However, in this paper only oxides of vanadium are considered. Effects of pressure, temperature and moisture on the bulk resistivity of the oxides in powder, sintered, and crystalline form were determined and static and dynamic volt-ampere characteristics were obtained. Sintered samples tested showed better electrical stability than the compressed powder samples. Two types of commercially available vanadium pentoxide were heat treated to obtain various crystalline oxide forms which were mounted on alumina substrates and terminated by thick film conductors for making electrical connections. Indications are that these materials could have applications as sensors, critical temperature resistors, high speed switches and temperature compensation elements in hybrid microelectronic circuits.

5. Evaluation Tests on Commercial Thick Film Resistors, by Leo Williams, Jr., paper No. 27-E1-74F, presented at the Electronics Division, NICE Joint Fall Meeting of the American Ceramic Society, Denver, Colorado, September 19, 1974

ABSTRACT

3:35–3:50 p.m.

27–EI–74F. Evaluation Tests on Commercial Thick Film Resistors

LEO WILLIAMS, JR., North Carolina A. and T. State University, Greensboro

Thick film resistive inks printed on alumina substrates were processed and tested. Load, drift, TCR, relative humidity, peak firing temperature and X-ray diffraction tests were conducted on several inks. Test results and evaluations are presented. (Sponsored in part by NASA grant NGR-34-012-004.)

6. Metallic Oxide Switches Using Thick Film Technology, by Dalpat N. Patel and Leo Williams, Jr., presented at the 1974 International Symposium of International Society for Hybrig Microelectronics (ISHM), Boston, Massachusets, October 21-23, 1974, Published in Proceedings.

ABSTRACT

Metallic oxide thick film switches were processed on alumina substrates using thick film technology. Vanadium pentoxide in powder form was mixed with other oxides e.g., barium, strontium copper and glass frit, ground to a fine powder in a micromill and pastes and screen printable inks were made using commercial conductive vehicles and appropriate thinners. Some switching devices were processed by conventional screen printing and firing of the inks and commercial cermet conductor terminals on 96% alumina substrates while others were made by applying small beads or "dots" of the pastes between tiny platinum wires. Processing involved heat treatment at varying temperatures up to 1000 degrees C in vacuum, argon, reducing atmospheres, and air firing in a tunnel kiln. Resistance - temperature tests showed resistance changes by factors of 1000 to 10,000 at various critical temperatures between 50 and 90 degrees C. Static and dynamic volt - ampere and pulse tests performed indicate that the switching and self oscillatory characteristics of these devices could make them useful in memory element, oscillator, automatic control applications, etc.

7. Oscillator Devices Using Thick Film Technology, by Leo Williams, Jr., currently being considered for publication in the December issue of Journal of IEEE, special edition devoted to University contributions to Hybrid Microelectronics,

ABSTRACT

The Electrical Engineering Department of North Carolina Agricultural and Technical State University has developed a microelectronics Laboratory as a result of research efforts involving evaluation of commercial microelectronic components and studies on metallic oxides under a grant from NASA over the past five years. This paper gives details on the fabrication of eight oscillator devices on a one inch square alumina substrate using metallic oxide materials developed at A & T as a result of the research program. Significant technological capabilities of the laboratory relative to the microelectronics industry are also considered.

B. Progress Reports Made to NASA on Microelectronic Components and Metallic Oxide Studies:

8. Semi - Annual Status Report, covering period of June - December, 1970, by Leo Williams, Jr., December 1970

9. Annual Report, for the year of 1971, by Leo Williams, Jr., January, 1972.

10. Progress Report for January - August 31, 1972, by Leo Williams, Jr., September, 1972.

11. Progress Report for September, 1972 to October, 1973, by Leo Williams, Jr., and Donald A. Edwards, November, 1973.

12. Semi - Annual Status Report, for September 1, 1973 to March 31, 1974, by Leo Williams, Jr., April, 1974.

13. Semi - Annual Status Report, April - November, 1974, by Leo Williams, Jr., and Jason Gilchrist, December, 1974.

C. Other References

14. The Processing and Evaluation of Screened Resistors, by R. L. Stermer, Jr., and R. E. Dolan, LWP - 190.

15. Effect of Preliminary Illumination on the Conductivity of Cuprous Oxide, by Klier, Kuzel, and Pasternak, Czechoslov. J. Phys. 5, 421 - 4 (1955).

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