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Environmental Effects on the Resistivity of Palladium-Silver Alloy Films in High Vacuum

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OF PALLADIUM-SILVER ALLOY FILMS IN
HIGH VACUUM

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INTRODUCTION

AND

HISTORY

During the last decade our vastly increased knowledge of atomic and molecular structure of materials, and the new technologies and techniques based on this knowledge, have spurred several approaches to integrated circuits. Specifically, the integrated circuit approaches today are thick films, thin films and semiconductor techniques.

The beginning of integrated circuits can be traced to World War II, the proximity fuse program, and techniques developed in 1945 by the National Bureau of Standards and Centralab, for forming resistance and capacitance on a ceramic substrate by silk screening of conductive inks. However, the key event signaling the advent of true integration in electronics was unquestionably the development during 1958 by Jack S. Kilby of a concept of processing the equivalent elements for a complete circuit such as resistors, capacitors, transistors, and diodes in a monolithic bar of pure silicon.

An alternate approach to integrated circuits involved the use of thin film techniques to deposit all components, including active and passive elements upon a substrate. The electrical isolation of the components afforded by the insulating substrate permits construction of more coupled circuits covering much larger areas. The use of metals to fabricate integrated passive circuits (R-C) appeared in the literature in 1959. Tantalum films, which have been used extensively, possess the unusual advantage of being suitable for both resistors and capacitors.

The rate of development of thin film integrated circuits has been limited by the properties of the available thin film transistors. At present, thin film circuits assume the form of "hybrid" circuits (for example, deposited R-C networks with attached discrete chip transistors and diodes) since the development of practical deposited active devices is still in the laboratory stage.

However, it has been difficult to mass produce thin film (100Å) resistors and capacitors. The uniform thin layer of material is deposited in a vacuum. Attention has recently been focused on thick film (250,000Å) resistors and capacitors. They are used as R-C networks or hybrid circuits as described above by depositing the desired material at a given thickness upon a substrate by silk screen techniques. The process is simple, easy to control and the component values can be adjusted after the initial process to obtain high precision resistors with the added advantage of economic feasibility. This thesis will treat the thick film resistor in detail with special emphasis given to relating environmental effects on resistivity to microstructure properties.

Particulate oxides dispersed in a glass binder have been proposed as thick film resistors. Forrest, for example, obtained 0.2-50 megohms by using Fe_2O_3 as pigment in a glaze. (1) He assumed that conductivity was developed by reduction to Fe_3O_4 in firing. These resistor glazes have the high negative temperature coefficients of resistance typical of oxide conductors. Huttar (2) attempted to use mixtures of finely divided silver and oxides such as Cu_2O-CuO mixtures, but was not able to reproduce resistivities. Attempts have also been made to produce stable carbon-glass frit resistors by adding powdered boron as a scavenger to prevent oxidation. (3)

These attempts to utilize powdered conductors dispersed in glassy binders failed not only because of poor resistance-temperature relationship but also because of a critical dependence of resistivity on the concentration of the powdered conductor. Auerbach (4) has shown that the resistivity of powdered conductors or semiconductors with insulating binders changes by orders of magnitude over a narrow concentration range. D'Andrea (5) was able to overcome this difficulty by using palladium alone or as one of the conductive particulate materials in glaze resistors.

Hoffman (6), of du Pont, undertook research in 1962 to develop resistor compositions based on this idea. The oxidation-reduction behavior of palladium on firing in air was studied by measuring weight gain and loss and is thought to be responsible for welding and sintering of particles into chainlike aggregates. This effect is catalyzed by the presence of a second precious metal powder and, when this powder is silver, extremely good resistor properties can be obtained.

The reported usage of the palladium-silver alloy films as resistors in the electronics industry has been in encapsulated form. By mounting the resistor inside vacuum electron devices, there is the possibility of eliminating the encapsulation. A literature search has revealed no reported efforts of experiments with unencapsulated resistors and certainly no reports of the palladium-silver alloy resistor in vacuum tubes or other high vacuum environments. Therefore, the research reported in this thesis will concentrate on the environmental effects on resistivity of palladium-silver alloy films in high vacuum.

THEORY

AND

PROPERTIES

I. Definition of the Thick Film Resistor

The real question is, "What is a thick or thin film?" Thin film resistors reported in the literature have a thickness range of 100 to 1000Å. Thin film capacitors have a thickness of 500 to 2400Å, while thin film transistors are reported to have a thickness from 500 to 2000Å. Therefore, thin film generally means film thickness of 100 to 2500Å. The thick film resistors reported in the literature have a range of 175,000 to 330,000Å. Thick film resistors are at least two orders of magnitude greater in thickness than thin film resistors.

II. Properties of Thick Film Resistor

The work of Hoffman (6) and others have considered the most important properties of the thick film resistors to be resistance, temperature coefficient of resistance and drift. A brief description of previous research efforts on palladium-silver alloy film resistors with relation to these properties has been included in this paper for continuity of thought.

A. Resistance (6)

The concept of film or square resistivities is used freely in discussing thick film resistors. It follows from observation that:

$$R = \rho\left(\frac{l}{tw}\right)$$

where R = resistance
p = resistivity of the material
l = length
w = width
t = thickness

In the special case where length and width of the glazed area are the same, any square of material of constant resistivity and thickness will have the same resistance. It is customary to talk of resistance per square at some constant thickness. In this work all resistivities are in ohms per square per mil thickness (one-thousandth inch). Glaze resistor compositions (Pd-Ag) are available with resistance values ranging from 1-20,000 ohms per square per mil.

B. Temperature Coefficient of Resistance (6)

Insensitivity to temperature is often a requirement for resistors. Since the passage of current generates heat in resistors, it is difficult to compensate for large changes in resistance due to heat. The changes in resistance with temperature as reported by Hoffman (6) is shown in figure 1 on page 8. An increase in resistance (positive TCR) is obtained in the temperature range 25-105°C with palladium-silver compositions with resistivities ranging from 1 ohm up to almost 20,000 ohms per square per mil. In the temperature range +25° to -75°C an increase in resistance (negative TCR) is obtained up to 1,000 ohms per square per mil, above which resistance decreases. From 1,000 to 20,000 ohms per square per mil the resistance decreases when the temperature is lowered. Compositions with resistivities above 1,000 ohms per square have an increasing, almost linear, curve of resistance versus temperature from -75 to +105°C. The 4,000 ohms per square compositions have very small temperature coefficients of 100-125 ppm/°C.

C. Drift

The drift in resistance value is the change (ΔR) with respect to time and temperature. Melan and Mones (7) have reported relationships of firing parameters, composition parameters, power density to drift. Their data on glazed resistors using a broad range of firing temperatures (730° to 775°C) and a somewhat limited range of composition parameters is quite significant. Data based

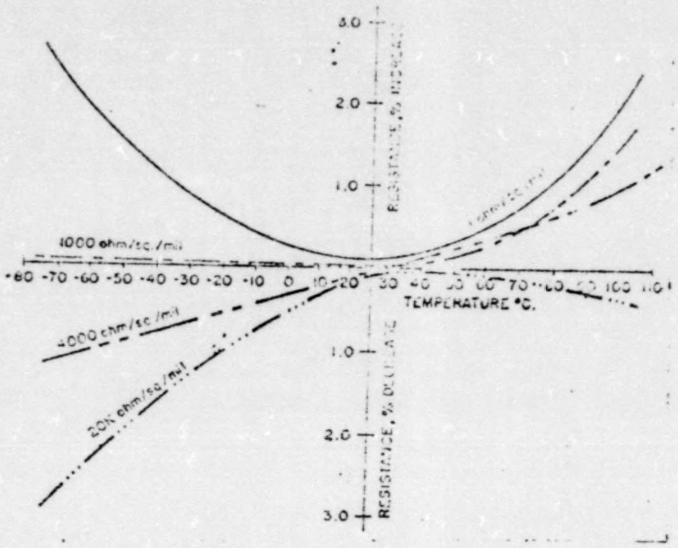

Fig. 1. - Changes in resistance with temperature as a function of resistivity of the compositions (6)

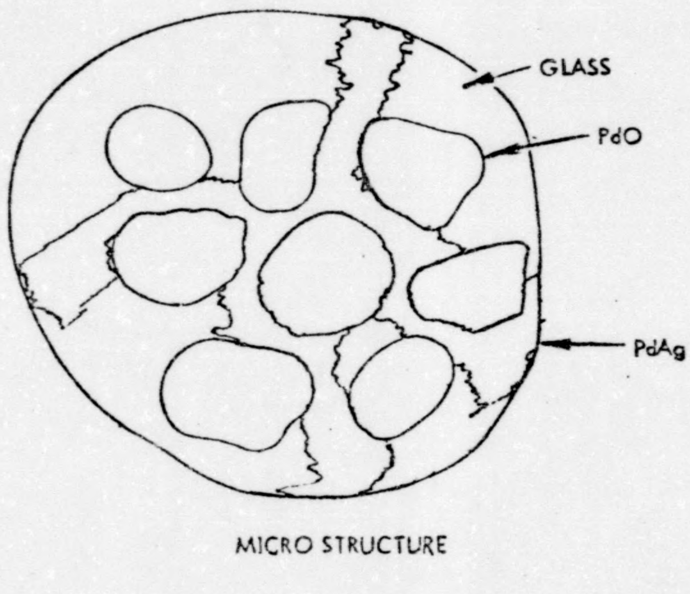

Fig. 2. - Proposed microstructure of the Pd-Ag resistor (7)

on 60 million component hours of testing indicated the Pd-Ag resistor drift characteristics under relatively severe environmental conditions to be essentially predictable and small.

III. Resistor Structure

In 1964, Melan and Mones (7) described the structure of the palladium-silver-glass glaze resistor. The structure of the glaze resistor is essentially a dispersion of conductive particles in a glass base or matrix. Firing the palladium-silver-glass material at moderately high temperatures in an oxidizing atmosphere results in certain crystalline phases which have been identified as palladium oxide and a palladium-silver alloy. A high temperature X-ray diffraction study of the process indicates the following reaction to occur:

$$\mathrm{Pd} \xrightarrow[>330°\mathrm{C}]{\mathrm{O}} \mathrm{PdO} \xrightarrow[>520°\mathrm{C}]{\mathrm{Ag}} \mathrm{PdAg} + \mathrm{PdO}$$

As shown, the alloy forms by parasitic attack of silver on the palladium oxide. It is believed that the Pd-Ag alloy at least partially encapsulates the residual PdO during the reaction. However, X-ray techniques in this case were not sufficiently sensitive to verify this. (7)

The thermodynamic equilibrium data for the system

$$\mathrm{PdO} = \frac{1}{2}\,\mathrm{O_2} + \mathrm{Pd}$$

has been established; the equilibrium relationship can be expressed by

$$K = \left[a_{\mathrm{Pd}}\right]\left[P_{\mathrm{O_2}}\right]$$

where K is the equilibrium constant, a_{Pd} is the activity of palladium in the alloy, and the $P_{\mathrm{O_2}}$ is the partial pressure of oxygen. (8)

For a 750°C air firing of typical compositions, the alloy phase has been found to consist of 65-70% Ag, which is consistent with thermodynamic data. (9) It is evident from the preceding that the higher the initial silver content in the material, the lower the ultimate PdO content in the reacted mixture. At 750°C in air apparent equilibrium is established within 20 minutes. Although longer firing time does not change the apparent constitution, it does increase resistivity. The reasons for this are proposed in the discussion below. A proposed microstructure (7) is shown in figure 2.

X-ray fluorescence analysis indicates that the resistor is essentially homogeneous in cross section. Also, electron probe measurement show some solubility of silver in the glassy phase. As might be supposed from this picture either decreasing the glass content or increasing the silver content (and thereby the alloy phase) decreases resistivity. This has also been observed by Hoffman. (6)

IV. Conduction Process

Although the detailed conduction mechanism of this relatively complex system is not fully clear, the evidence is that palladium oxide primarily controls the conduction process (7). The evidence for the role of PdO is as follows(7):

A. Thermal probe measurements have shown that the resistor itself is a "p" type conductor. A study of sintered pellets of PdO has shown that the oxide is a "p" type semiconductor with essentially temperature independent carrier concentration. The latter observation is consistent with the picture of conduction in "p" type semiconductor oxides such as NiO, CoO, and CuO which is controlled by lattice site to site hole transport. The mobility of hole transport in turn is associated with an activation energy α. The resistivity, ρ, can be shown to have the relationship.

$$\rho = ATe^{\alpha/kT}$$

where A is a constant for the system, T is the Kelvin temperature, and k is Boltzmann's constant.

A plot of p vs. T would show a minimum at T = α/k. This means that both positive and negative temperature coefficients of resistance (TCR) can occur for a given material depending on where the minimum occurred relative to the measurement temperature. Positive and negative TCR's are normally observed for a given PdO glaze resistor.

B. The extent and type of conductivity in palladium oxide and similar semiconductors is associated with metal ion vacancies or an excess of oxygen. Each Pd^{+2} vacancy can be thought to result in 2 Pd^{+3} centers to maintain charge neutrality. Hole transport occurs from Pd^{+3} to an adjacent Pd^{+2} site. If Melan and Mones' opinion of conductivity in palladium oxide were correct and, more important, if palladium oxide largely governs resistivity in the glaze resistor, then appropriate charge control in the palladium oxide would strongly influence resistivity of the resistor. Introduction of univalent ions such as Li^+ would tend to stabilize a Pd^{+3} ion and consequently increase conductivity. On the other hand, introducing trivalent or higher valency ions, e.g., Sb^{+3}, would tend to decrease the concentration of Pd^{+3} centers and reduce conductivity. All this is observed in PdO. For resistors prepared with PdO, which is treated with lithium and antimony the result is that resistivity can be varied over several orders of magnitude. Thus for compositions that are otherwise fixed with respect to Pd, Ag and glass, a wide range of resistivity may be obtained by appropriate additives.

The observed (7) increase in resistivity with prolonged firing time can be qualitatively accounted for on the basis of the palladium oxide becoming more stoichiometric, therefore less conductive, by loss of excess oxygen. Resistors subjected to elevated storage temperatures drift predominantly in a positive direction. This too can be accounted for on the basis of increased stoichiometry.

The foregoing obscures the role of the silver in the system. Resistors can in fact be made without silver. Silver does modify the conductivity of the system possibly by improving the conductive linkages between the PdO granules (7). It also appears to increase the drift stability of the system at elevated storage temperatures. This may be due to silver partially encapsulating the PdO as the alloy and inhibiting oxygen loss.

The role of the glass is twofold. It serves the purpose of bonding the system to the substrate and provides some moisture protection. The moisture sensitivity of the resistor becomes more pronounced for glass concentration below 40% (7).

F. R. White and Dr. L. C. Hoffman of du Pont have developed the resistor pastes which were used for this study. Even in 1966 they were not in complete agreement on the conductivity mechanism in the resistor materials which involve the Pd-PdO-Ag-PdAg-glass system (10). White ascribes conductivity to "filaments" through the resistor which consist probably of "chained" metal particles coated with an oxide skin. Doped semiconducting PdO controls the electrical properties of the material. The glass constituents contribute heavily to the doping as evidenced by data from a large number of controlled experiments. Impurities in the Pd powder also can have significant influence as dopants.

Hoffman feels that doped PdO cannot explain all phenomena observed. He suggests that Pd-Ag alloy films coat particles in the fired resistor, particularly for low ohms per square materials. He pointed out that PdO does not decompose completely even at very high firing temperatures.

V. Resistor Compositions

Du Pont has available a variety of palladium-silver resistance pastes. These materials are given a number such as 7800, 8000, etc. and the actual composition is not given. Several compositions of palladium-silver-glass are available on the commercial market such as 150, 500, 3500, 10,000 ohms per square per mil. These pastes can be blended to obtain intermediate values (11) of resistance.

The resistor pastes made by du Pont (6) are prepared by mixing precious metal powders and finely divided glasses, produced by melting and fritting, with specially developed organic vehicles. The particulate silver and palladium used has an average size of 0.1 to 0.5 microns. Many frit compositions were studied by du Pont. The only frit composition identified by Hoffman (6) in the literature was PbO-B_2O_3-SiO_2. The frit or glassy compositions were prepared by melting the batch components together, pouring into water, and ball-milling until the average particle diameter was about 5 microns. The frit composition is then mixed with the palladium and silver powders. The resistor pastes are composed of two-thirds inorganic solids (Pd-Ag-glass) and one-third organic vehicle (6) (12).

When palladium powder is a component of the glaze resistor system, the dependence of resistance on concentration is low enough for practical use. The effect of concentration of precious metal powders on resistivity in ohms per square per mil is shown in figure 3 on page 16. (6)

The dependence of resistivity on gold or silver concentration is very steep. Silver powder has a resistivity of less than one ohm per square per mil at 48% and over 100K ohms at 46%. Palladium has useful resistivities over a range of 33 to 70%. When palladium and silver are used together the concentration dependence is even less precipitous. It is possible, therefore, to formulate mixtures of palladium and glass or palladium, silver, and glass over a range of resistivities, and obtain reproducible resistances in resistor manufacture.

Resistor compositions containing palladium powder alone are inferior to those which also include silver. The superiority of silver-containing compositions is particularly evident when measuring temperature coefficient of resistance and noise (6). Table 1 shows the effect of adding silver to palladium and low melting lead borosilicate compositions.

TABLE 1. - Effect on TCR and noise of percent silver in palladium-lead borosilicate compositions (6)

Silver (%)	Resistivity (ohm/sq/mil)	TCR at 25-105°C (ppm/°C)	Noise (db/decade)
0	200,000	+1720	+22
10	7,300	+ 440	+12
20	400	+ 380	+ 4
30	20	+ 175	- 8
40	0.5	+ 320	- 4

From the table it can be seen that silver additions lower resistivity, temperature coefficients, and noise. There are indications also that the silver concentration reaches an optimum value and that very large additions are precluded on the basis of precipitous resistance changes and deleterious effects on the other electrical properties.

The lower concentration-resistivity dependence of palladium and palladium-silver mixtures and the excellent electrical properties obtained when palladium and silver are combined, require explanation. (6) As the palladium powder is heated in the air, it oxidizes at a relatively low temperature until a maximum oxygen content (PdO) is reached. After the temperature reaches a given value, the palladium oxide begins to decompose. The decomposition is not complete, however, and small amounts of oxygen are left in the metal phase. The presence of small amounts of oxygen tends to raise the resistivity of the particles, thereby reducing the tendency toward metallic conductivity which is very strong in the case of a noble metal such as silver. At the same time, the decomposition exposes high-energy palladium surfaces which have a tendency to sinter with the silver powder into alloy phases.

Dr. L. C. Hoffman has summarized previous work on palladium-silver alloys. (6)

> The system palladium-silver has been studied by Ruer. The system is a complete series of solid solutions with no minimums or maximums. Grube has shown that the resistivity of Pd-Ag alloys goes through a maximum at 56% (wt) palladium and the temperature coefficient of resistance is essentially zero at the same point. [This is shown in figure 4 on page 16.] This is thought to be a consequence of the completion of the d-shell of palladium by a quantum mechanical sharing of the silver valence electron. This alloying tendency is thought to result from the similar ionic radii of palladium and silver and the sharing of the extra electron from silver in the holes of the d-shell of palladium. Ubbelohde has shown by magnetic measurement that palladium has 0.55 holes per atom. In the system Pd-H, palladium becomes diamagnetic at a hydrogen concentration of 55% (at.), indicating ionization to H^+ and an electron which goes into the d-shell. The dissolution of silver in palladium eliminates the anomolous high hydrogen solubility in addition to affecting the resistivity and TCR. The affinity of palladium for silver is therefore as strong as its affinity for hydrogen. The tendency of the particulate precious metals to weld or sinter is enhanced by the active palladium surface exposed when the PdO formed in firing decomposes. This decomposition is favored by the lower decomposition temperature of PdO in the presence of silver. (6)

Since the Pd-Ag alloys go through a maximum of resistivity at approximately 56% (weight) palladium and the temperature coefficient of resistance is essentially zero at the same point (6) (11), it seems logical that manufacturers of palladium-silver-glass pastes would endeavor to obtain something close to the ratio of palladium to silver of 55/44.

This information will only give a relative measure of the percent composition of palladium and silver in the palladium-silver-glass resistor pastes since PdO and Pd-Ag are both present in the finished resistor. The percent compositions of du Pont resistor paste are not available.

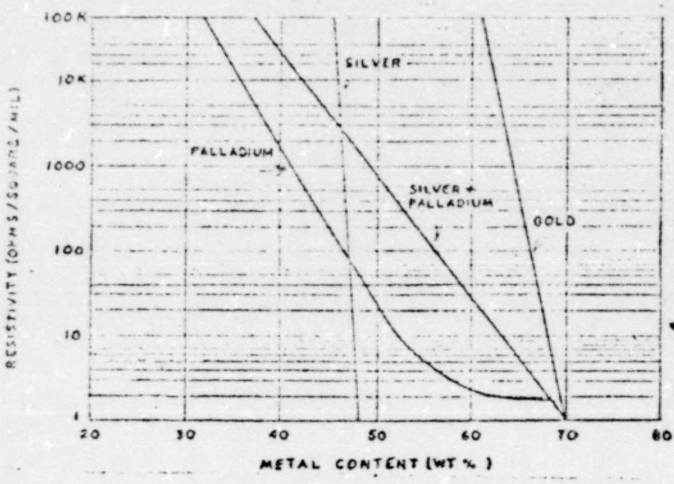

Fig. 3. - Resistivity vs. concentration of metal powders in $PbO-B_2O_3-SiO_2$ frit (6)

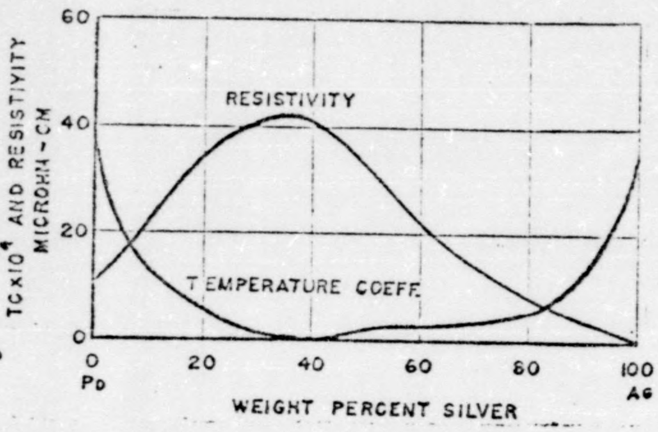

Fig. 4. - Resistance and temperature coefficient of palladium-silver alloys (13)

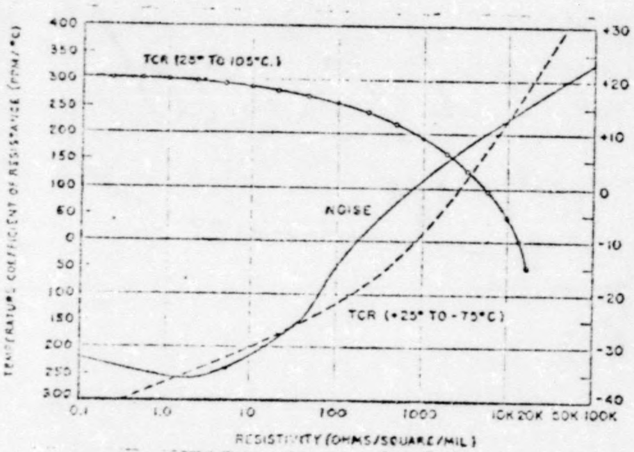

Fig. 5. - Noise and TCR of glaze resistors. Substrate, 96% aluminum oxide; terminals, high-temperature silver; single fired at 760°C with 10 minutes at peak temperatures and belt speed of 3 in./minute (6)

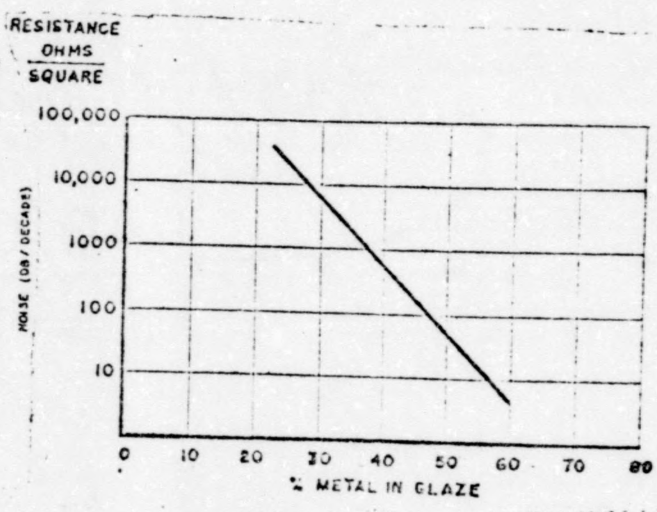

Fig. 6. - Dependence of glaze resistance on metal content (13)

One other consideration is the percentage of glass frit in the resistor paste composition. Casey, Mulligan and Woods have discussed the importance of the glass frit. (13)

> The glass used must be chosen so as to give a proper thermal expansion "fit" to the underlying ceramic substrate. Preferably, the glaze should have a thermal expansion somewhat lower than the substrate material so that it will be in a state of compression. If the glaze is placed in tension, crazing results and poor electrical properties are obtained. It has been found that the glass plays a significant role in determining the overall temperature coefficient of the system. (13)

Hoffman (6) has provided the information on how the fit of the resistor to the base material affects the temperature coefficient of resistance.

> In figure 5 [on page 16] the numerical values of both temperature coefficients of resistance increase as the resistivity of the glaze composition decreases. Since the thermal expansion of the precious metals is much higher than that of the frit or the substrate, the resistivity can be decreased by increasing the proportion of palladium-silver to frit. (6)

Hoffman (6) prepared a series of Pd-Ag-lead borosilicate frit resistor compositions and applied them to 96% alumina substrates which had an expansion of 8 ppm/°C. Bars, 3 by 0.5 inch, were dry-pressed from the Pd-Ag-frit mixtures and fired on graphite plates at 760°C, allowing 10 minutes at peak temperature. Thermal expansions were measured with the Gaertner dilatometer. The results are shown in table 2. (6)

The expansion of the substrate is nominally 7.9 ppm/°C. in the temperature range 25-700°C; the frit or glaze was chosen about 5% lower in order to obtain stress-free fit at room temperature (6). The precious metals have much higher expansions, but do not affect the combined expansion until their concentration exceeds 30%. Even then, they do not affect expansion markedly until their concentration exceeds 50%. The TCR's react to the fit situation as can be seen from table 2, especially in the low temperature direction where differential contraction is believed to cause pressure on the conducting phase.

TABLE 2. - Thermal expansion and temperature coefficients of resistance (6)

Composition (%) Lead Boro-silicate Frit	Precious Metal	TCR 25-105°C (ppm/°C)	TCR 25 to -75°C (ppm/°C)	Thermal Expansion Coeff. 0-300°C (ppm/°C)
100	0			7.5
70	30 Pd-Ag	+160	+ 50	7.6
60	40 Pd-Ag	+240	- 80	8.2
40	60 Pd-Ag	+300	-250	8.5
10	90 Pd-Ag	+320	-320	8.9
0	100 Pd-Ag			16.8
0	100 Ag			17.0*
0	100 Pd			11.0

* American Society for Metals, Metals Handbook, Eighth Edition, Reinhold Publishing Corp., New York, 1961. 1300 pp.

Another reference for resistor composition is given by Casey, Mulligan and Woods of the International Resistance Company (13). Figure 6 on page 16 shows a curve of resistance in ohms per square versus percent metal content, based upon a coating thickness of 12 microns.

Du Pont resistor paste #7826 and .001" thickness were used in the experiments reported in this paper. The performance characteristics of #7826 paste are shown in table 3 as per du Pont published data.

TABLE 3. - Performance characteristics of the 7800 series resistor compositions

Resistor Composition	Fired Thickness (mils)	Resistivity as fired (ohms/sq.)	TCR 25 to +125°C (ppm/°C)	TCR 25 to -55°C (ppm/°C)
7800	0.52	0.2	+725	+331
7826	0.79	159	+738	+401
7827	0.98	1092	+495	+169
7828	0.91	2827	+243	-25
7832	0.93	6743	+263	+38
7860	0.75	9722	+402	+115

As mentioned previously, du Pont has not published the composition of their resistor paste. One may use figures 3,4,5,6; tables 1,2,3, and the written material of this section to make educated guesses.

VI. Environmental Effects on Resistivity

To date, the reported experimental usage of the palladium-silver alloy resistor in the electronics industry has involved encapsulation. By mounting the resistor inside vacuum electron devices, there is the possibility of eliminating the encapsulation. A literature search has revealed no reported efforts of experiments with unencapsulated resistors and certainly no reports of palladium-silver alloy resistors in vacuum tubes.

The receiving tube type 17BF11 with a single resistor on a substrate mounted 5 mm above the top mica of the cage was chosen as the test vehicle for investigating the environmental effects on resistivity of palladium-silver alloy films in high vacuum. A sample of this test vehicle is shown in figure 7.

The receiving tube is indeed a complex electronic device. The addition of the palladium-silver alloy resistor inside the vacuum receiving tube adds to the complexity of the device. Consequently there are several aspects of this complex system that need to be investigated. There are many combinations of 17BF11 parts materials and processing schedules available to the design engineer.

A. Random Balance Test

A first effort to get a better idea of the important variables in tube making that affect the palladium-silver alloy involved the use of a random balance test.

The concept of random balance in experimental design, created by F. E. Satterthwaite, has been criticized by some authorities and praised by others. Much of the controversy has been due to a lack of understanding of the objectives of random balance experimentation. A brief description of the random

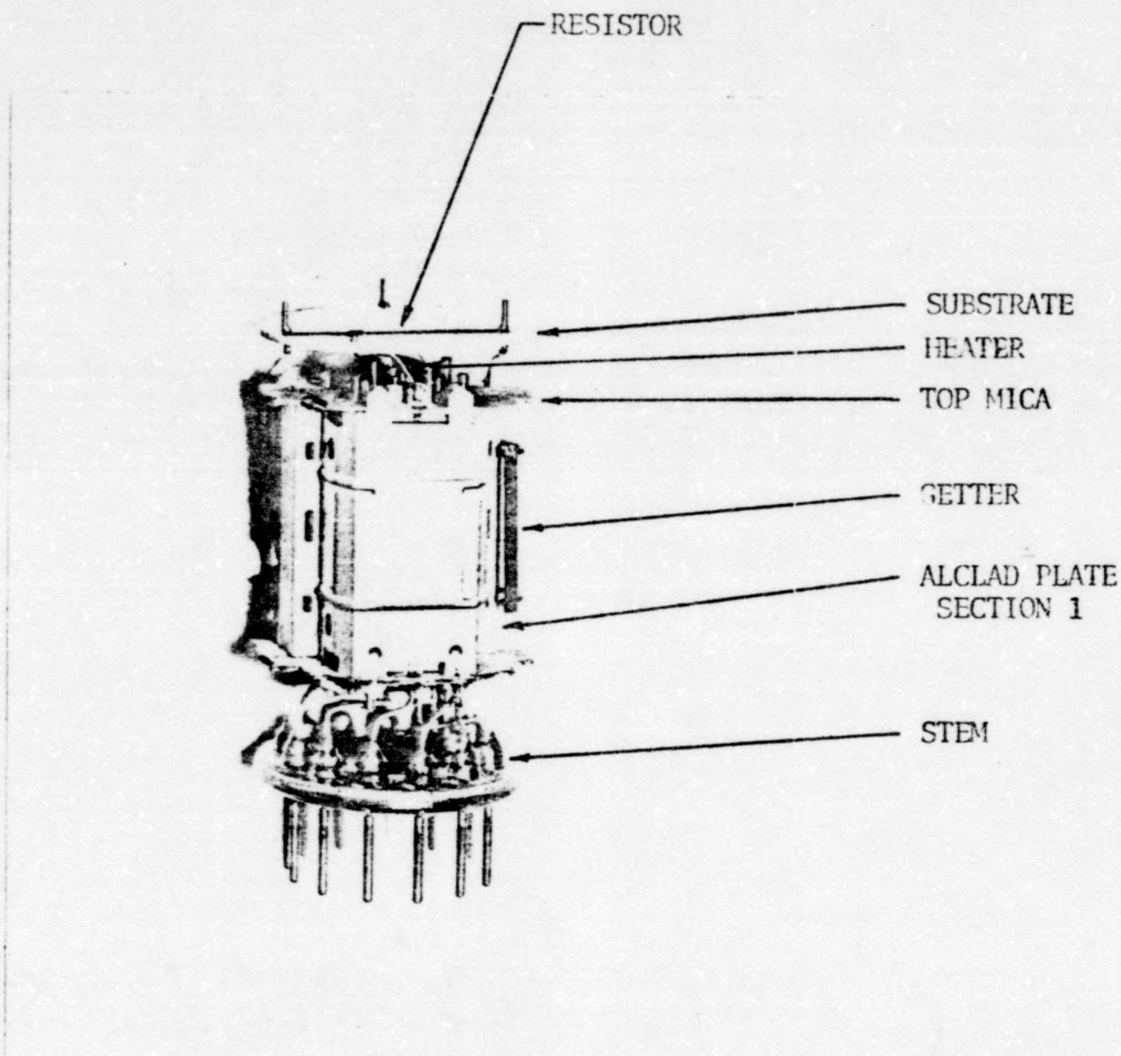

Fig. 7. - 17BF11 mount with resistor, without bulb

balance test has been included in this paper for continuity of thought and a better understanding of the results.

The following material has been, in part, extracted from articles written by Thomas A. Budne, published in Industrial Quality Control. For a more comprehensive view the reader is referred to the April, May and June 1959 issues of Industrial Quality Control. Mr. Budne is a Statistical Engineering Consultant located at Great Neck, New York.

When a large number of variables are believed to influence the measurable output or response of a device, the scientist or engineer is primarily interested in knowing which of the variables are responsible for the variation in output. The isolation of significant variables becomes important in several specific cases.

An attempt to identify the significant variables of the complex receiving tube-resistor device was made by conducting a random balance test. This test sought to answer the following questions:

1. Identify those variables in design and manufacturing process of tubes which can be changed to achieve a more satisfactory performance of an unencapsulated resistor.
2. Identify those variables in the manufacturing process which cause undesirable variation in performance characteristics of both the resistor and tube.
3. Identify those variables which can be changed to obtain a better manufacturing yield, within specified performance characteristic limits.

A random balance experiment contains all of the variables of potential significance to the problem. While two levels of each variable result in maximum simplicity, any number may be used. Between 30 and 50 test runs are required, depending on the number of levels used.

Random balance experiments rest on the assumption of mal-distributions of causes to a total effect. A large body of experience shows that within a large number of variables only 2, 3 or 4 of the largest are often responsible for as much as 50 percent or more of the total effect. This phenomenon may be called the mal-distribution principle. Frequency distributions of phenomena exhibiting this mal-distribution are sometimes called "Pareto" distributions or "Lorenz" Curves after experimenters in this field, although there are distinctions between the two. Regardless of the terminology employed, the mal-distribution principle has been noted in many unrelated areas. Variation in product, variation in measurements, variation within units measured repetitively, variation from unit to unit, variation from one time period to another, variation from machine, or variation from operator to operator is evidence of a problem when the variation becomes excessive. Whenever the variation exists, there are one or more factors.

The random balance design is a method for screening all possible contributing variables in a limited number of test runs. Its primary objective is to identify all of the relatively major contributors to variation by a rough analysis of all the contributors. It is possible that one or more critical variables may escape inclusion in the design; such variables will reflect themselves into the unexplained variation which the analysis may reveal.

The random balance design test for the 17BF11 with resistor is shown in tables 4 and 5. Ten variables with two and three levels were included in the test. A total of 30 runs was sufficient to represent the 5184 possible combinations of this test.

TABLE 4. - Statistical design of preliminary tests

Variables	Code	Variables	Levels
Sealex	A	Filament lighting	1 700 ma. 2 720 ma. 3 740 ma.
	B	Bombarder setting (Induction heating)	1 High 2 Normal 3 Low
	C	Exhaust machine speed	1 600 tubes/hr. 2 800 tubes/hr.
	D	Filament lighting sequence	1 Early 2 Simultaneous
Aging	F	Filament hot shot	1 38 volts for 2 min. 2 34 volts for 2 min. 3 30 volts for 2 min.
	G	Plate step	1 E_f=18V, Ip=36ma W_p=3.6 watts, for 30 min. 2 E_f=18V, Ip=49ma W_p=5.8 watts, for 30 min.
Life Test	H	Regular life test with	1 No load on resistor 2 1/8 watt on resistor 3 1/4 watt on resistor
Materials	I	Cathode alloy	1 Normal K22-K09 2 Passive K51-K51
	J	Grid lateral wire	1 Perma nickel 2 Silver plate nickel
	K	Plate	1 Converted alclad 2 Unconverted alclad

TABLE 5. - Random balance test design and life test summary

Run #	Sealex A	Sealex B	Sealex C	Sealex D	Aging F	Aging G	Life Test H	Materials I	Materials J	Materials K	Resistor Initial Value in ohms	After Exhaust	After Aging	After 16 Hr.	After 289 Hr.	After 541 Hr.	Run #
1	3	3	2	2	3	2	2	1	2	1	1 903	1 890	1 914	1 909	1 870	1 869	1
2	3	3	2	1	1	2	1	2	1	1	1 666	1 246	1 300	1 367	991	816	2
3	2	1	2	1	2	1	1	1	2	1	1 789	1 353	1 386	1 330	1 270	1 241	3
4	3	1	1	2	2	1	2	1	2	1	1 922	1 738	1 735	1 654	1 602	1 592	4
5	2	3	2	2	2	1	3	2	1	1	1 797	1 036	1 130	1 022	447	316	5
6	2	3	1	1	3	1	1	2	1	2	1 719	1 617	1 610	1 555	1 517	1 560	6
7	1	1	1	2	1	1	2	1	1	1	2 324	2 035	2 037	1 894	1 777	1 717	7
8	3	2	2	2	3	1	3	1	2	1	1 773	1 287	1 321	1 280	1 237	1 217	8
9	2	3	1	1	3	1	3	2	2	1	2 070	1 261	1 316	1 197	649	514	9
10	1	3	1	1	2	2	2	2	2	2	1 718	1 436	1 430	1 358	1 283	1 252	10
11	1	3	2	1	3	2	1	2	1	2	1 785	1 251	1 311	Open	Open	Open	11
12	2	1	2	1	2	2	2	2	2	2	2 004	1 620	1 616	1 533	1 474	1 452	12
13	1	1	1	2	2	1	1	1	2	1	1 841	1 696	1 691	1 633	1 564	1 553	13
14	1	2	2	2	2	2	3	2	1	1	1 858	1 104	1 349	1 083	636	372	14
15	2	2	1	2	3	2	1	1	1	2	1 423	1 311	1 308		1 234	1 221	15
16	3	2	2	1	3	2	3	1	2	2	1 869	1 073	1 226	1 075	674	464	16
17	3	1	2	2	1	2	1	2	2	2	2 184	2 140	2 133	2 086	2 120	2 181	17
18	2	2	1	2	1	2	3	1	1	2	1 731	1 602	1 592	1 516	1 463	1 454	18
19	3	1	2	1	1	1	2	2	2	1	2 179	1 353	1 423	1 351	1 195	1 054	19
20	1	1	2	1	2	2	3	2	2	1	2 292	1 176	1 373	1 194	662	486	20
21	2	1	2	1	3	1	1	1	1	2	2 153	1 759	1 765	1 680	1 600	1 550	21
22	2	2	1	2	3	1	1	1	1	2	1 735	1 606	1 604	1 561	1 522	1 520	22
23	2	3	2	2	1	1	2	1	1	2	1 791	1 098	1 138	1 080	885	758	23
24	1	2	1	1	2	1	2	2	1	2	1 974	1 847	1 855	1 788	Open	Open	24
25	3	2	1	2	2	2	3	2	2	2	1 846	1 782	1 783	1 726	1 702	1 706	25
26	1	1	1	2	1	1	1	2	1	2	1 927	1 870	1 861	1 798	1 768	1 810	26
27	1	2	1	1	1	2	2	1	2	2	2 064	1 759	1 778	1 689	1 603	1 560	27
28	3	3	2	2	2	2	3	1	2	1	1 855	1 413	1 454	1 356	1 210	1 117	28
29	3	3	1	1	3	2	2	2	1	1	1 705	1 075	1 150	1 078	752	550	29
30	3	2	1	1	1	1	3	1	1	1	1 882	1 054	1 257	1 176	876	707	30

The resistors were made in the Tube Technology Engineering area of the General Electric plant in Owensboro, Kentucky. The room was lint free and had an air controlled atmosphere. A model 100C PRESCO printer was used. The resistor material was #7826 du Pont paste while the platinum gold conductor was #7553 du Pont paste. The finished resistors were exposed to the room atmosphere over the weekend due to exhaust machine schedule. The resistors were connnected to pin #4 and 5 of the special 17BF11 tubes and were independent of the tube operation. Fabrication of the palladium-silver resistors will be discussed in more detail in a later section devoted to fabrication.

The combination tube and resistor were evacuated on the 16-head compactron exhaust machine in the Engineering Development Shop, General Electric, Owensboro, Kentucky. The bulb was sealed to the stem in one revolution of the machine. The stem tubulation was then inserted into an exhaust machine port. On the second revolution the tube was evacuated, filament lighted and the metal parts were heated by induction heat (bombarder). At the end of this cycle the stem tubulation was tipped off and machine processing was over. The vacuum level was approximately 10^{-5} torr. After the getter was flashed, the vacuum inside the tube was approximately 10^{-6} torr or lower.

All resistor measurements were made with a Leeds and Northrup Company #5305 wheatstone bridge and in the same room under the same conditions.

Several observations were apparent after the completion of the random balance test. They are as follows:

1. After sealing and evacuating the 17BF11 tube, all

resistance values decreased. There is a reversal of process for the oxide resistor. The individual and median values are shown in figure 8. The design of the random balance test was good because there were extreme variations. The most detrimental variables were high filament lighting, low induction (bombarder) heat, high exhaust machine speed and converted alclad plates. The median change of 30% in resistor values due to the exhaust cycle is more than one would want. Especially when a ± 10% resistor is the desired end product.

2. The hot shot aging process, where the filament and oxide cathode are heated above the levels of the exhaust cycle processing, tends to recover the resistors. Many resistors increased in value. This is shown in figures 9 and 11.

3. The life test has accentuated the variables that decrease the resistor value from the initial reading as listed above in the first observation. This is shown in figures 10, 13 and 17.

4. The overrated (1/4W) life test of resistor is very detrimental to most resistors. A forty-eight percent median change in resistance due to 1/4W life was observed in the 541 hours of life as shown in figures 10, 13, and 17. However, there were a couple of individual exceptions with very small resistance change in 541 hours.

5. Certain combinations of the variables resulted in very

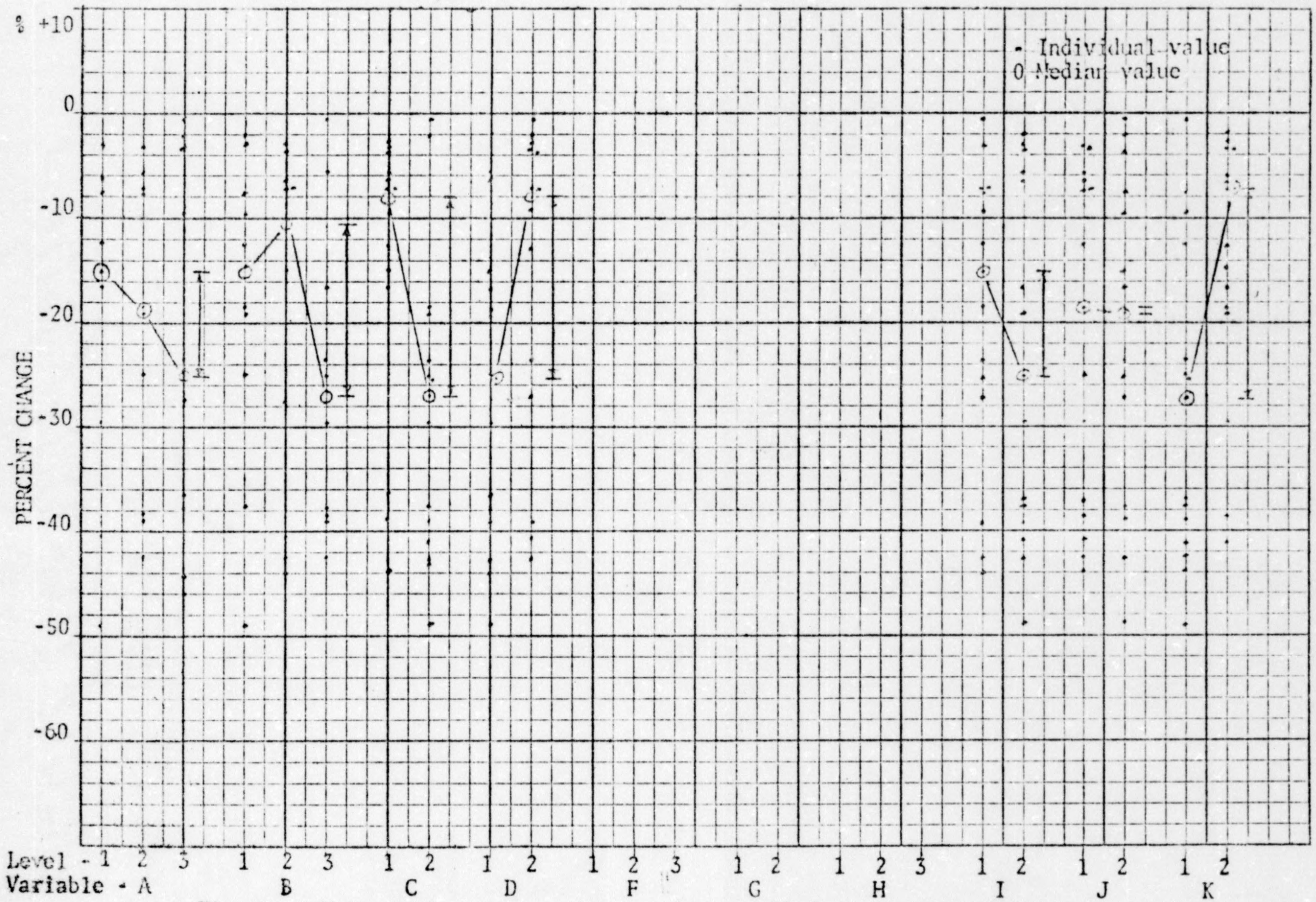

Fig. 8. - Percent change in resistance from initial values through exhaust

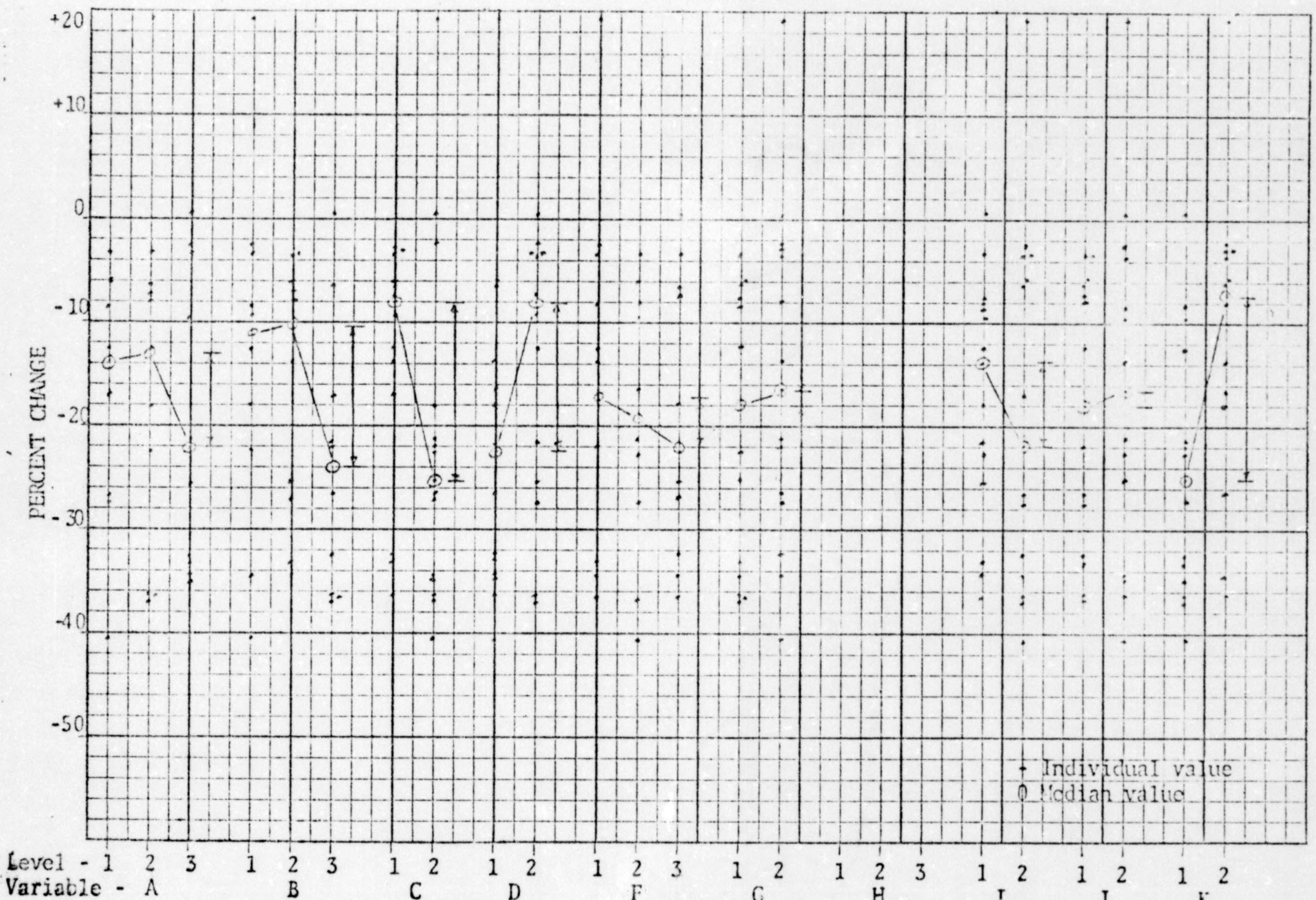

Fig. 9. - Percent change in resistance from initial values through aging

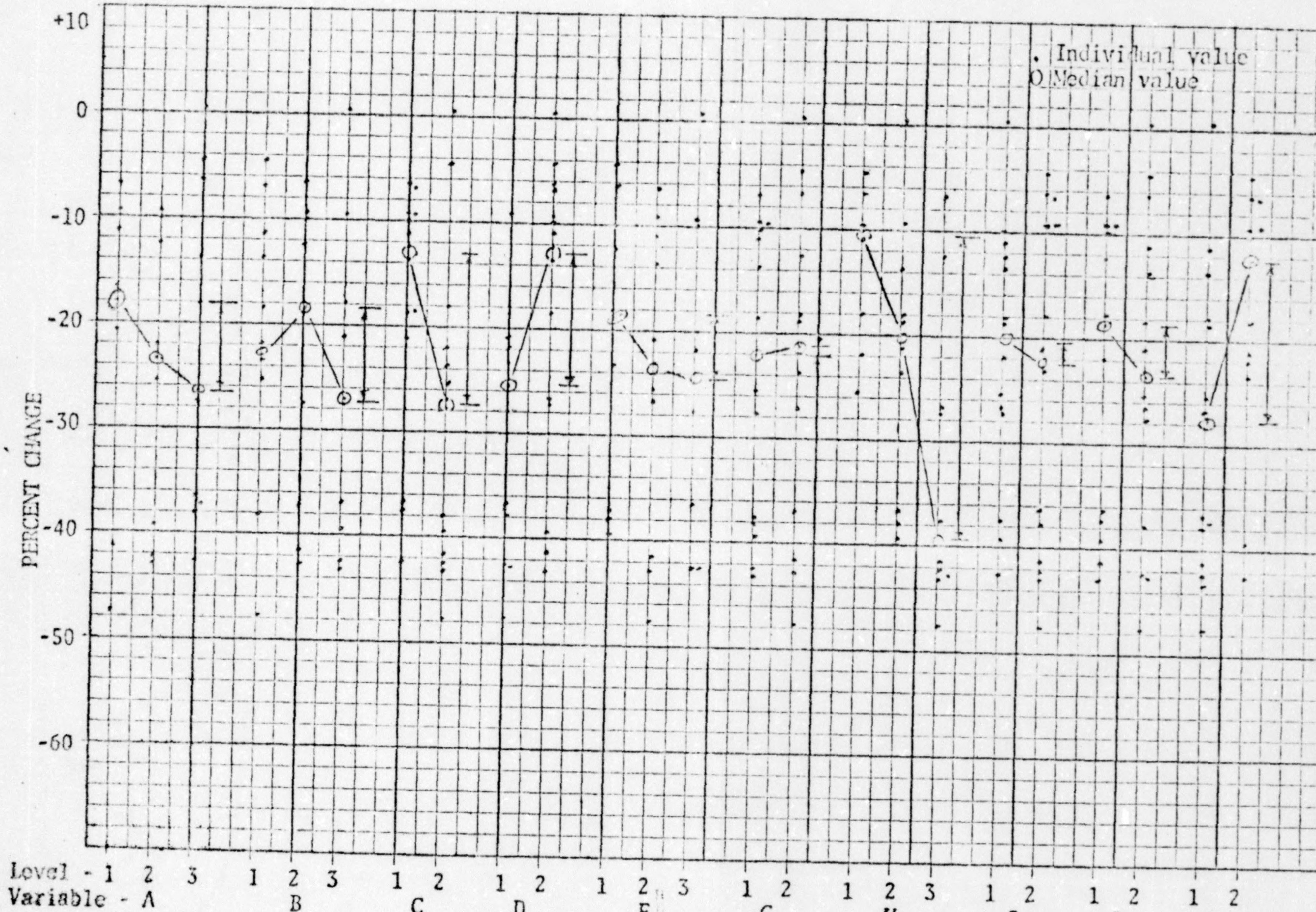

Fig. 10. - Percent change in resistance from initial values through 16 hours of life test

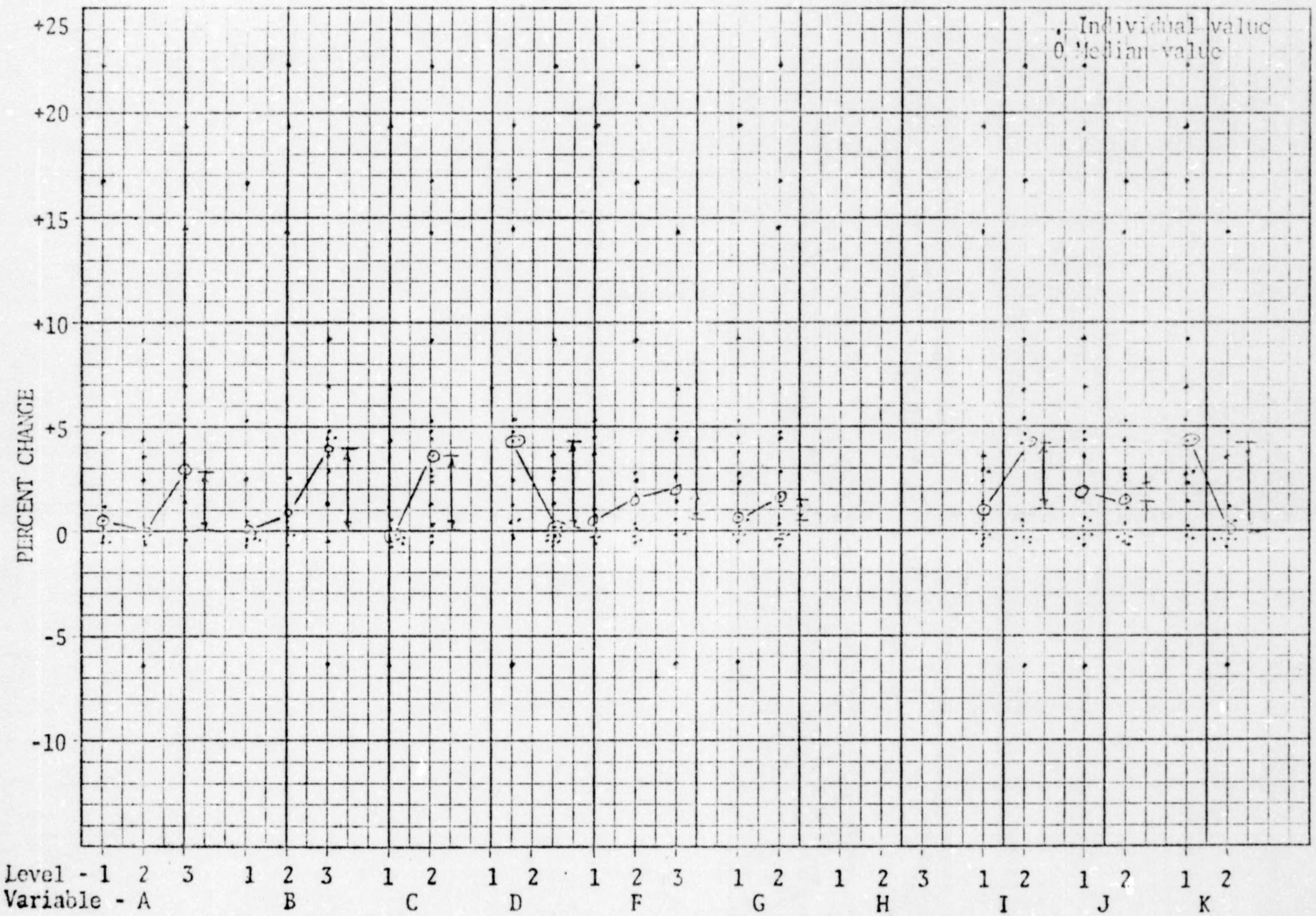

Fig. 11. - Percent change in resistance from exhaust through aging

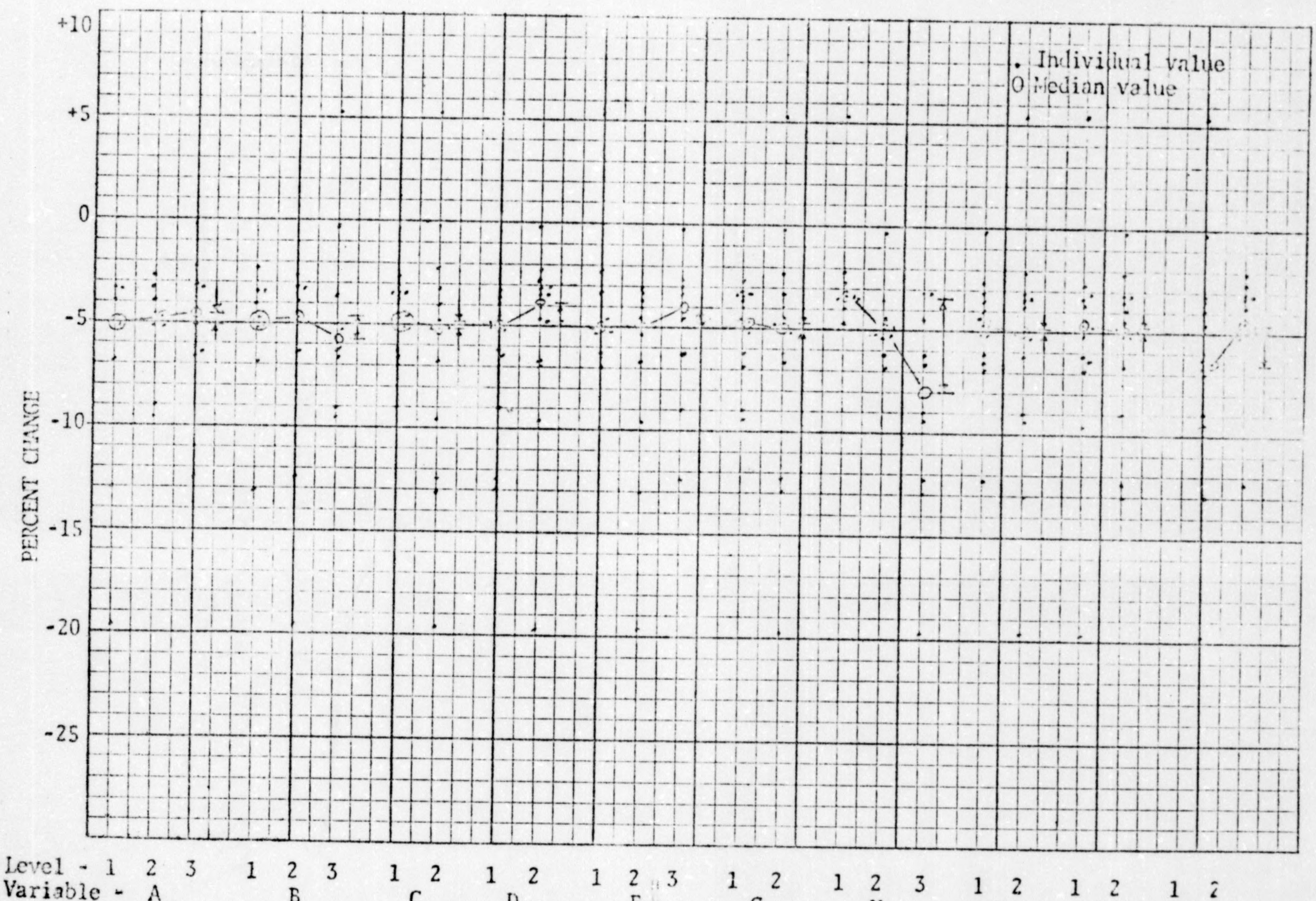

Fig. 12. - Percent change in resistance from aging through 16 hours of life test

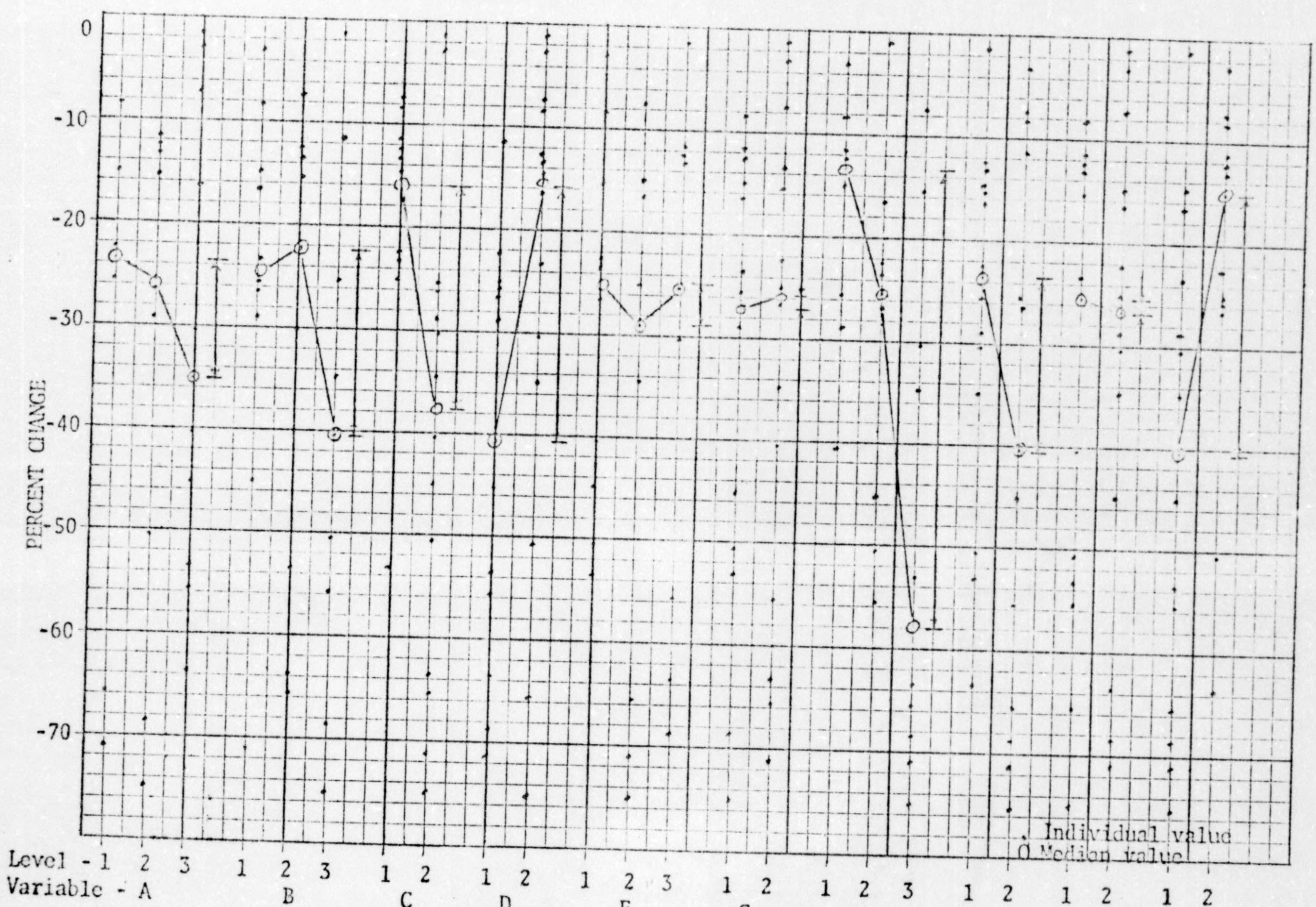

Fig. 13 - Percent change in resistance from initial values through 289 hours of life test

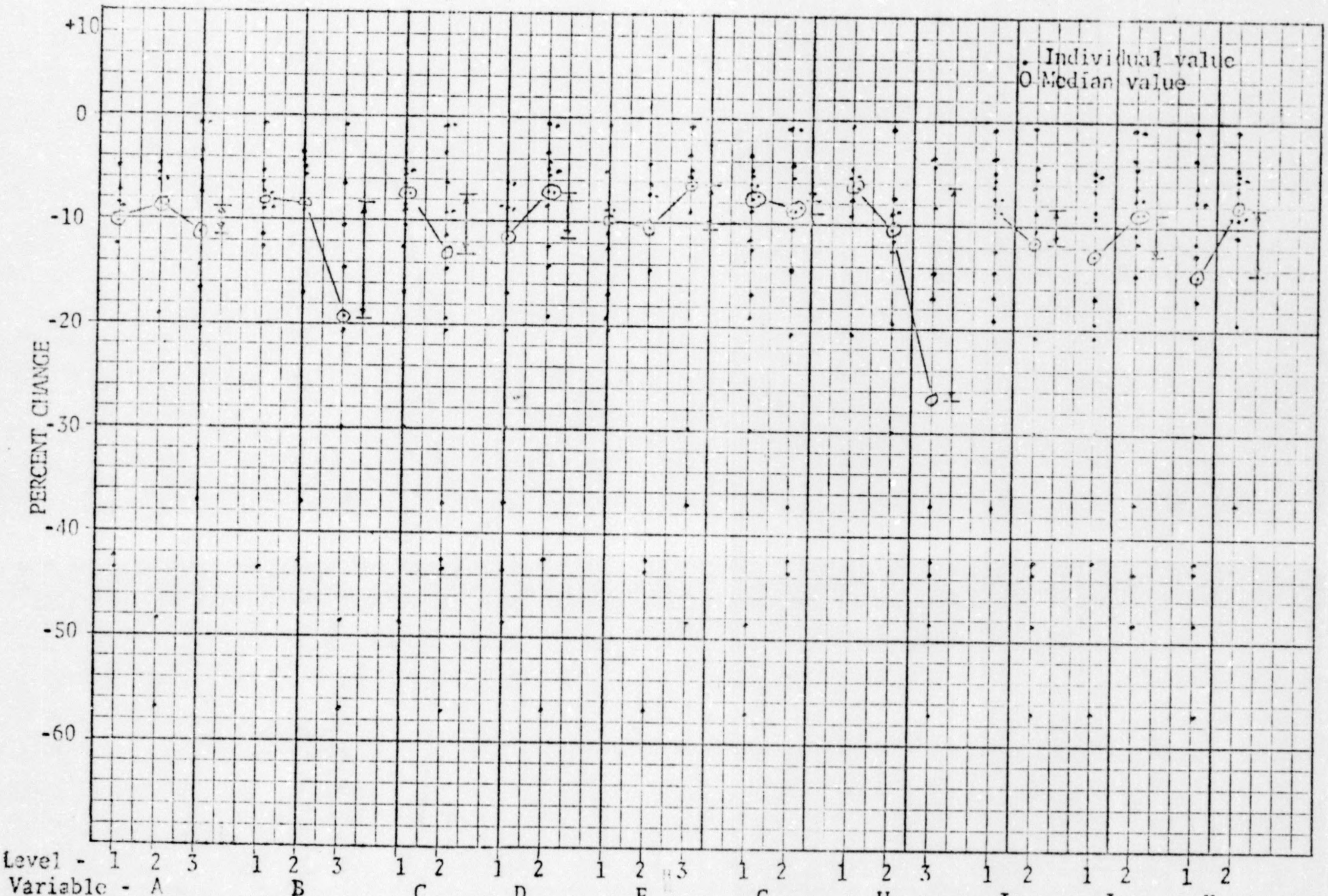

Fig. 14. - Percent change in resistance from exhaust through 289 hours of life test

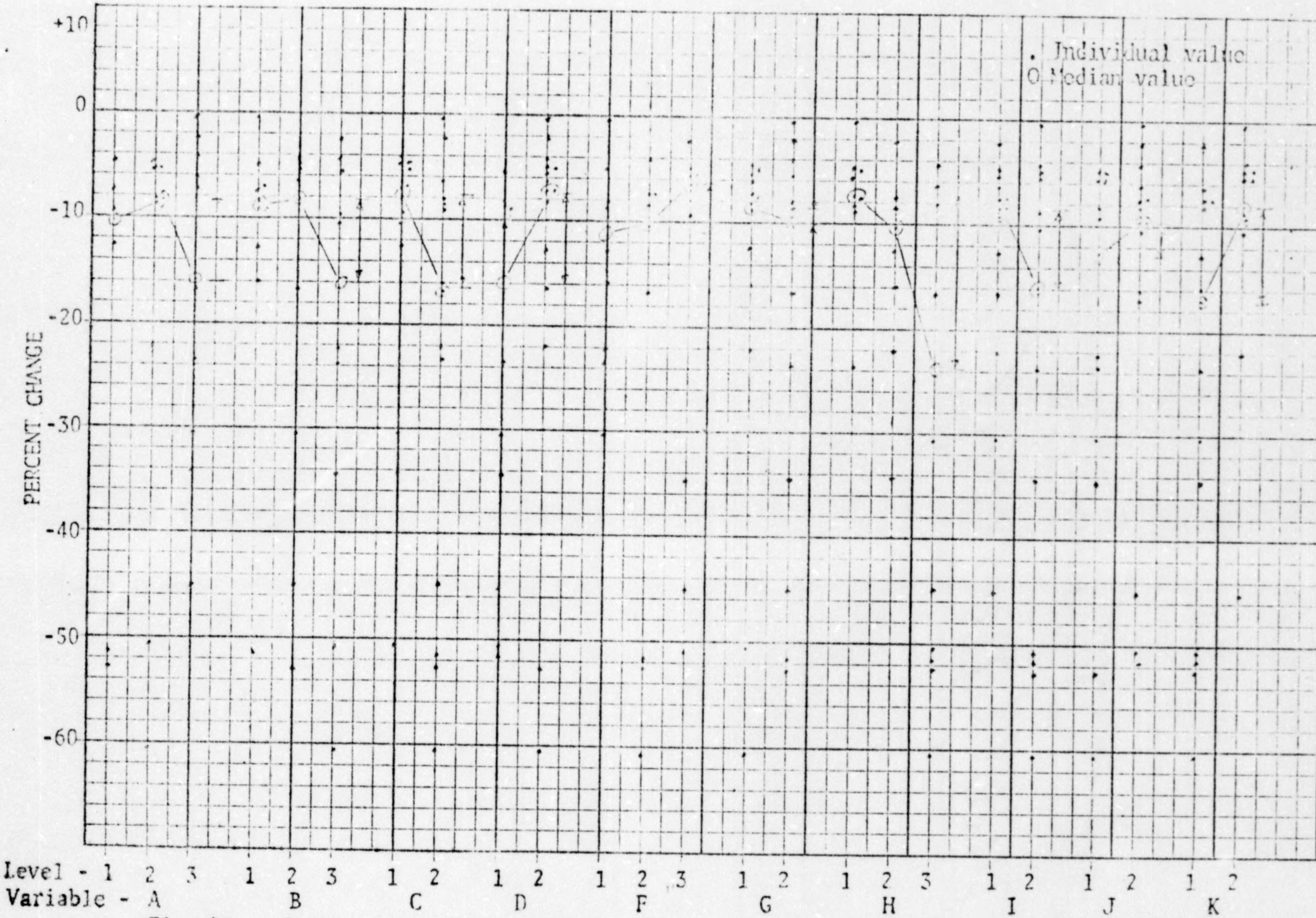

Fig. 15. - Percent change in resistance from aging through 289 hours of life test

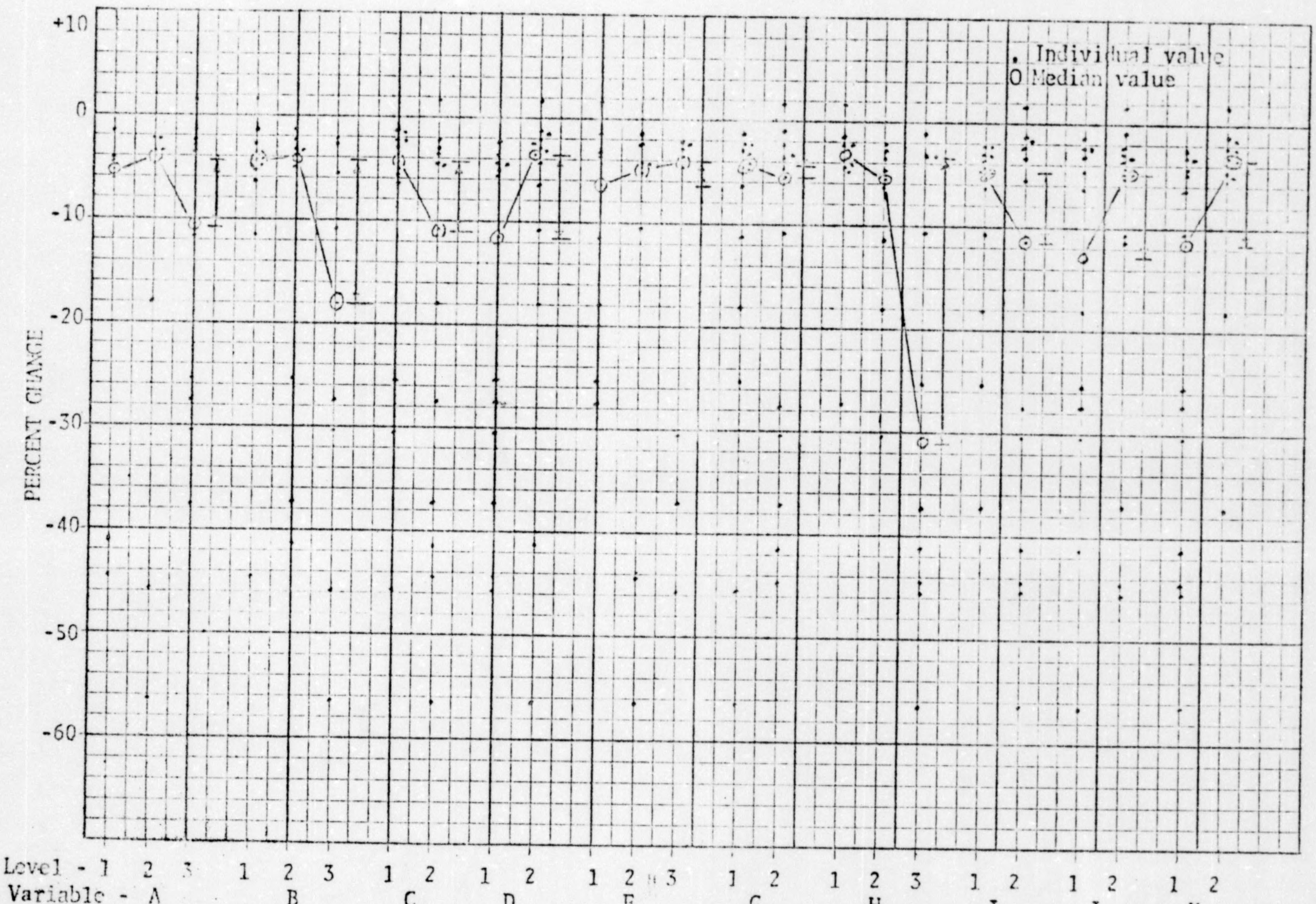

Fig. 16. - Percent change in resistance from 16 hours of life test through 289 hours of life test

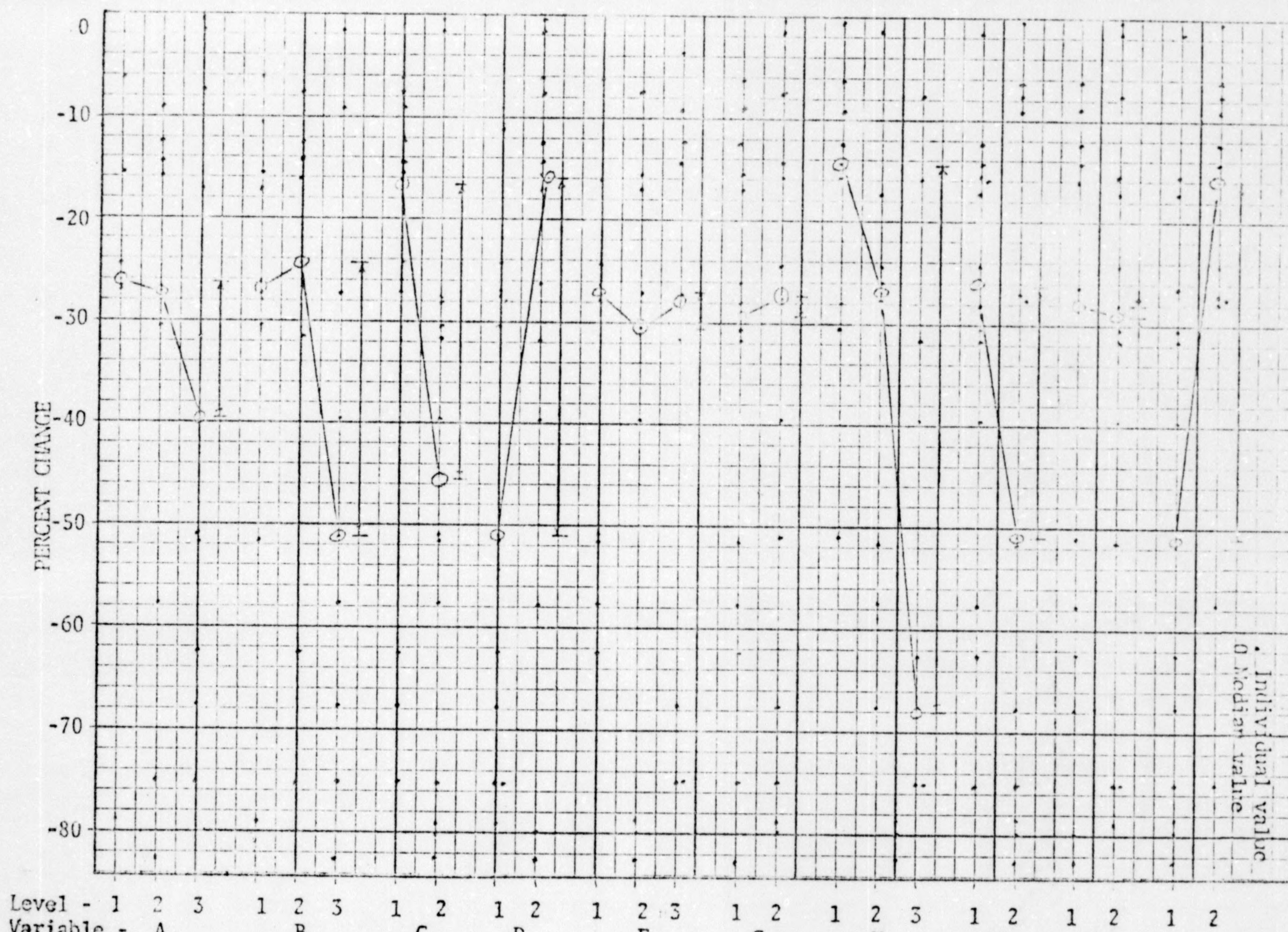

Fig. 17. - Percent change in resistance from initial values through 541 hours of life test

small resistance changes as shown in table 6.

TABLE 6. - Summary of test runs with less than 10% change in resistance due to life test

Individual Resistor Run #	Before Exhaust (ohms)	After Exhaust (ohms)	% Change from Initial	After 541 hrs. life test (ohms)	% Change due to life	Type of Resistor life
R1-1	1903	1914	+ .58	1869	-2.35	1/8W
R6-1	1719	1610	-6.35	1560	-3.1	0
R13-2	1813	1691	-6.72	1553	-8.15	0
R15-3	1423	1308	-8.08	1221	-6.65	0
R17-2	2184	2133	-2.34	2181	+2.25	0
R18-2	1731	1592	-8.0	1454	-8.7	1/4W
R22-3	1735	1604	-7.55	1520	-5.2	0
R25-1	1846	1783	-3.40	1706	-4.3	1/4W
R26-1	1927	1861	-3.42	1810	-2.74	0

The complete preliminary test data is shown in table 5 and appendix A. Table 5 includes individual values.

6. The plate aging step and grid lateral wire variables have very little effect on the resistance value when 541 hours of life test data was reviewed.

7. The resistor operation (with and without load) did not affect the operation or life of the 17BF11 tube. This is shown in table 7. The initial life test readings on section one are in error. Apparently this section oscillated on the test set. The section two plate current (I2p) and screen current (I2g2) levels are not right due to the necessity of an internal connection of grid #3 to cathode to permit separate pin connections for the resistor. The rest of the

TABLE 7. - Summary of 17BF11 life test with Pd-Ag resistor operation

Lot		681					682					683				
		Regular Life Test					Regular Life Test					Regular Life Test				
Misc.		Resistor Dissipation @ 0					Resistor Dissipation @ 1/8 W					Resistor Dissipation @ 1/4W				
Hours Life		0	16	289	541	Init. Limit	0	16	289	541	Init. Limit	0	16	289	541	Initial Limit
I1g1	Min.	.05	.02	0			.01	.01	0	0		.05	.01	0	0	µa
	Avg.	.13	.09	.04	.02		.09	.07	.04	.05		.14	.01	.05	.004	µa
	Max.	.28	.26	.11	.10	1.0	.15	.45	.25	.45	1.0	.29	.05	.25	.02	1.0 µa
I1p	Min.	56.0	25.9	29.0	29.0	21	57.5	28.0	[illegible]	27.0	21	60.0	30.1	28.6	28.2	21 ma
	Avg.	68.3	32.9	34.1	33.5		68.1	35.7	32.6	35.1		67.2	35.0	34.2	33.2	ma
	Max.	84.0	36.9	37.8	37.1	51	92.5	47.9	45.0	39.9	51	78.0	41.8	42.1	40.5	51 ma
I1g2	Min.	5.05	.96	.80	.80		5.02	1.55	1.4	1.4		5.5	1.5	.96	.76	ma
	Avg.	5.58	1.13	1.67	1.69		6.18	1.72	1.66	1.59		7.09	1.85	1.81	1.72	ma
	Max.	9.20	2.0	2.0	2.30	8.5	7.70	2.79	2.50	2.25	8.5	13.5	2.39	2.69	2.11	8.5 ma
Po1	Min.	1.78	2.05	2.15	2.18	1.8	2.0	2.18	2.18	2.18	1.8	1.78	2.18	2.22	2.22	1.8 watt
	Avg.	2.0	2.32	2.34	2.34		2.03	2.34	2.28	2.27		1.94	2.37	2.33	2.35	watt
	Max.	2.18	2.50	2.50	2.50		2.15	2.52	[illegible]	2.52		2.18	2.60	2.52	2.52	watt
I2g1	Min.	.01	0	0	0		0	0	0	0		0	0	0	0	µa
	Avg.	.73	.17	.16	.18		.77	.23	.03	.10		.16	.21	.07	.36	µa
	Max.	2.70	.65	.91	.95	1.0	2.85	.91	.21	.50	1.0	.80	1.85	.42	1.30	1.0 µa
I2p	Min.	1.14	1.65	1.71	1.24	1.0	1.82	1.87	1.71	1.71	1.0	1.76	1.85	1.78	1.81	1.0 ma
	Avg.	2.10	2.02	1.98	1.98		2.11	2.06	1.89	1.88		2.10	2.14	2.07	2.03	ma
	Max.	2.31	2.25	2.11	2.11	1.8	2.25	2.25	2.01	1.99	1.8	2.30	2.35	2.30	2.32	1.8 ma
I2g2	Min.	1.14	1.18	1.31	1.24	1.5	1.29	1.25	1.10	1.06	1.5	1.24	1.29	1.30	1.24	1.5 ma
	Avg.	1.38	1.32	1.36	1.31		1.37	1.39	1.31	1.25		1.44	1.43	1.41	1.33	ma
	Max.	1.62	1.38	1.48	1.38	2.5	1.56	1.51	1.42	1.35	2.5	1.67	1.61	1.61	1.55	2.5 ma
Accum. Tube Defects			0	0	0			0	0	0			0	0	0	
Test Rating			100	100	100			100	100	100			100	100	100	

Life Conditions

Life Conditions			End Points	Req. Rating
E_f=17.6V	R_{1g1}=1.0 megohm	R_{2k}=150 ohm		
$E_{1g2}=E_{2g2}$=150V	R_{1k}=80 ohm	$R_{2g1}=R_{2g3}$=.5 megohms	Po1=1.2 watts	90%
E_{1p}=150V	E_{2p}=300V	E_{HK}=-180V		

regular life test readings are the same as those expected on normal regular life test.

8. The resistors which decreased the most on exhaust processing continued to decrease on life test. These same resistors had the maximum change or resistance decrease on life test.

9. The resistors which decreased by less than 10% on exhaust processing had a less than 10% decrease in resistance value due to life test.

10. The 541 hour life test data showed simultaneous lighting and conduction heating with normal alloy cathodes was preferred. There was a -35% drop in median resistance value due to the early lighting as shown in figure 17. (Initial value through 541 hours of life.) There was a -25% drop in median resistance values due to usage of passive alloy cathodes as shown in figure 17. Additional data shown in figures 18, 19, 20 and 21 confirm the above observation.

11. Since there are seven very significant variables out of ten, it would be difficult to extract any additional information from the random balance test by use of further statistical methods. Six of the variables have about the same median level as shown in figure 21.

B. Various Atmospheres

1. Hydrogen

A 17BF11 cage with resistor was sealed without forming gas and placed on a mass spectrometer with a

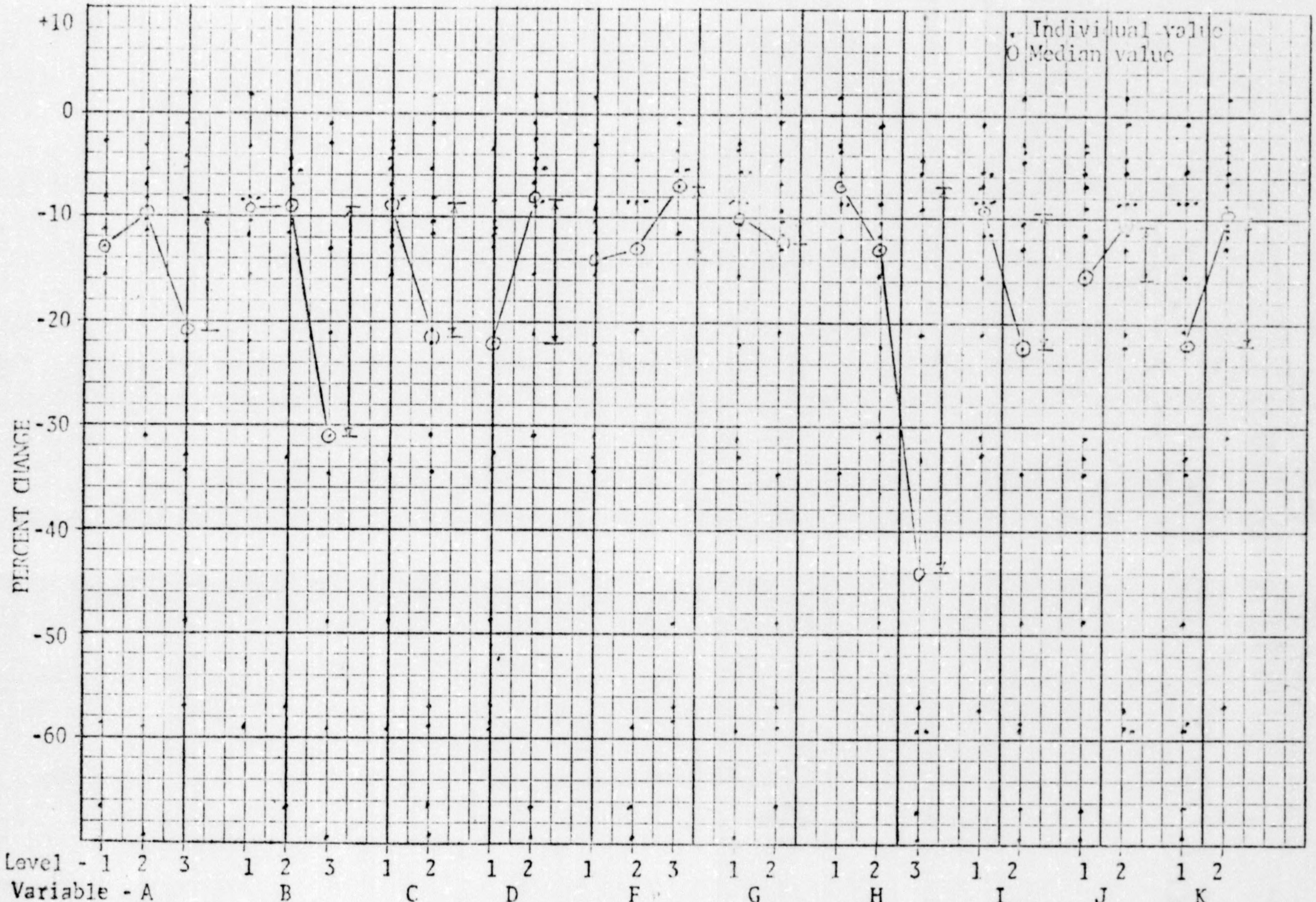

Fig. 18. - Percent change in resistance from exhaust through 541 hours of life test

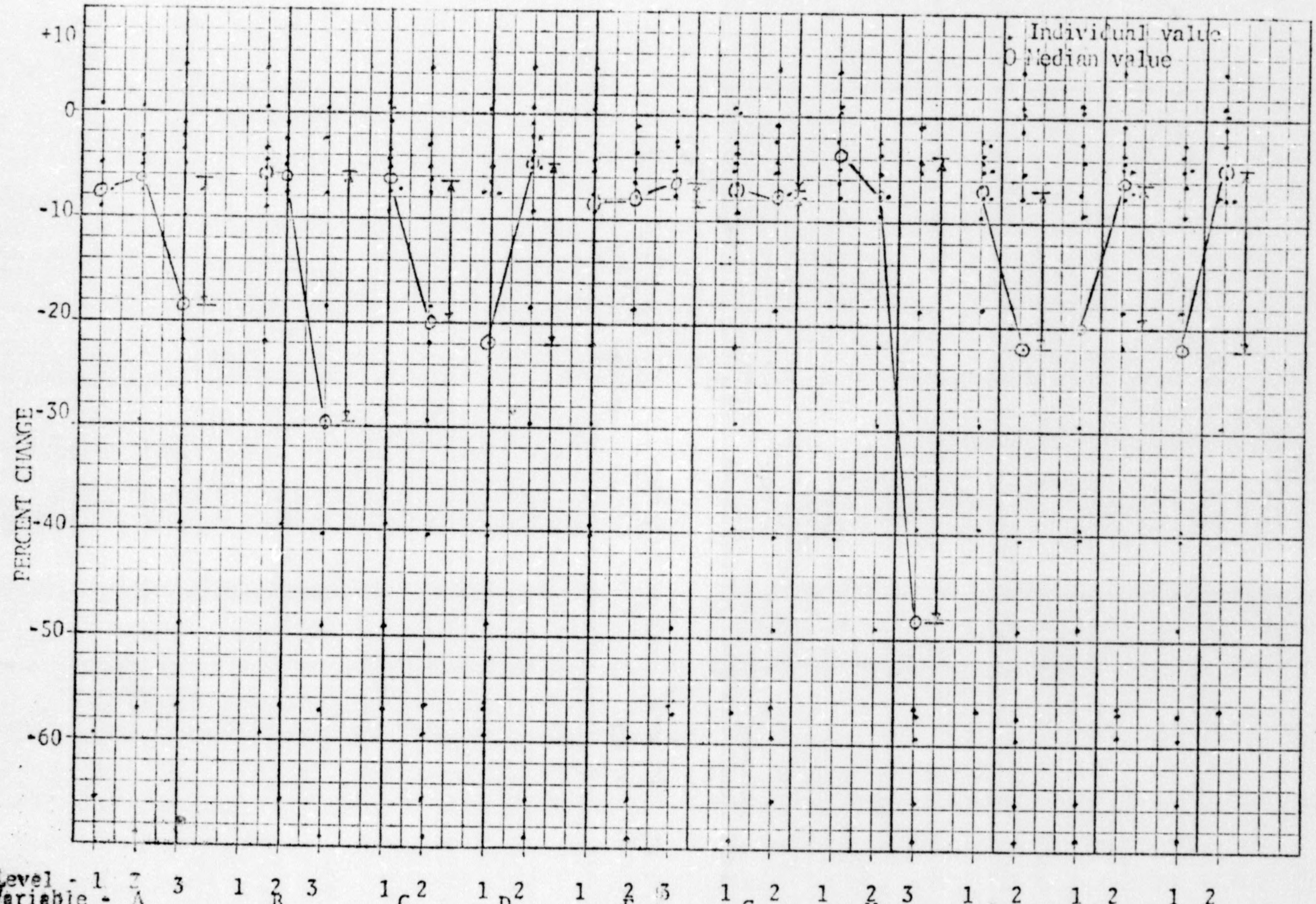

Fig. 19. - Percent change in resistance from 16 hours of life test through 541 hours of life test

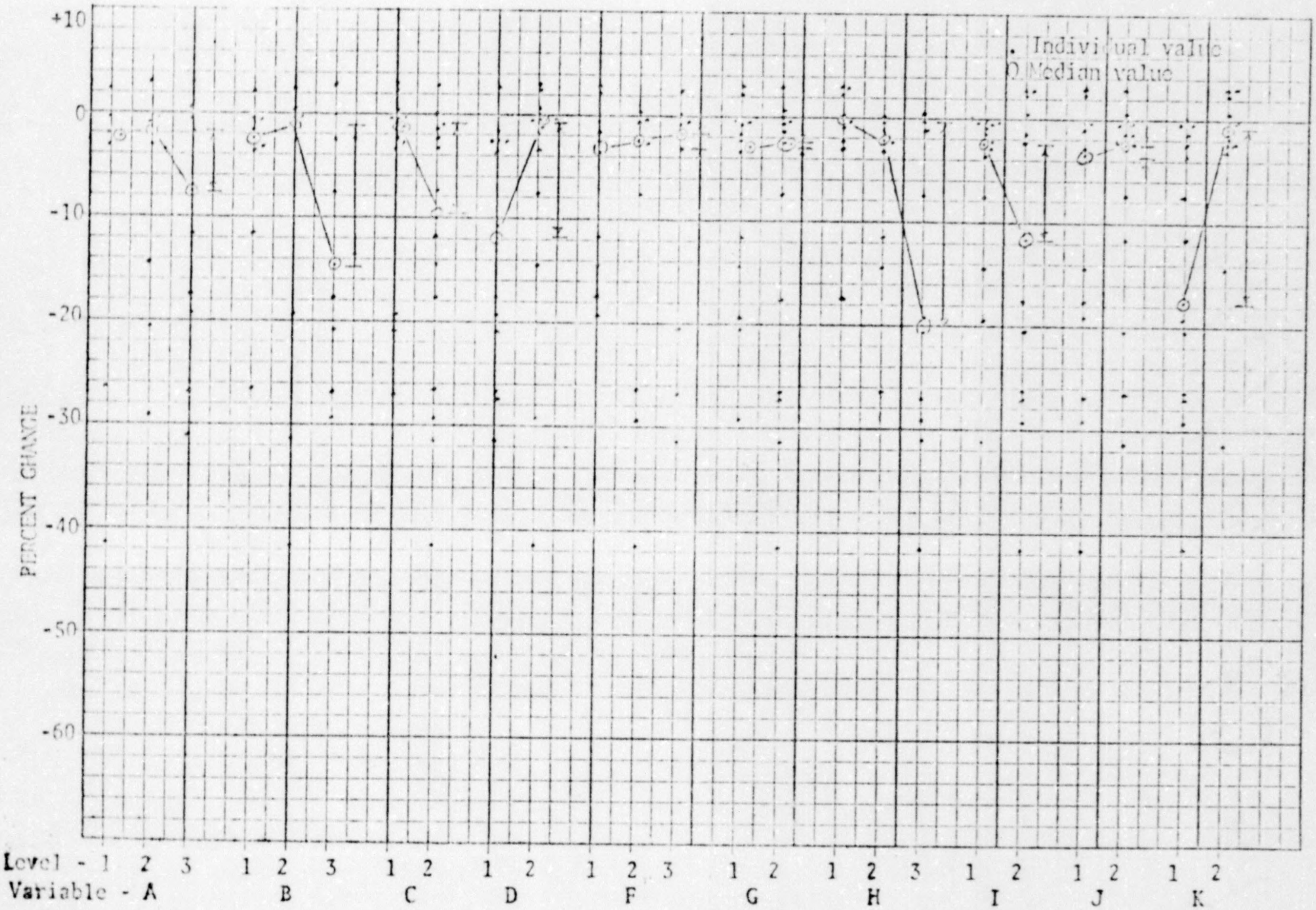

Fig. 20. - Percent change in resistance from 289 hours of life test through 541 hours of life test

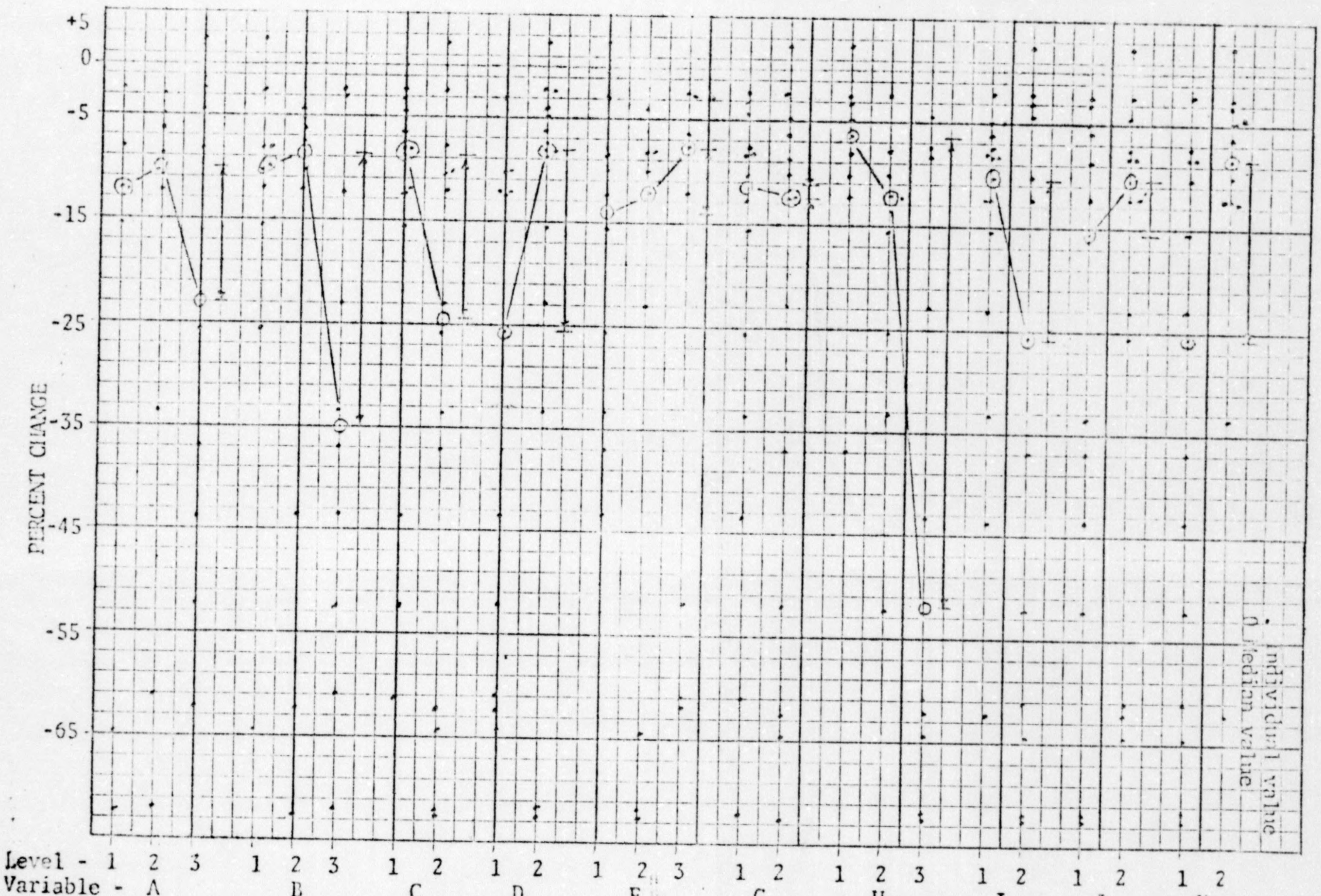

Fig. 21. - Percent change in resistance from aging through 541 hours of life test

pressure of 10^{-3} torr. The mass spectrometer was a model 21-620 manufactured by Consolidated Engineering Corporation, Pasadena, California. A flask was filled with hydrogen and slowly released in the tube. Then the tube could be isolated from the system and a resistor reading taken.

The data for this experiment is shown in table 8. The tube, with 4700 10^{-6} mm of hydrogen and filament on, was left for 20 or 30 minutes. Under these conditions hydrogen had no effect on a hot or cold resistor.

TABLE 8. - Hydrogen test on resistor R1-3

OHMS	BACK-FILLED H_2 PRESSURE	MISCELLANEOUS
1 831	0.	Without Filament
1 831	.55 x 10^{-6} mm	" "
1 831	1.1	" "
1 831	1.7	" "
1 831	3.08	" "
1 831	4.7	" "
1 831	11.3	" "
1 831	22.0	" "
1 831	49.0	" "
1 833	100.0	" "
1 833	214.0	" "
1 832	510.0	" "
1 833	1000.0	" "
1 833	2080.0	" "
1 929	310.0	With Filament
1 934	502.0	Ef = 17.0
1 930	1000.0	"
1 932	1780.0	"
1 945	2000.0	"
1 946	2950.0	"
1 948	4700.0	"
1 833	4700.0	Without Filament
1 831	0.	" "

2. Forming Gas

There are two sources of hydrogen in tube processing. The metal parts give off hydrogen when heated and the forming gas which contains 3% hydrogen. Forming gas, AGA Class 223, has the following normal compostion, percent by volume: (14)

N_2	96.9
CO	0.05
CO_2	0.05
H_2	3.0

A two-by-two factorial test was designed to evaluate the forming gas. The test design and results are shown in table 9. Encapsulation of the resistor confined the change of resistance due to sealing and exhaust to limits of $\pm$ 1%. Encapsulation would certainly be a solution in eliminating large variations in resistors due to processing.

It would, however, be highly desirable from a manufacturing viewpoint to eliminate the encapsulation process when placing the resistor inside a vacuum tube. The data shown in table 9 for lots S2 and S3 (with and without forming gas, unencapsulated resistors) is not conclusive. It is very evident that there is a variable or combination of variables that cause an average -16.0% drop in resistance value on the exhaust machine.

An additional test was run as shown in table 10. A control lot T1 was compared to lot T2 (removal of heater and cathode) and lot T3 (removal of grids,

TABLE 9. - Two-by-two factorial test* (Resistance values in ohms)

	Before exhaust	After exhaust but not flashed	After flashing of getter	% Change from initial	After aging 2 min Ef=30V; 30 min Ef=18V, Ip=38 ma		Before exhaust	After exhaust but not flashed	After flashing of getter	% Change from initial	After aging 2 min Ef=30V; 30 min Ef=18V, Ip=38 ma
S1-1	2765	2756	2763	- .07	2752	S3-1	3549	2938	2900	-18.4	2919
S1-2	3487	3503	3492	+ .14	3488	S3-2	2735	2249	2214	-19.0	2245
S1-3	2868	2890	2885	+ .59		S3-3	1865	1336	1298	-30.3	1325
S1-4	2495	2510	2495	.00		S3-4	1766	1419	1408	-20.2	
S1-5	3318	3311	3315	- .09		S3-5	1836	1405	1388	-24.5	
S1-6	3426		3420	- .17		S3-6	1832		1342	-26.7	
S1-7	2617		2573	- 1.68		S3-7	1742		1190	-31.6	
S1-8	3370		3370	.00		S3-8	2154		1677	-22.1	
S1-9	2863		2840	- .81							
S1-10	2604		2604	.00							
S2-1	1680	1298	1295	-23.0	1275	S4-1	3468	3465	3477	+ .26	3465
S2-2	1696	Open				S4-2	2538	2550	2542	+ .16	2535
S2-3	3750	3275	3262	-13.0	3267	S4-3	3464	3528	3519	+ 1.58	
S2-4	2084	1876	1864	-10.5	1837	S4-4	2960	3035	2957	- .10	
S2-5	1814	1447	1464	-19.4		S4-5	3306	3334	3333	+ .82	
S2-6	1856		1417	-23.7		S4-6	3133		3133	.00	
S2-7	1658		1407	-16.1		S4-7	2749		2729	- .73	
S2-8	3615		3019	-16.5		S4-8	3144		3130	- .45	
S2-9	1598		1459	- 8.75		S4-9	3444		3433	- .32	
S2-10	2151		1679	-21.9		S4-10	2894		2888	- .21	

* Lot S1 Resistor with encapsulation with forming gas
S2 Resistor without encapsulation without forming gas
S3 Resistor without encapsulation with forming gas
S4 Resistor with encapsulation without forming gas

Construction of the 17BF11 cage and processing was as follows:

A1 - 700 ma filament lighting
B2 - Normal bombardment
C1 - 600 tubes/hour
D2 - Simultaneous bomb. and lighting

I1 - Normal cathode alloy K22-K09
J1 - Permanickel grids
K2 - Unconverted alclad plates

TABLE 10. - Parts removal and exhaust processing test

Test	Before Exhaust	After Complete Exhaust Process	After Exhaust with seal and tipoff only	% Change from Initial	After Aging - 2 min Ef=30V; 30 min Ef=18V, Ip=38ma	Construction
T1-1	2650					Lot T1 had a full cage and was used as a
T1-2	2370	1549		-34.6	1565	control. Construction of the 17BF11 cage
T1-3	2060	1399		-32.1	1407	and processing was as follows:
T1-4	3740	2769		-25.9	2793	A1- 700ma filament lighting
T1-5	3302	2443		-26.8		B2- Normal bombardment
T1-6	2152					C1- 600 tubes/hour
T1-7	3132					D2- Simultaneous bomb. and lighting
T1-8	2112		2107	- .24		I1- Normal cathodes alloy K22-K09
T1-9	2615		2600	- .56		J1- Permanickel grids
T1-10	3255		3252	+ .09		K2- Unconverted alclad plates
T2-1	1905	1501		-21.6		Lot T2 was the same as Lot T1 except for
T2-2	1866	1415		-24.1		removal of heater and cathode.
T2-3	2854	2367		-17.0		
T2-4	2534	2058		-18.9		
T2-5	1964	1902		- 3.2		
T2-6	3284					
T2-7	2260					
T2-8	2690		2693	+ .11		
T2-9	2730		2720	- .37		
T2-10	1860		1864	+ .22		
T3-1	2420					Lot T3 was the same as Lot T1 except for
T3-2	2059	1612		-21.7		removal of grids, beam plate and
T3-3	2453					section 2 plate.
T3-4	2333	1858		-20.3		
T3-5	Open					
T3-6	2578					
T3-7	1878					
T3-8	2048		Open			
T3-9	2317		2242	- 3.24		
T3-10	2447		2447	.00		

beam plate and section 2 plate). Three tubes from each lot were sealed as per standard practice with forming gas and evacuated on the machine. No filament lighting was applied and the induction (bombarder) heat was turned off. Under these conditions the forming gas has a very, very small effect on the resistor.

Ten tubes from lot S were placed on life test. The encapsulated resistor have a median change of -.073% in 504 hours of life as shown in table 11. This confirms the previous statement that encapsulation would certainly be a manufacturing solution in eliminating large variations in resistors due to processing.

TABLE 11. - Resistor life test summary for two-by-two factorial test * lot 774

	0 Hr. (ohms)	16 Hr. (ohms)	247 Hr. (ohms)	504 Hr. (ohms)	% Change Due to Life
S1-1	2752	2733	Open	2750	- .073
S1-2	3488	3477	3414	3204	- 8.142
S2-1	1275	1207	1099	1050	- 17.647
S2-3	3267	3037	2877	2797	- 14.386
S2-4	1837	Open	Open	Open	--
S3-1	2919	2747	2597	2527	- 13.429
S3-2	2245	2117	1995	1919	- 14.521
S3-3	1325	1259	1138	1067	- 19.471
S4-1	3465	3459	3468	Open	--
S4-2	2535	2539	2556	2567	+ 1.262

* Lot S1 - Resistor with encapsulation with forming gas
S2 - Resistor without encapsulation without forming gas
S3 - Resistor without encapsulation with forming gas
S4 - Resistor with encapsulation without forming gas

The unencapsulated resistors had approximately the same decrease in resistance value due to life as experienced in the random balance test. The average median change was -14.521% as shown in table 11.

The resistor, whether encapsulated or unencapsulated, did not affect the performance of the 17BF11. A summary of the life test data is shown in table 12. If the resistor were to affect tube performance, one would expect poisoning of the cathode and lower levels of plate current, power output, etc.

3. Water Vapor

A recent test of preconverted and unconverted alclad plates by Bernard Grady of the General Electric Tube Department indicates water as a source of trouble. Converted alclad plates evolve low H_2 and H_2O levels when heated by r.f. for 20 seconds. This is shown in figure 22.

Unconverted alclad plates evolve high H_2 and low H_2O levels under r.f. heating for 20 seconds. A tube will certainly be heated by r.f. for more than 20 seconds.

The good results with the use of unconverted alclad plates in the random balance test, the hydrogen experiments and the above information confirm the observation that the presence of H_2 in the tube is not detrimental to the resistor performance.

TABLE 12. - Life test summary for two-by-two factorial test, 17BF11 characteristics

Lot		774			
		Regular life test*			
Misc.		Resistor dissipation @ 1/8 watt			
Hours Life		0	16	247	504
I1g1	Min.	.05	0	0	0 μa
	Avg.				
	Max.	6+	6+	6+	4.8 μa
I1p	Min.	37.8	33.9	33.2	31.0 ma
	Avg.	41.99	39.26	37.63	35.3 ma
	Max.	47.0	42.9	41.1	40.0 ma
I1g2	Min.	2.00	2.05	1.90	1.79 ma
	Avg.	2.46	2.57	2.39	2.24 ma
	Max.	2.90	3.20	2.85	2.75 ma
Po1	Min.	2.43	2.52	2.43	2.22 w
	Avg.	2.52	2.58	2.53	2.36 w
	Max.	2.75	2.75	2.70	2.55 w
I2g1	Min.	0	0	0	0 μa
	Avg.	.01	0	.005	.012μa
	Max.	.05	0	.05	.05 μa
I2p	Min.	1.98	1.90	1.91	1.92 ma
	Avg.	2.07	2.00	2.04	2.05 ma
	Max.	2.20	2.11	2.19	2.19 ma
I2g2	Min.	1.36	1.22	1.30	1.32 ma
	Avg.	1.44	1.31	1.36	1.40 ma
	Max.	1.50	1.38	1.42	1.49 ma
Accum. Tube Defects		0	0	0	0
Test Rating		100	100	100	100

* Life Conditions

E_f=17.6V
$E_{1g2}=E_{2g2}$=150V
E_{1p}=150V
R_{1g1}=1.0 megohm
R_{1k}=80 ohm
E_{2p}=300V
R_{2k}=150 ohm
$R_{2g1}=R_{2g3}$=.5 megohms
E_{HK}=180V

* End Points

Po_1=1.2 watts

Req. Rating

90%

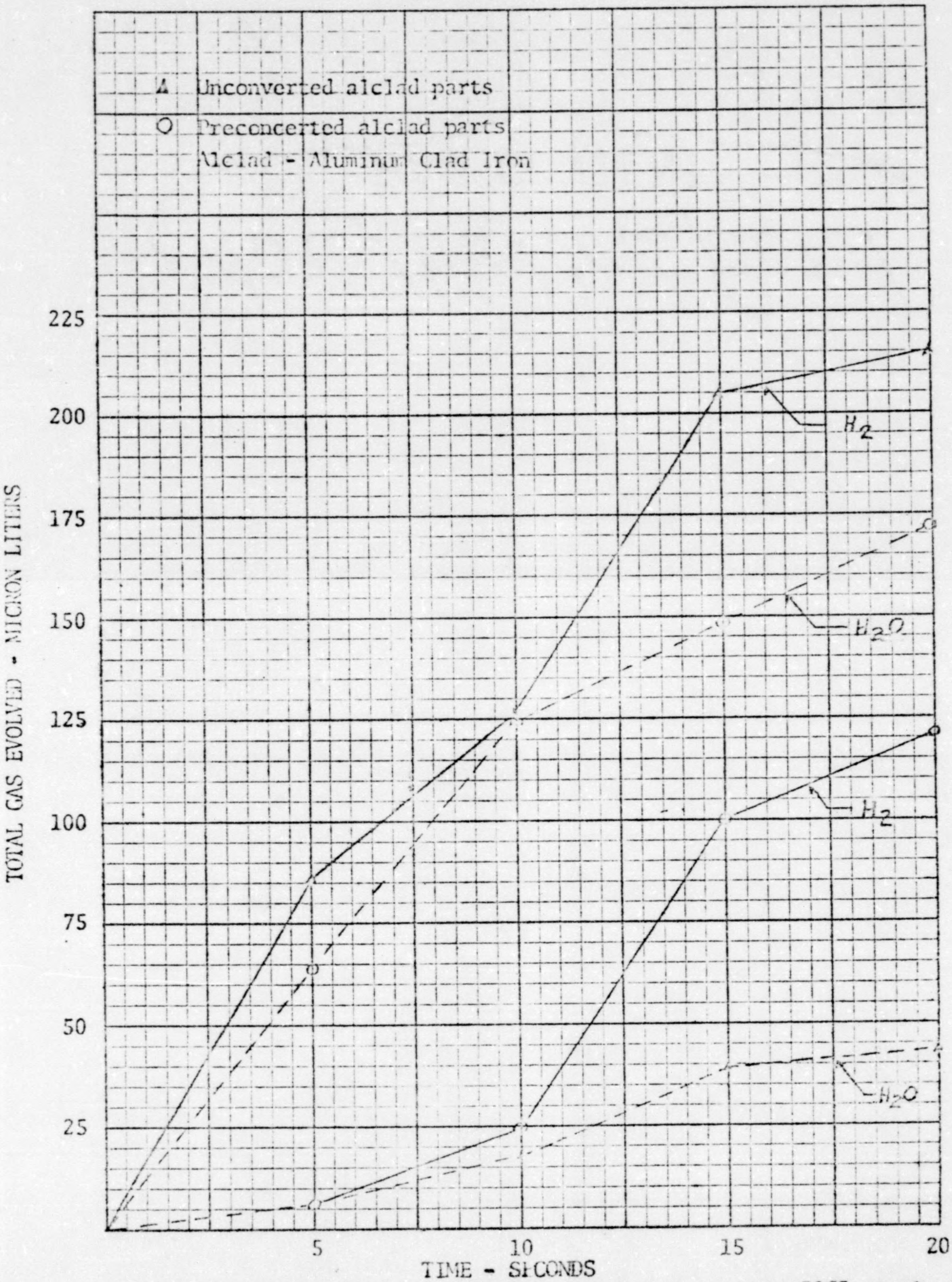

Fig. 22. - Hydrogen and water evolved from tube type 50C5 mount when induction heating is applied

C. High Vacuum

Will the resistor value change when it is placed in a vacuum? The unencapsulated resistor has a very, very small change in its resistance value because it is placed in a vacuum. This was apparent in seal and tip-off only test in table 10 where the median percent change from initial resistance value was -.09%. It was also evident in the two-by-two factorial test of table 9 where five tubes from each test lot (S1, S2, S3, S4) were checked before and after flashing of the getter. The flashing of the getter improves the vacuum level from 10^{-5} to 10^{-6} torr or lower. The median percent change of resistance value was -.23% in the four lots with a very tight grouping around the -.23% value.

D. Sublimation

The palladium-silver resistor was positioned across the large cathode sleeve of the vertical pentode section of the 17BF11 as shown in figure 7 on page 20. The 17BF11 has an integral heater with the connecting bar at the top. The heater bar is 3 mm above the top mica and only 2 mm from the bottom of the resistor substrate. The resistor was placed on top of the substrate in the random balance test tubes which were run for 541 hours of regular 17BF11 life test with direct current operation of the tube at near rated dissipation.

A large dark spot of sublimation was observed on the bottom of the substrate and directly over the large cathode sleeve in these 541 hour life test tubes. All tubes with the dark sublimation on the bottom of the substrate used the K22-K09 cathode alloys. This nickel sublimation from the cathode was independent of the life test wattage in the resistor.

A light spot of sublimation was observed on the substrates in the same position on the remaining tubes with K22-K09 alloy cathodes and one-third of the tubes with K51 alloy cathodes. This sublimation was also independent of the life test wattage in the resistor.

The other tubes with passive K51 cathode alloy had no visible sublimation after 541 hours of life. The K22-K09 alloy cathodes are prone to sublimate more than K51 alloy cathodes in vacuum tubes. Therefore, the sublimation in these tests is normal. Cathode sublimation may preclude usage of unencapsulated resistors in certain positions inside vacuum tubes.

In two cases sublimation occurred on top of the substrate around the platinum gold conductors. Both of these tubes had K22-K09 alloy cathodes and wattage in the resistor. There was also dark sublimation on the bottom of these substrates.

There were two tubes with no sublimation on the bottom of the substrate but they had feathering of the platinum gold conductor on top of the substrate. Each tube contained K51 alloy cathodes.

The visible sublimation in all of these tests did not cover the resistors and did not affect the resistance values. However, sublimation is a potential source of problems.

E. Reheating

The sealing of the glass bulb to the glass stem requires preheating of the glass. The preheat temperature of the glass, tube cage and substrate with resistor is approximately 100°C with all components exposed to air for several minutes.

These component parts are placed on the sealing portion of the exhaust machine where the glass bulb and stem are melted to form a seal. During the sealing cycle the internal components are at 400-450°C temperature for one minute. The forming gas fills the bulb to prevent oxidation of the metal parts. Will this reheating of the substrate affect the resistance value? The seal and tip-off only test shown in table 10 yielded a median percent change from initial resistance value of -.09%. The first firing of the silk screened resistor was 730°C in air. One would not expect the brief intervals of reheating below 730°C to seriously affect the resistance values. The reheating of the resistor in the sealing cycle can be neglected.

F. Effects of Previous Resistor Processing on Resistance Changes in Vacuum Environment

The evidence of -25 to -50% median change in resistor value due to exhaust, aging and life test in the preliminary tests certainly raises the question of effects of previous resistor processing on resistance changes in vacuum environment. An attempt to identify the significant variables of prior processing of resistors was a 2^6 factorial test as shown in table 13. The complete statistical design of the 64 combinations is shown in table 14.

TABLE 13. - Design of the 2^6 factorial test

Variables	Level 1		Level 2	
Conductor material	A1	Pd-Ag	A2	Ag
Squeegee speed	B1	2"/sec.	B2	1"/sec.
Drying time	C1	Force dry	C2	Air dry
Firing temperature	D1	730°C	D2	760°C
Air flow	E1	5 CFH	E2	10 CFH
Encapsulating	F1	Yes	F2	No

Each combination or test lot had five tubes and each 17BF11 vacuum tube contained a substrate with four different values of resistance. The four resistors had different designs of resistor area with all resistors using #7826 du Pont paste. The encapsulate material was #8125 du Pont paste. The resistor substrate was placed 9 mm above the 17BF11 top mica to minimize the substrate ambient temperature variable as shown in section G on page 67.

The variables C and D, drying time and firing temperature, were the major variables in the screened resistor. This was true for all four resistor values as shown in figures 23, 24, 25 and 26. Each level and variable shown in these illustrations is a median value of thirty-two test lots with five tubes each. Air dry and 730°C firing temperature combinations, variables C2 and D1, were the best for minimum change in resistor value.

TABLE 14. - Complete statistical design of the 2^6 factorial test

	Variables							Variables					
Run	A	B	C	D	E	F	Run	A	B	C	D	E	F
1	1	1	1	1	1	1	33	2	1	1	1	1	1
2	1	1	2	1	1	1	34	2	1	2	1	1	1
3	1	2	1	1	1	1	35	2	2	1	1	1	1
4	1	2	2	1	1	1	36	2	2	2	1	1	1
5	1	1	1	1	1	2	37	2	1	1	1	1	2
6	1	1	2	1	1	2	38	2	1	2	1	1	2
7	1	2	1	1	1	2	39	2	2	1	1	1	2
8	1	2	2	1	1	2	40	2	2	2	1	1	2
9	1	1	1	1	2	1	41	2	1	1	1	2	1
10	1	1	2	1	2	1	42	2	1	2	1	2	1
11	1	2	1	1	2	1	43	2	2	1	1	2	1
12	1	2	2	1	2	1	44	2	2	2	1	2	1
13	1	1	1	1	2	2	45	2	1	1	1	2	2
14	1	1	2	1	2	2	46	2	1	2	1	2	2
15	1	2	1	1	2	2	47	2	2	1	1	2	2
16	1	2	2	1	2	2	48	2	2	2	1	2	2
17	1	1	1	2	1	1	49	2	1	1	2	1	1
18	1	1	2	2	1	1	50	2	1	2	2	1	1
19	1	2	1	2	1	1	51	2	2	1	2	1	1
20	1	2	2	2	1	1	52	2	2	2	2	1	1
21	1	1	1	2	1	2	53	2	1	1	2	1	2
22	1	1	2	2	1	2	54	2	1	2	2	1	2
23	1	2	1	2	1	2	55	2	2	1	2	1	2
24	1	2	2	2	1	2	56	2	2	2	2	1	2
25	1	1	1	2	2	1	57	2	1	1	2	2	1
26	1	1	2	2	2	1	58	2	1	2	2	2	1
27	1	2	1	2	2	1	59	2	2	1	2	2	1
28	1	2	2	2	2	1	60	2	2	2	2	2	1
29	1	1	1	2	2	2	61	2	1	1	2	2	2
30	1	1	2	2	2	2	62	2	1	2	2	2	2
31	1	2	1	2	2	2	63	2	2	1	2	2	2
32	1	2	2	2	2	2	64	2	2	2	2	2	2

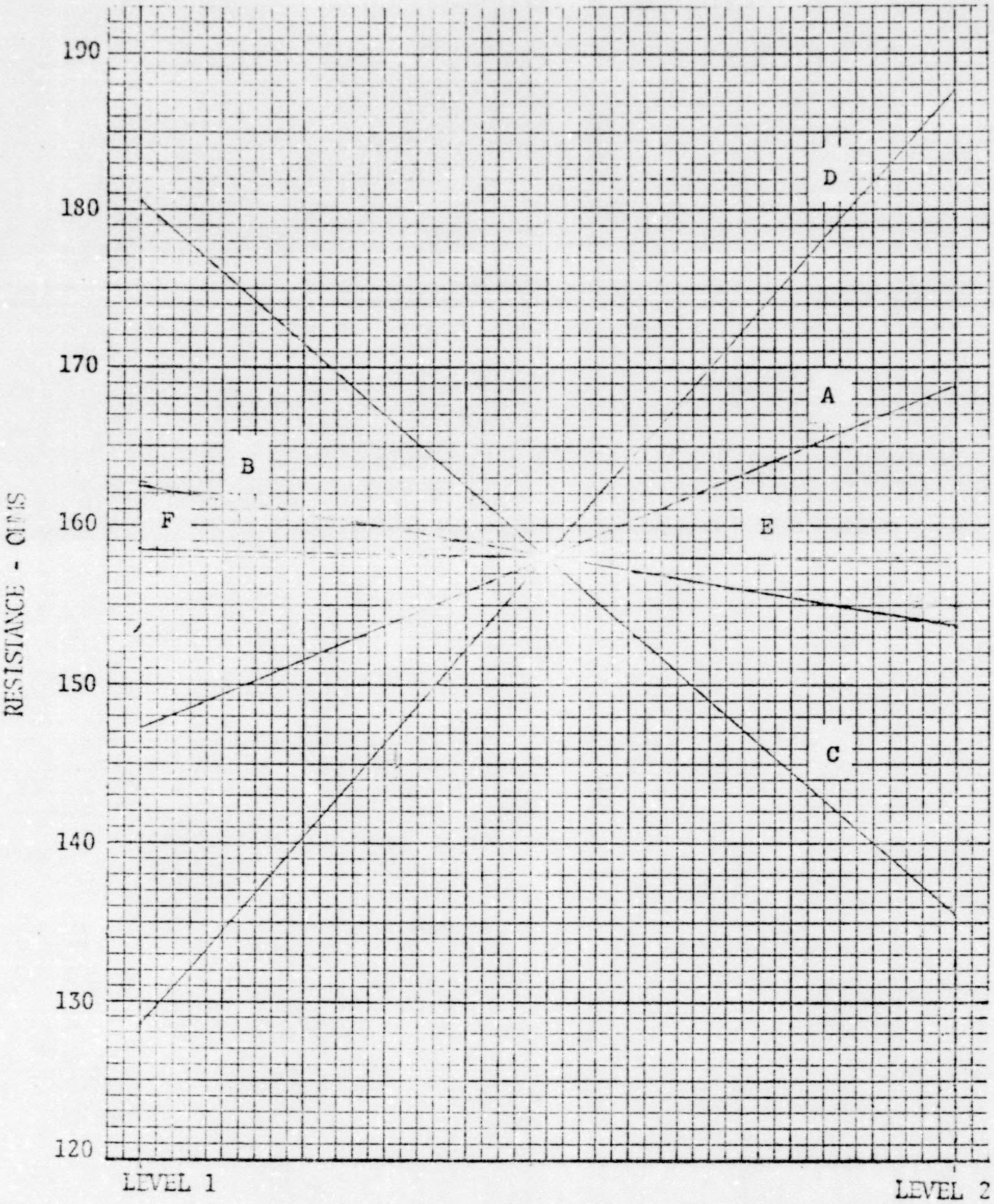

Fig. 23. - Summary of the effects of prior processing variables on resistor "a" in the 2^6 factorial test

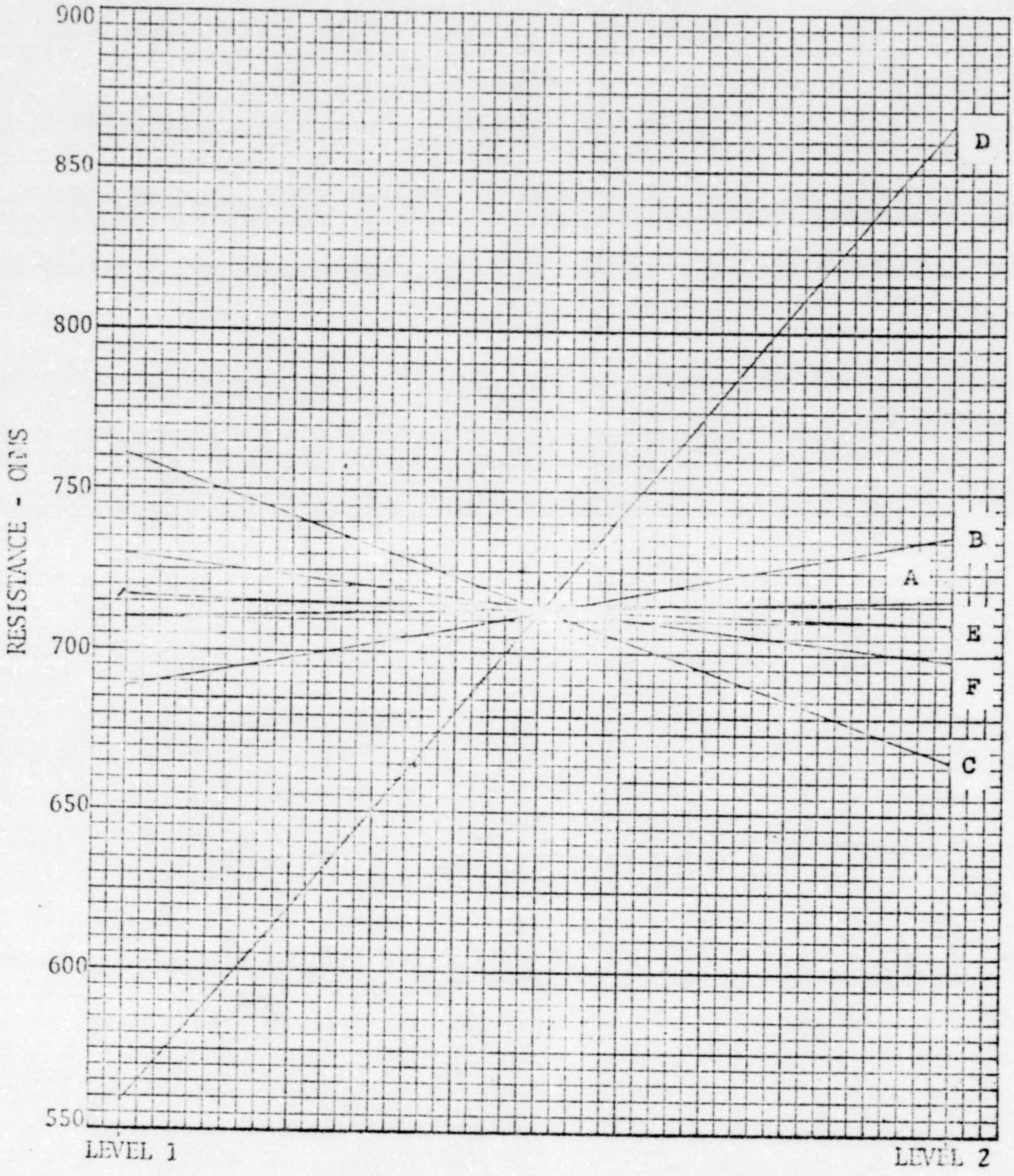

Fig. 24. - Summary of the effects of prior processing variables on resistor "b" in the 2^6 factorial test

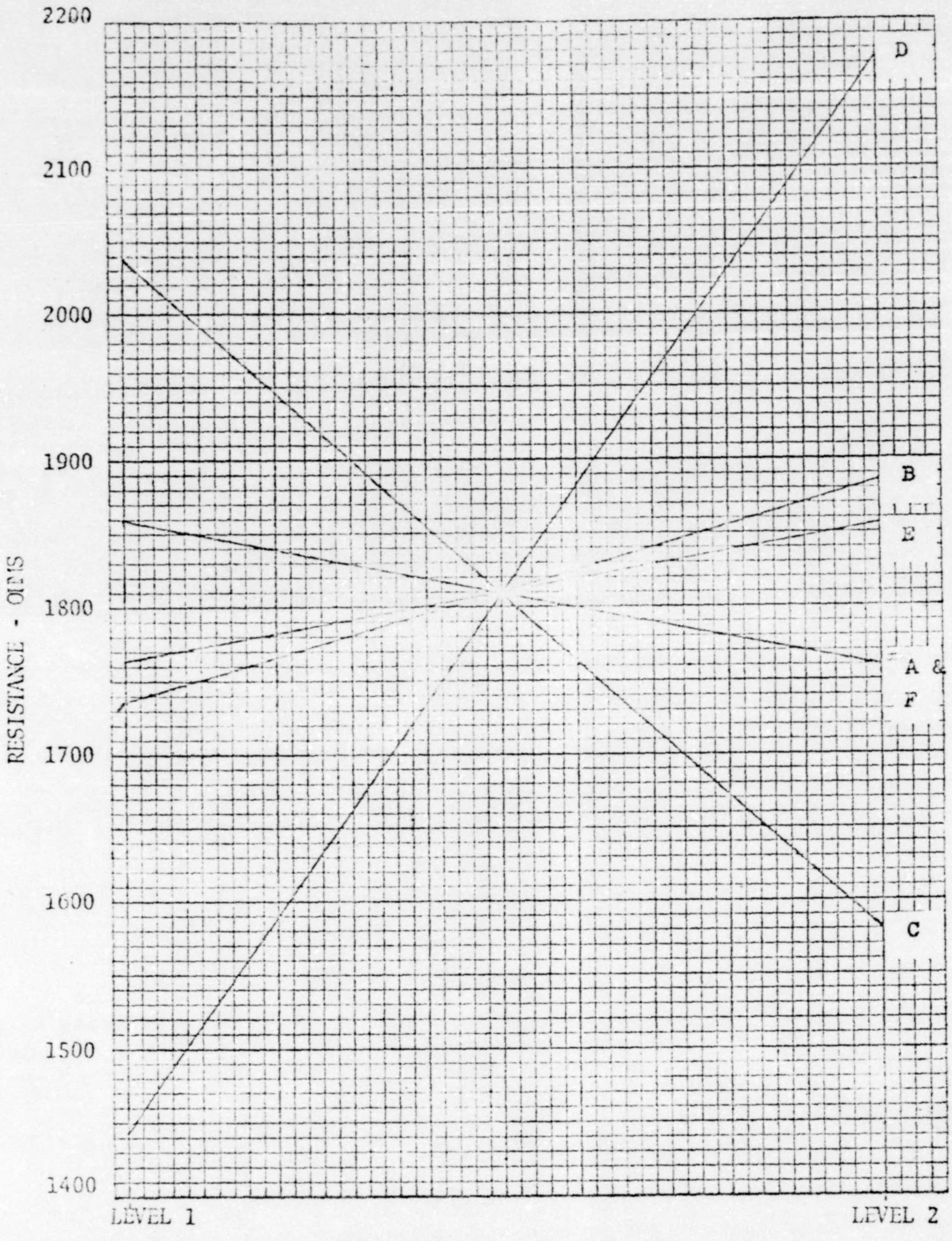

Fig. 25. - Summary of the effects of prior processing variables on resistor"c"in the 2^6 factorial test

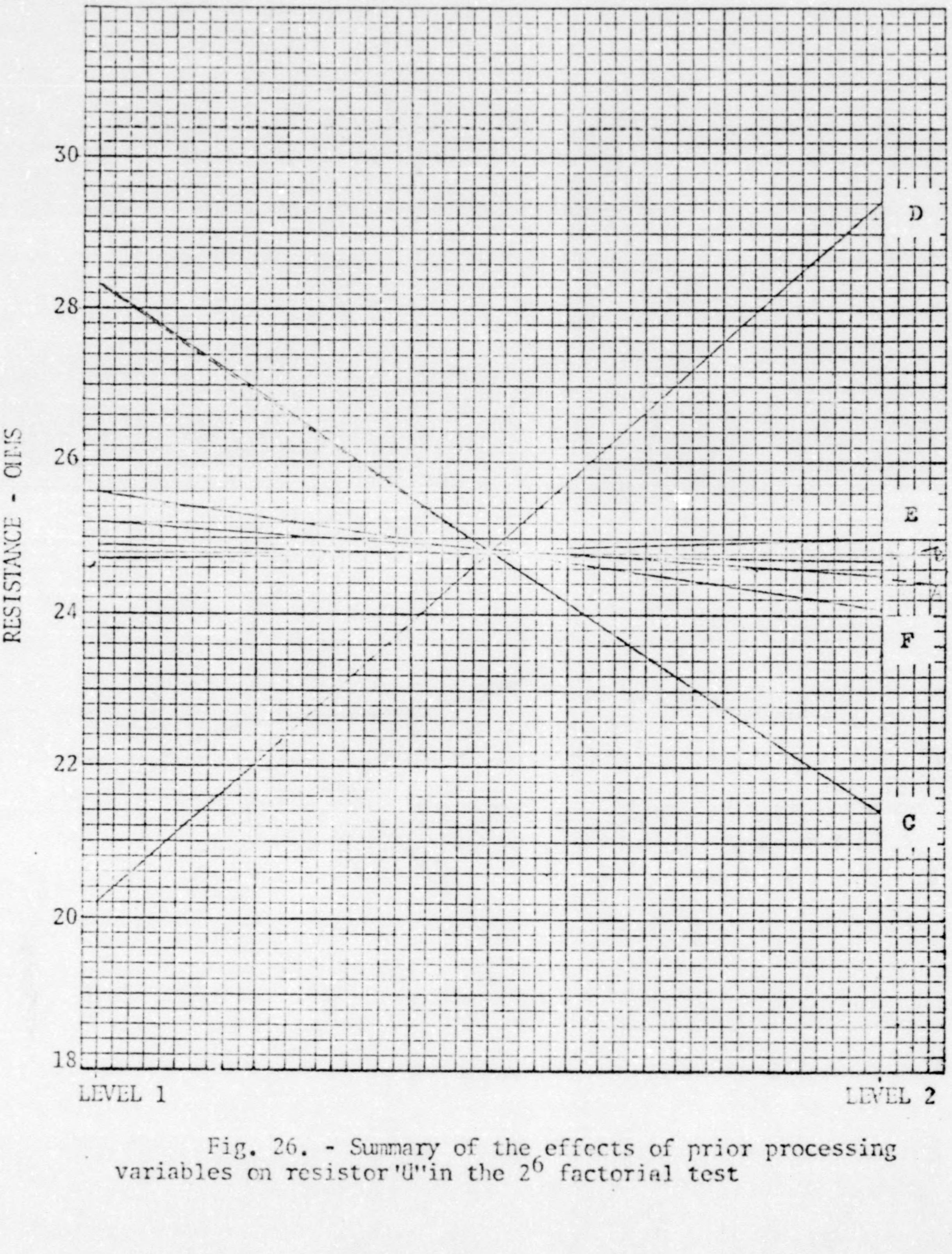

Fig. 26. - Summary of the effects of prior processing variables on resistor "U" in the 2^6 factorial test

The encapsulation of the printed resistors increased the resistance by approximately 5 to 10%. This was true for all four of the resistor values. This confirms previous random balance test observations that encapsulation increases the initial resistance value.

The 320 units used in evaluating the prior processing variables were then evacuated, etc. The combination of tube processing parameters selected was very similar to the R26 parameters of the random balance test with the most important feature being the use of unconverted alclad plates. The remaining tube materials and tube processing parameters were the same as those used in regular production. The tube processing parameters used in the 2^6 factorial test are shown in table 15.

TABLE 15. - Tube processing parameters for 2^6 factorial test

Variables		Level
A1	Filament lighting	700 ma
B1	Bombarder setting	High
C1	Exhaust machine speed	600 tubes/hr.
D2	Filament lighting sequence	Simultaneous
F1	Filament hot shot	38 volts for 2 minutes
G1	Plate step	Wp=3.6 watts for 30 min.
I1	Cathode alloy	Normal K22-K09
J2	Grid lateral wire	Silver plate nickel
K2	Plate	Unconverted alclad

The complete summary of the effects of vacuum tube processing on the 2^6 factorial test resistors is shown in tables 16, 17, 18, and 19. Each test run shown in the summary is a median value of three to five units. The following observations were made with respect to the 2^6 factorial test as shown in these tables:

TABLE 16. - Data summary for resistor"a"in 2^6 factorial test (Resistance values in ohms)

Run #	Before Exhaust	After Encapsulation	After Exhaust	After Aging	% Change Due to Exh. & Age	Run #	Before Exhaust	After Encapsulation	After Exhaust	After Aging	% Change Due to Exh. & Age
1	87.48	90.5	90.7	90.6	+ .11	33	151.86	158.3	157.78	157.96	- .215
2	144.85	153.55	153.6	153.35	+ .13	34	164.40	171.80	171.43	171.7	- .058
3	163.07	172.92	172.9	172.7	- .13	35	152.24	157.2	156.56	157.22	+ .013
4	99.13	104.97	105.0	104.9	- .067	36	107.28	112.4	112.24	112.28	- .011
5	95.9		96.0	95.92	+ .021	37	161.7		158.52	158.40	-2.041
6	143.4		143.5	143.44	+ .028	38	141.4		136.62	136.26	-3.635
7	153.52		154.2	153.75	+ .15	39	158.5		153.18	153.0	-3.47
8	108.62		108.9	108.87	+ .23	40	99.0		92.58	92.28	-6.788
9	84.96	92.7	92.6	92.6	- .108	41	139.47	139.52	142.37	142.45	+2.1
10	104.68	111.3	110.8	111.16	- .126	42	106.6	111.5	111.28	111.40	- .09
11	136.45	143.9	143.8	143.72	- .125	43	177.76	185.4	184.52	191.76	+3.41
12	89.05	92.4	92.4	92.34	- .065	44	99.26	103.3	102.84	105.42	+2.052
13	75.4		75.6	75.54	+ .186	45	112.2		109.52	109.32	-2.59
14	101.4		101.7	101.6	+ .197	46	104.2		100.18	100.82	-3.244
15	172.52		172.87	172.83	+ .18	47	182.8		177.84	181.98	- .449
16	93.6		93.92	93.8	+ .214	48	108.37		104.47	106.47	-1.753
17	167.54	175.4	175.0	175.02	- .217	49	254.5	275.0	274.16	274.56	- .160
18	200.93	220.33	220.07	219.96	- .168	50	207.45	219.02	217.36	218.45	- .260
19	158.2	165.95	165.7	165.75	- .121	51	148.06	157.7	156.54	157.06	- .406
20	104.6	111.23	111.1	111.13	- .09	52	109.36	115.16	114.53	115.40	+ .208
21	156.2		156.4	156.28	+ .051	53	330.13		316.90	316.93	-3.99
22	196.77		197.4	197.4	+ .320	54	178.87		165.3	167.90	-6.133
23	185.00		185.37	185.32	+ .173	55	175.7		165.78	166.10	-5.464
24	106.2		106.7	106.56	+ .339	56	125.6		114.64	114.70	-8.678
25	178.17	192.8	192.27	192.17	- .327	57	227.83	260.0	259.64	258.94	- .408
26	151.72	169.42	171.12	169.2	- .118	58	175.24	182.3	181.50	183.70	+ .768
27	239.4	263.7	263.90	263.86	+ .061	59	273.70	284.72	281.52	281.95	- .973
28	151.96	163.2	163.0	162.90	- .184	60	126.92	133.15		132.55	- .676
29	186.5		186.66	186.58	+ .043	61	223.8		214.54	212.8	-4.915
30	135.82		138.58	136.2	+ .280	62	135.7		126.80	126.24	-6.971
31	232.9		233.08	233.62	+ .309	63	278.02		266.53	266.1	-4.216
32	128.07		128.15	125.97	-1.64	64	147.3		138.56	138.06	-6.273

TABLE 17. - Data summary for resistor "b" in 2^6 factorial test (Resistance values in ohms)

Run #	Before Exhaust	After Encapsulation	After Exhaust	After Aging	% Change Due to Exh. & Age	Run #	Before Exhaust	After Encapsulation	After Exhaust	After Aging	% Change Due to Exh. & Age
1	311.14	328.8	329.3	328.28	- .158	33	265.0	298.2	296.90	297.14	- .355
2	750	784.75	784.3	782.9	- .236	34	776.83	807.13	801.96	802	- .636
3	830.2	883.0	882.6	880.6	- .272	35	767.7	794.3	788.98	789.12	- .652
4	463.95	485.95	485.5	485.7	- .051	36	502.2	525.0	523.26	523.58	- .270
5	336.0		336.0	335.9	- .03	37	266.2		260.7	260.84	-2.01
6	715.4		715.5	714.62	- .109	38	688.9		178.56	654.32	-5.02
7	759.52		761.8	759.4	- .016	39	764.1		734.0	733.0	-4.33
8	514.30		514.3	514.27	- .006	40	500.3		483.02	482.38	-3.582
9	341.96	370.4	370.2	369.42	- .265	41	221.1	230.80	230.27	230.12	- .29
10	536.66	568.4	566.8	566.74	- .292	42	515.3	534.6	533.82	534.70	+ .019
11	717.47	754.25	751.6	751.37	- .382	43	828.5	862.6	860.0	869.46	+ .795
12	452.42	468.7	468.97	469.25	+ .117	44	488.7	506.0	520.66	506.74	+ .146
13	305.6		305.4	304.6	- .327	45	239.1		233.20	233.02	-2.543
14	531.4		530.8	530.6	- .151	46	517.2		492.52	491.66	-4.938
15	816.7		833.97	834	+1.996	47	844.8		811.74	811.60	-3.93
16	463.9		463.46	463.44	+ .124	48	557.05		542.27	542.20	-2.666
17	815.76	856.2	853.2	853.8	+ .280	49	1058.0	1143.6	1140.0	1140	- .315
18	1038	1125.33	1120.66	1120.0	- .473	50	948.25	1002.2	997.53	999	- .319
19	840.15	879.40	876.7	876.7	- .307	51	683.4	731.0	727.36	727.6	- .465
20	581.25	617.72	612.5	612.55	- .837	52	610.23	629.96	627.1	628.33	- .259
21	802.0		801.9	801.34	- .082	53	1118.8		1077.0	1077	-3.736
22	987.75		980.44	989.25	+ .150	54	801.75		734.5	732.5	-8.637
23	997.50		998.25	997.75	+ .025	55	837.0		799.90	798.18	-4.636
24	571.2		571.0	570.58	- .109	56	651.4		598.50	598.76	-8.081
25	916	992.2	989.25	988.75	- .380	57	953.4	1010.7	1007.0	1007	- .366
26	807.25	886.50	887.48	887.25	+ .085	58	701.6	754.8	746.26	751.06	- .495
27	1019	1115	1134.0	1113	- .179	59	1161	1188.0	1175.0	1179	- .758
28	787.1	837.0	836.78	836.06	- .112	60	601.45	631.05	--	627.3	.594
29	923.4		925.0	918.44	- .537	61	1038.0		993.76	1005.5	-3.131
30	737.25		736.35	736.47	- .106	62	516.2		475.94	476.0	-7.79
31	1151.2		1151.0	1151	+ .017	63	1279		1211.6	1209.6	-5.426
32	675.95		675.95	676.70	+ .111	64	662.0		622.94	620.82	-6.22

TABLE 18. - Data summary for resistor "c" in 2^6 factorial test (Resistance values in ohms)

Run #	Before Exhaust	After Encapsulation	After Exhaust	After Aging	% Change Due to Exh. & Age	Run #	Before Exhaust	After Encapsulation	After Exhaust	After Aging	% Change Due to Exh. & Age
1	1125.72	1199.9	1199	1197.1	-.023	33	1158.8	1208	1202	1202.3	- .474
2	1388.2	1476.5	1473.8	1489	+.846	34	1721	1784	1781	1781	- .168
3	2079.5	2207.7	2206	2202.5	-.240	35	1907.2	1956.6	1947	1350	- .337
4	1249.5	1313.0	1311	1309	-.305	36	1239.4	1290.6	1288	1287	- .279
5	1400.6		1401.8	1399.4	-.086	37	1007.6		990.2	989.46	-1.80
6	1338.4		1338	1336	-.179	38	1389.0		1311	1305	-6.048
7	1953.5		1958.5	1954	+.026	39	1910.6		1807	1804.8	-5.538
8	1390.0		1391.5	1390.2	+.014	40	1203.4		1135.6	1132	-5.93
9	1274.4	1411.0	1409	1406.8	-.298	41	754.62	785.47	784	783.97	- .191
10	1269.2	1340.4	1338	1336.4	-.298	42	1141.8	1197.6	1193	1194	- .301
11	1458.5	1526	1524	1523	-.197	43	2002.2	2075.8	2070	2073	- .135
12	1037.7	1073	1071	1069.5	-.419	44	1188.8	1225.2	1219	1220	- .424
13	1055		1055.5	1055.2	+.19	45	956.8		927.44	925.92	-3.221
14	1262.6		1263.4	1263	+.032	46	1116.8		1043	1040	-6.877
15	2074.5		2075	2073.7	-.039	47	2159.8		2106	2124	-1.658
16	1225.8		1215.8	1215	-.881	48	1263.5		1209	1209	-4.313
17	1927.8	2029.0	2023	2023	-.296	49	2196.0	2358.4	2349	2356	- .102
18	2558	2777.3	2773.3	2771	-.226	50	2376	2500.75	2501.25	2491	- .390
19	2049.7	2166.0	2157	2156	-.231	51	1722	1802.5	1784	1805.5	+ .166
20	1523.7	1600.0	1595	1595.5	-.281	52	1275	1321	1315.3	1315	- .454
21	1750.6		1751.2	1750	-.034	53	2614.0		2504	2509	-4.017
22	2306.7		2311.2	2308	+.087	54	1947.5		1772.2	1764	-9.422
23	2346.6		2348.6	2347	+.017	55	1907.2		1795	1791	-6.093
24	1582.2		1398.6	1583	+.051	56	1578.2		1452	1447	-8.313
25	2436.5	2610.8	2604.5	2602.5	-.318	57	2585.4	2693.4	2685	2682	- .423
26	1811.2	2008.5	2003.5	2004	-.215	58	1760.0	1821.8	1808	1816	- .318
27	3002	3282.5	3273	3276	-.198	59	3024	3105.0	3093	3089	- .515
28	1831.2	1958.2	1954	1953	-.317	60	1601	1662	--	1652.2	- .590
29	2496.8		2501	2500	+.128	61	2570.8		2382.4	2374.0	-8.005
30	1713.5		1710.2	1711	-.146	62	1518.8		1393	1384.1	-11.239
31	3187.8		3188	3188	+.006	63	3004		2812	2807.0	-6.558
32	1636.0		1627	1631	-.306	64	1811.4		1703	1696.4	-6.349

TABLE 19. - Data summary for resistor "d" in 2^6 factorial test (Resistance values in ohms)

Run #	Before Exhaust	After Encapsulation	After Exhaust	After Aging	% Change Due to Exh. & Age	Run #	Before Exhaust	After Encapsulation	After Exhaust	After Aging	% Change Due to Exh. & Age
1	18,824	20,100	20,010	19,940	-.796	33	19,080	19,800	19,760	19,800	.0
2	21,533	22,800	22,860	22,770	-.132	34	23,900	24,960	24,830	24,860	-.400
3	27,250	28,850	28,900	28,800	-.173	35	25,700	26,800	26,560	26,580	-.821
4	17,075	18,070	18,100	18,050	-.111	36	16,975	17,620	17,570	17,550	-.397
5	19,100		19,200	19,080	-.105	37	16,700		16,340	16,340	-2.156
6	21,700		21,700	21,620	-.369	38	20,000		19,060	18,980	-5.100
7	26,250		26,300	26,220	-.114	39	26,300		25,260	25,260	-3.954
8	17,250		17,300	17,250	.0	40	16,500		15,220	15,200	-7.879
9	18,960	20,700	20,700	20,660	-.193	41	13,300	13,925	13,870	13,850	- .539
10	18,340	19,500	19,500	19,420	-.410	42	16,160	16,800	16,840	16,820	+ .119
11	24,787	26,175	26,200	26,100	-.287	43	27,660	29,200	28,960	28,960	- .822
12	15,150	15,750	15,730	15,700	-.317	44	14,120	14,800	14,500	14,680	- .811
13	17,400		17,400	17,360	-.230	45	14,500		14,180	14,180	-2.207
14	17,600		17,560	17,580	-.114	46	15,800		14,800	14,740	-6.709
15	29,550		29,550	29,550	.0	47	28,400		28,120	27,260	-4.014
16	14,200		14,160	14,160	-.282	48	15,550		14,620	14,570	-6.302
17	27,140	28,700	29,580	28,600	-.348	49	35,660	39,400	38,700	38,700	-1.777
18	33,200	36,660	36,530	36,460	-.546	50	29,770	31,420	31,270	31,270	- .477
19	30,475	31,675	31,630	31,630	-.142	51	25,500	27,100	26,920	26,940	- .590
20	18,275	19,425	19,670	19,600	+.901	52	17,230	18,130	18,030	18,030	- .552
21	27,700		27,740	27,720	+.722	53	37,000		35,340	35,320	-4.54
22	31,550		31,700	31,625	+.238	54	26,900		24,950	24,900	-7.435
23	31,250		31,180	31,275	+.080	55	27,100		25,280	25,220	-6.937
24	19,100		19,240	19,220	+.628	56	18,800		17,220	17,080	-9.149
25	32,375	34,400	34,300	34,350	-.145	57	32,160	34,100	34,040	33,920	- .528
26	26,550	29,650	29,650	29,670	+.067	58	24,820	25,900	25,400	25,760	- .543
27	40,230	44,130	44,460	44,130	.0	59	38,700	40,170	39,050	39,950	- .548
28	26,280	28,100	28,520	28,100	.0	60	20,550	21,600		21,480	- .556
29	31,500		29,400	31,520	+.063	61	33,300		30,740	31,520	-5.647
30	25,875		25,875	25,875	.0	62	21,200		19,420	19,480	-8.83
31	38,100		38,100	38,120	+.052	63	41,170		38,680	38,680	-6.437
32	21,700		21,700	21,700	.0	64	22,400		20,820	20,620	-8.632

1. The largest resistance change occurred on resistors using silver conductor material without encapsulation.
2. Encapsulating the resistor will permit use of the silver conductor. The resistance change was less than $\pm$ 1% on the resistors with silver conductors and encapsulation.
3. The remaining combinations of the 2^6 factorial test had less than $\pm$ 1% change in resistance caused by tube processing. The 9 mm distance between the substrate and top mica of the 17BF11 was probably the difference because the substrate was lower in temperature. The 2^6 factorial test shows a marked improvement when compared to the random balance test where many resistor values decreased by at least 30%. The distance between the substrate and top mica of the 17BF11 in the random balance test was 5 mm.
4. Encapsulation of the initial resistor before exhaust increased the resistance value in every case.
5. The right combination of filament lighting, bombarder setting, (induction heat) exhaust machine speed, filament lighting sequence, filament hot shot, plate aging, cathode alloy, grid lateral wire and unconverted alclad plates was apparently chosen.

6. Encapsulated resistors may decrease in value due to tube processing. This was the first time that this was observed.
7. Thick film, palladium-silver resistors can be fabricated with $\pm$ 1% resistance change due to processing.

G. Height of Substrate Above Mica

The 2^6 factorial test certainly suggests the importance of the ambient temperature of the palladium-silver resistor in a vacuum tube. Thermocouples were placed in four positions on the ceramic substrates 90° apart. A pin was attached to the ceramic and the thermocouple was attached to the pin. The substrate was positioned on the 17BF11 structure so that a thermocouple was directly over each cathode. Position #4 over the large cathode corresponds to the same position as the resistor in all of the tests.

The substrates were placed at 5, 7 and 9 mm heights above the top mica of the 17BF11. The data is shown in figures 27, 28, 29 and 30. The raw data has been listed in several tables and is shown in appendix B.

It was unfortunate that the position #4, 9 mm height tubes were lost in processing. This would have provided a direct comparison of the random balance test and 2^6 factorial test substrate ambient temperature environment. The total wattage for normal use of the 17BF11 is approximately 12 watts. Position #4, as shown in figure 30, was indeed the worst ambient temperature condition. Position #4 is 10 to

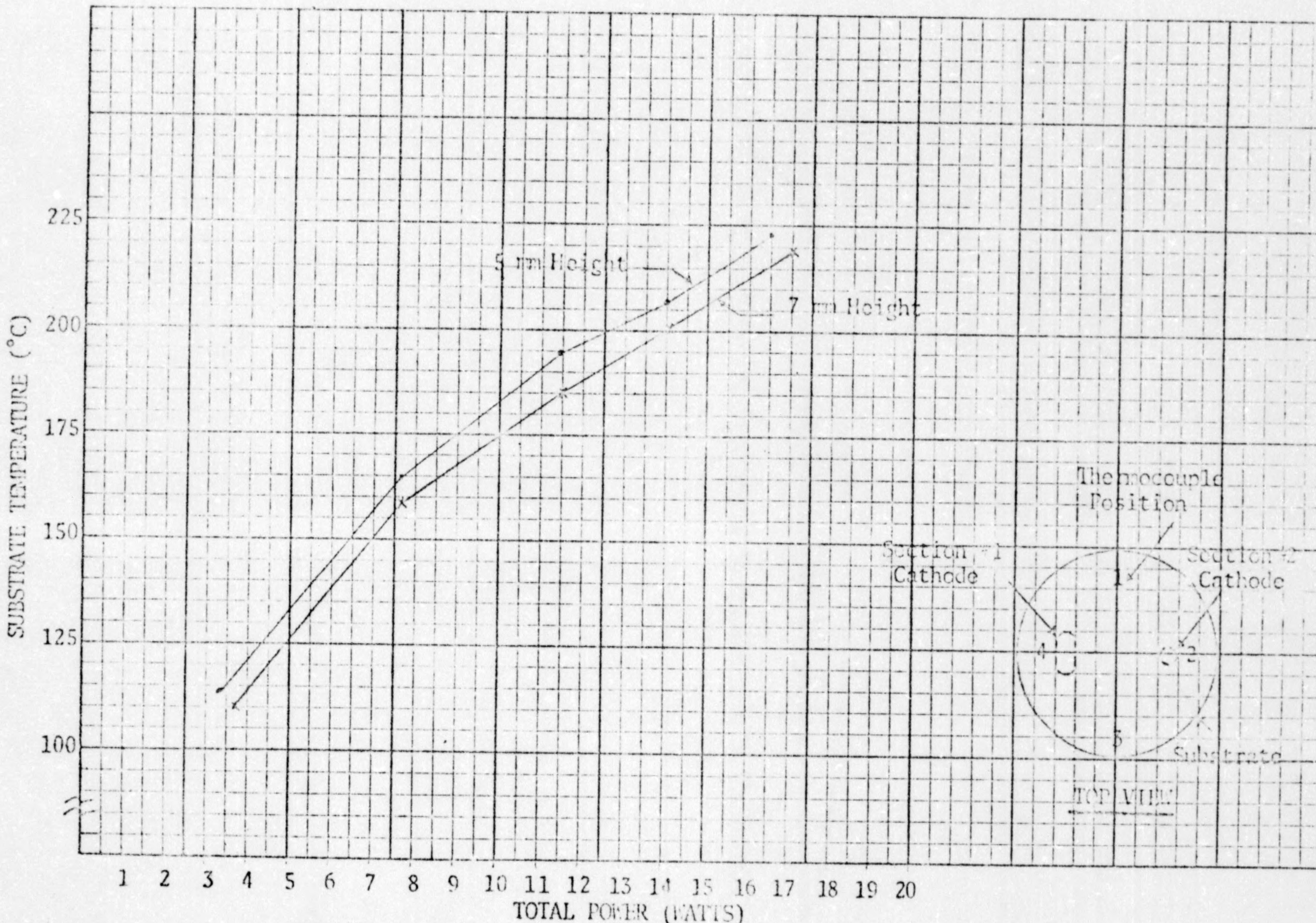

Fig. 27. - Substrate ambient temperature for position #4

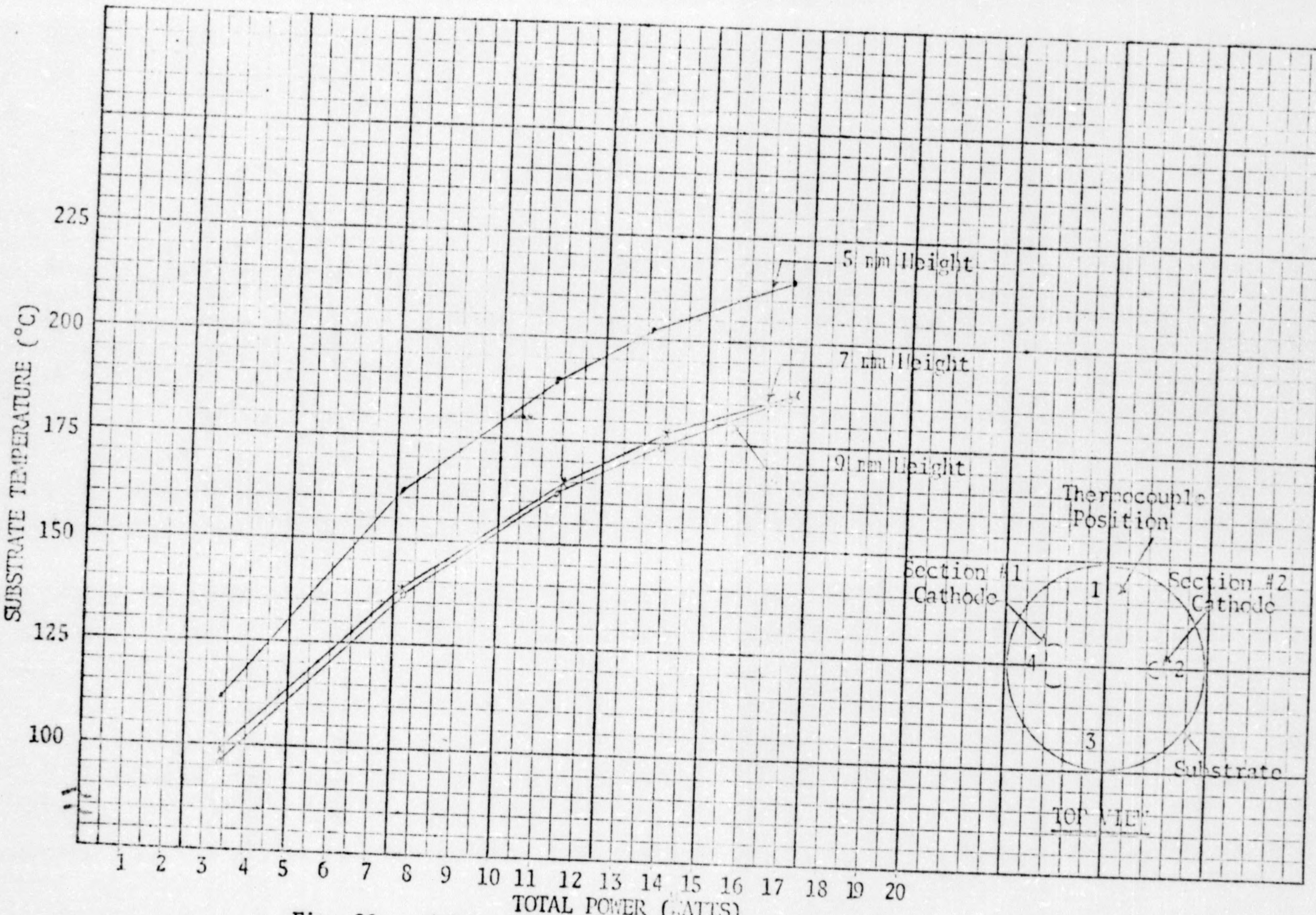

Fig. 28. - Substrate ambient temperature for position #2

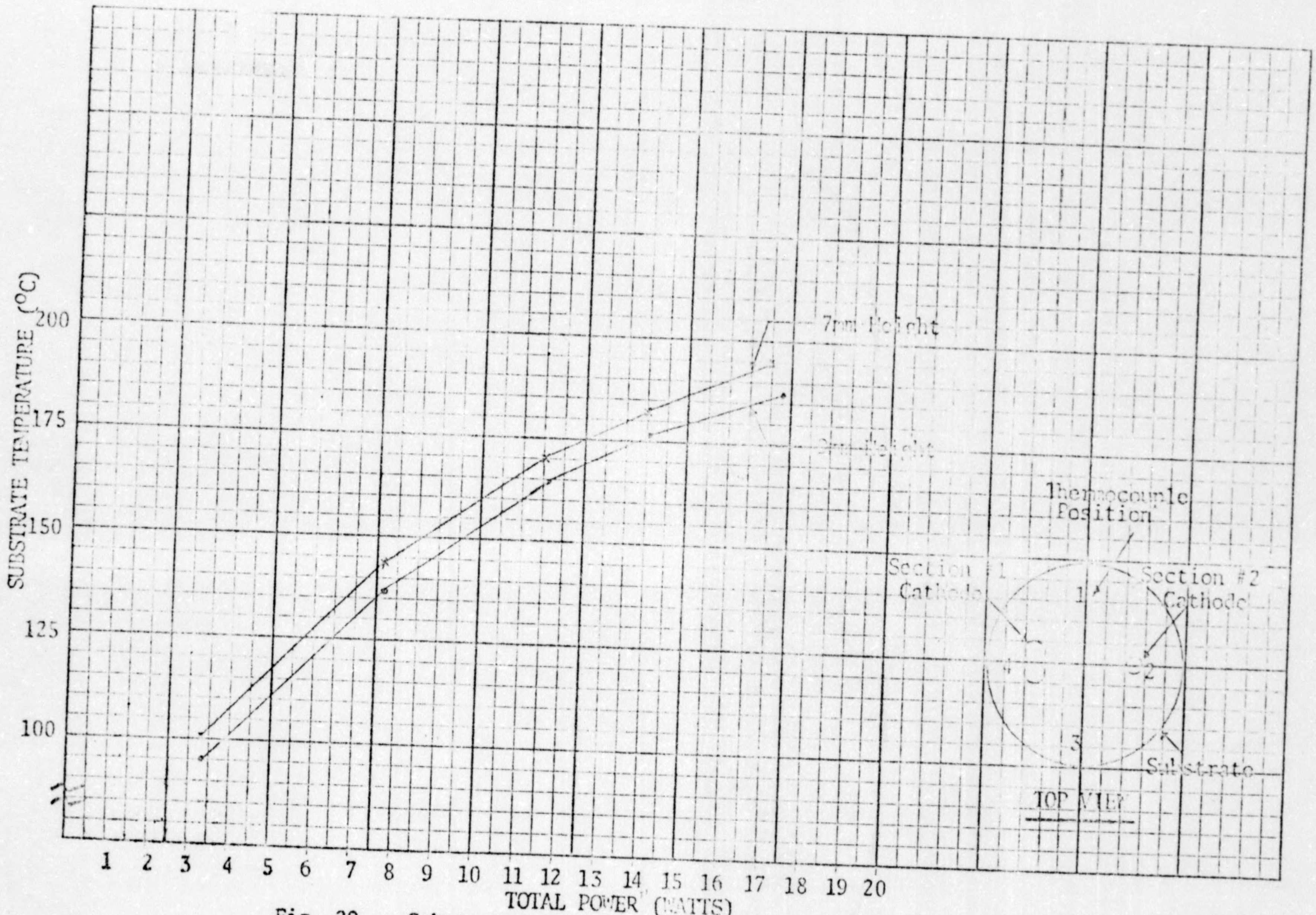

Fig. 29. - Substrate ambient temperature for position #1

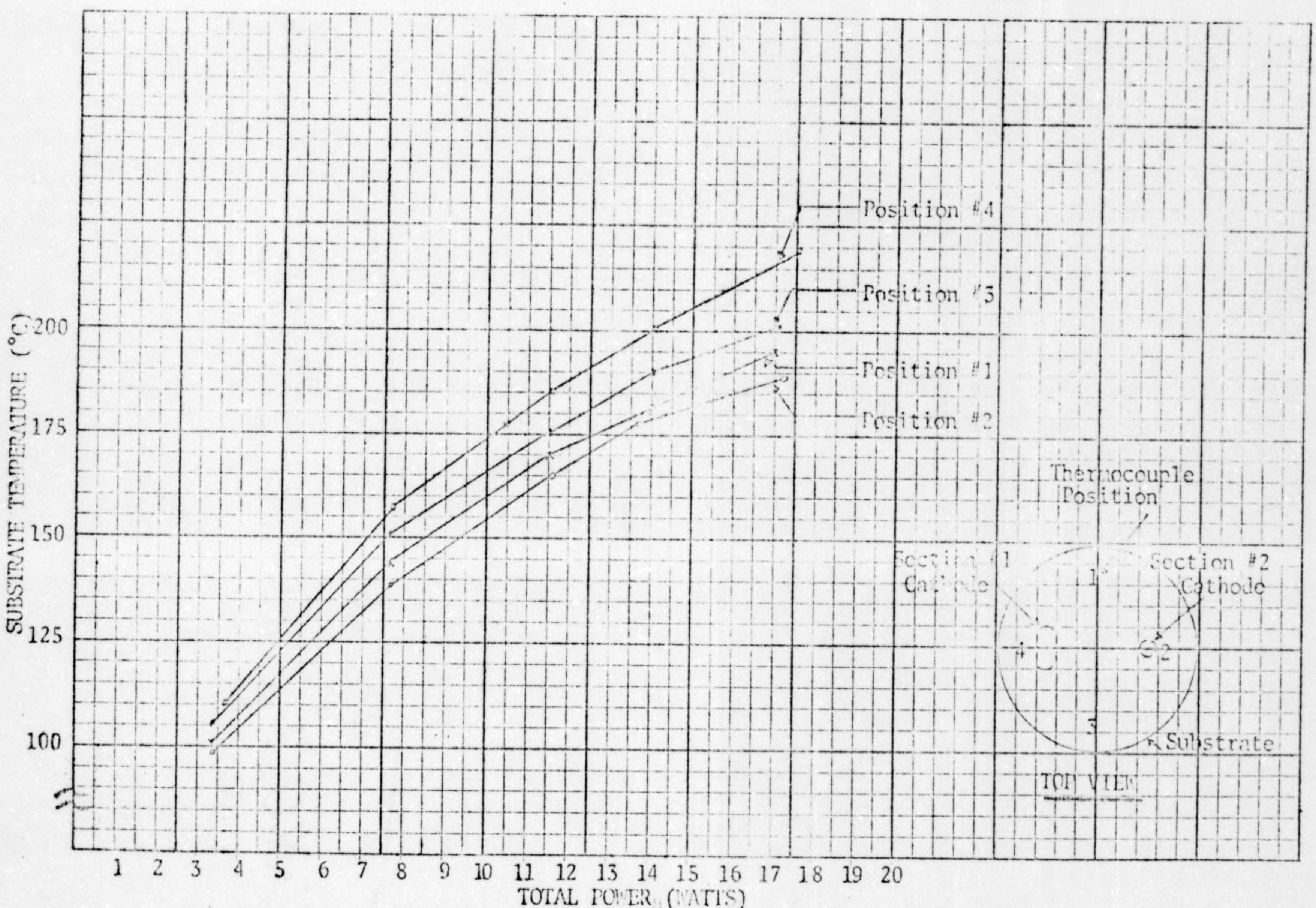

Fig. 30. - Substrate ambient temperature at 7mm height for all four positions

20°C hotter than the other positions. The difference between 5 mm and 9 mm substrate height would perhaps be 15 to 20°C. Position #2 data was used as a guide in making this observation.

How would a substrate ambient temperature of approximately 190°C affect the resistance value? Several resistors in the random balance test were checked for temperature coefficient of resistance. One recalls that these resistor substrates were 5 mm above the top mica. The change in resistance due to substrate ambient temperature for the random balance test was approximately +10% as shown in table 20. A Y-1670 development tube with a high value resistor was also checked with the same 17BF11 operation. The temperature coefficient of resistance was approximately +5%. The resistor for the Y-1670 tube was 9 mm above the top mica. Height of the substrate above the source of heat is an important variable.

TABLE 20.- Temperature coefficient of resistance for test samples

Random Balance Test	Tube Inoperative Resistor Value	Tube Operating* Resistor Value	Percent Change
R1-3	1814 ohm	2000 ohm	+ 9.3
R25-2	1673	1848	+ 9.5
R25-3	1564	1735	+ 9.85
R26-2	1834	2030	+ 9.7
R26-3	1598	1765	+10.45
Y-1670 Development	180,000 ohm	190,000 ohm	+ 5.27

* 17BF11 Operating Conditions:
E_f=16.8 V E_{1g2}=110 V E_{2p}=150 V E_{2g1}=-2.5 V
E_{1p}=145 V E_{1g1}=-6.0 V E_{2g2}=100 V Tot. W 12 W

H. Analysis of Selected Palladium-Silver Resistors

The analysis of palladium-silver resistors reported in the literature has not included data or pictures. The analysis of resistors reported in this thesis will be supported by data and pictures.

The largest resistance variations in palladium-silver resistor values due to environmental effects occurred in the random balance test. Several resistors from this test were selected for analysis. The good resistors (R25-1) represented a minimum change in resistance of -3.4% due to processing and -4.3% change due to 541 hours of life test. An intermediate resistor (R21-3) had a change in resistance of -23.2% due to processing and -12.2% change due to 541 hours of life test. A so-called bad resistor (R20-2) had a -40.1% change due to processing and -65% change due to 541 hours of life test. The bad resistor was not an "open" but it certainly was well beyond a reasonable ± 20% limit for resistors.

1. X-ray Diffraction

The first attempt to analyze the resistor utilized the XRD-5 x-ray diffraction equipment to identify the materials in the resistors. The resistor paste #7826 as received from du Pont contained PdO, Ag, and Pd. The noise level of the x-ray diffraction equipment prevented further identification of the doping impurities. The 1° x-ray beam penetrated through the .001" Pd-Ag resistor film into the ceramic. Therefore the peaks for the ceramic appeared on all x-ray diffraction data as shown in figure 60 in appendix C.

The x-ray diffraction data has been summarized in table 21. The raw data for the bare ceramic, resistor paste #7826 as received, resistor R-28 as screened, resistor R20-4 exhaust only, resistor R20-2 with 541 hours of life test, and resistor R25-1 with 541 hours of life test is shown in appendix C.

The resistor paste #7826 as received had a relatively high peak for PdO. As the resistor was processed this PdO peak diminished. The chart of resistor R20-4 with exhaust processing only shows a large reduction in the PdO peaks when compared to the data for the as received paste.

2. Electron Transmission Microscopy

Since the x-ray diffraction data only identified the basic elements of the palladium-silver resistor, a study of the resistor surface was started to learn more about the resistor. The electron transmission microscopy technique used for this study was an indirect carbon replica method for surface examination. An RCA EML-1B microscope was used in the work.

Resistor (R-28), as screened and fired, had three significant types of surface elements. Figure 31 shows a cluster of small irregularly

TABLE 21. - Summary of x-ray diffraction data (d values - Å)

Al_2O_3 standard lines	Ceramic used in tests	Resistor paste 7826 as received	R28 as screened - 1° beam	R20-4 exhaust only - 1° beam	R20-2 541 hours of life - 1° beam	R25-1 541 hours of life - 1° beam	PdO standard lines	Ag standard lines	Pd standard lines
		3.59				3.77			
$^{4}3.48^{74}$	3.50^{5}		3.49^{4}	3.48^{4}	3.49^{4}	3.49^{4}			
		2.94					3.05^{3}		
	2.78								
		2.66^{2}	2.65			2.63	2.67^{33}		
$^{2}2.55^{92}$	2.56^{1}		2.56^{1}	2.55^{1}	2.56^{1}	2.55^{1}	2.64^{100}		
$^{6}2.38^{42}$	2.38^{8}	2.37^{1}	2.38	2.38	2.39	2.38			
			2.33	2.32	2.33	2.32		2.36^{100}	
									2.25^{100}
	2.24	2.26							
	2.17	2.16					2.15^{20}		
$^{1}2.09^{100}$	2.08^{3}		2.08^{3}	2.09^{2}	2.09^{2}	2.09^{2}			
	2.04	2.05^{3}	2.01	2.01	2.01	2.01		2.04^{40}	
									1.95^{42}
		1.96							
		1.89							
$^{5}1.74^{43}$	1.74^{4}		1.74	1.74	1.74	1.74			
	1.66	1.68					1.67^{28}		
$^{3}1.60^{81}$	1.60^{2}		1.60^{2}	1.60^{3}	1.60^{3}	1.60			
1.55^{3}		1.54					1.54^{18}		
1.51^{7}	1.51		1.51	1.51	1.51	1.51	1.52^{11}		
		1.45^{4}						1.45^{25}	
$^{7}1.40^{32}$	1.40^{7}		1.41	1.40	1.41	1.40			
$^{4}1.37^{48}$	1.37^{6}	1.38	1.37	1.37	1.38	1.37			1.38^{25}
		1.32					1.34^{4}		
1.28^{2}	1.27								
$^{8}1.24^{16}$	1.24	1.23^{5}	1.24	1.24	1.24	1.24		1.23^{26}	
1.19^{6}	1.19	1.18						1.18^{12}	1.17^{24}
1.15^{4}	1.15								
1.13^{5}	1.12						1.13^{5}		1.12^{8}
1.10^{6}	1.10								
1.08^{7}	1.08						1.08^{9}		
		.938						$.937^{15}$	

Fig. 31. - Resistor (R28) surface as screened. Small grains at 8465 magnification .

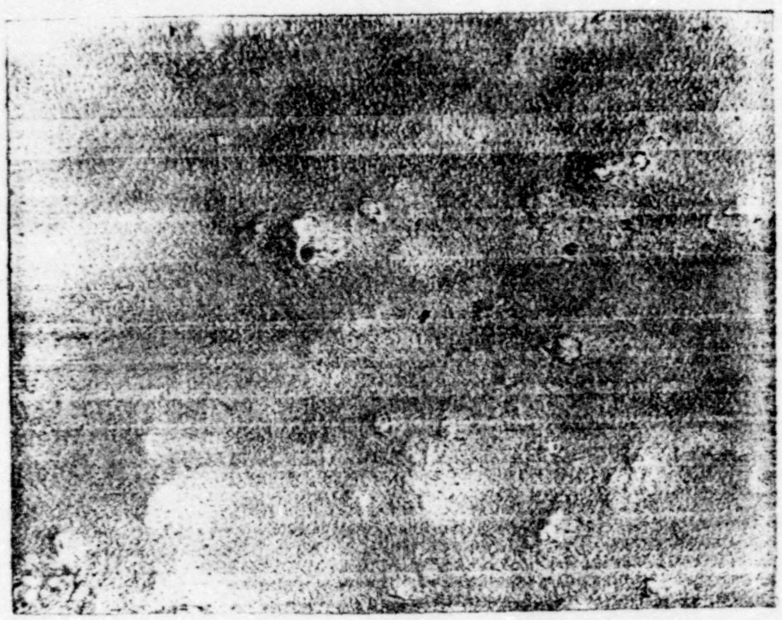

Fig. 32. - Resistor (R28) surface as screened. General appearance at 8465 magnification.

shaped grains. Figure 32 shows the general appearance of the (R-28) surface. Large areas of relatively smooth surface were observed. A cluster of large grains is shown in figure 33. The small and large grains were scattered throughout the surface in a random order. Figure 33 may be a picture of a thin layer of resistor material with the ceramic grains showing. This type of surface was an isolated occurrence.

Figure 34, ceramic substrate surface at 8465 magnification, has been included for comparison. The ceramics used in this study were very smooth compared to the ceramics used in making vacuum tubes in Owensboro, Kentucky. However, the resistor substrates do have a definite grain structure as shown in figure 34.

The good resistor (R25-1) surface after 541 hours of life test had large relatively smooth areas as shown in figure 35. However, many small hills are present. Several of these hills seem to be formed by small spherical grains.

The R25-1 resistor surface also had some large grain structure as shown in figure 36 at 8465 magnification. The black spots are thought to be caused by pits with the black replicating material filling the pits. A picture of a large grain depressed area in the R25-1 surface is shown

Fig. 33. - Resistor (R28) surface as screened. Large grains at 8465 magnification.

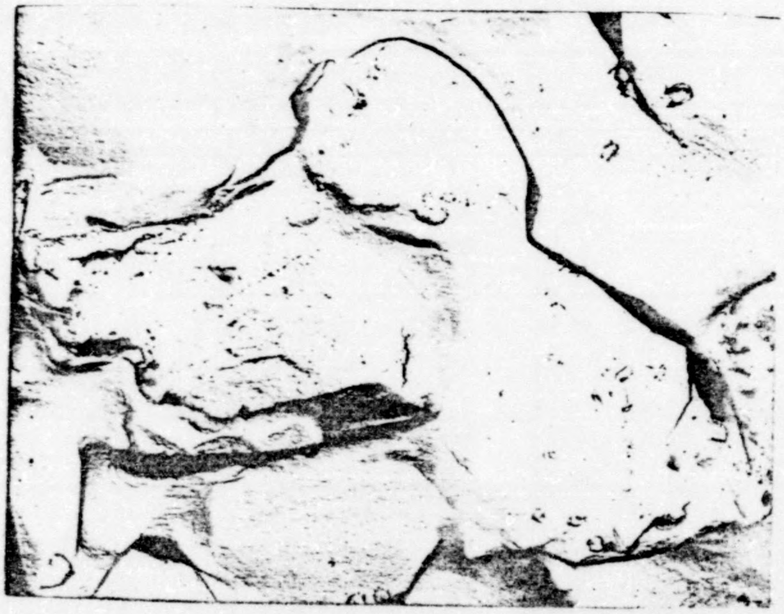

Fig. 34. - Ceramic substrate surface at 8465 magnification.

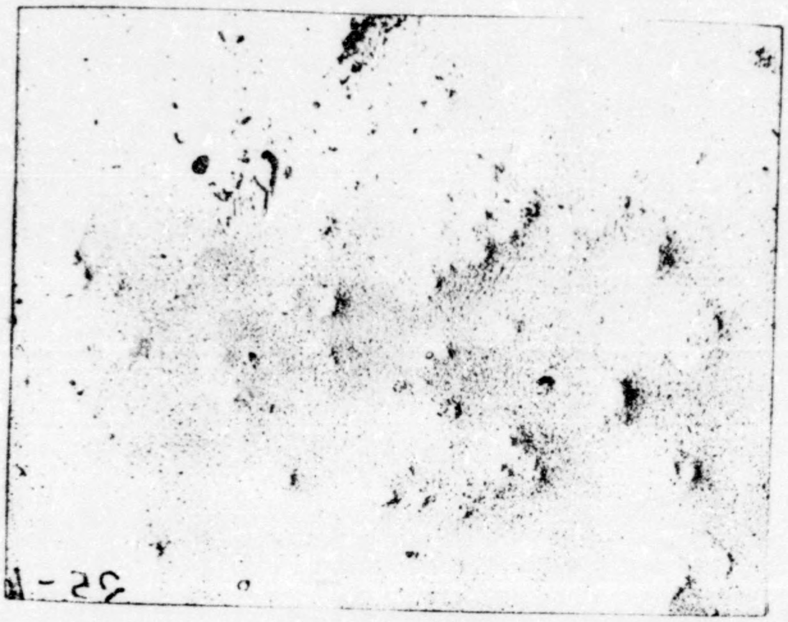

Fig. 35. - Good resistor (R25-1) surface after 541 hours of life test. General appearance at 8465 magnification.

Fig. 36. - Good resistor (R25-1) surface after 541 hours of life test. Grain structure at 8465 magnification.

in figure 37.

The bad resistor (R20-2) surface after 541 hours of life test had scattered grains as shown in figures 38 and 39. Figure 39 was the first observation of needle-like grains. The general appearance as shown in figure 40 looks like the good resistor in figure 35 except it has small indentations instead of protrusions.

3. Optical Microscope

A look at the good resistor (R25-1) surface through an optical microscope at 700 magnification revealed a surface that looked like a volcanic flow. Many protrusions and indentations are shown in figure 41. The protrusions contain many small white spherical parts surrounded by a grey mass.

A similar look at the bad resistor (R20-2) surface in figure 42 at 700 magnification shows the same type of surface as the good resistor. There is no apparent difference in the surface of the two resistors.

Many small pits or craters were observed in the surface of both the good and bad resistors. Figures 43 and 44 illustrate this point. Hoffman (6) gives a possible explanation for these craters. When the silver and palladium are with a glassy phase, as in the resistor compositions, the particulate metals oxidize, decompose and sinter together,

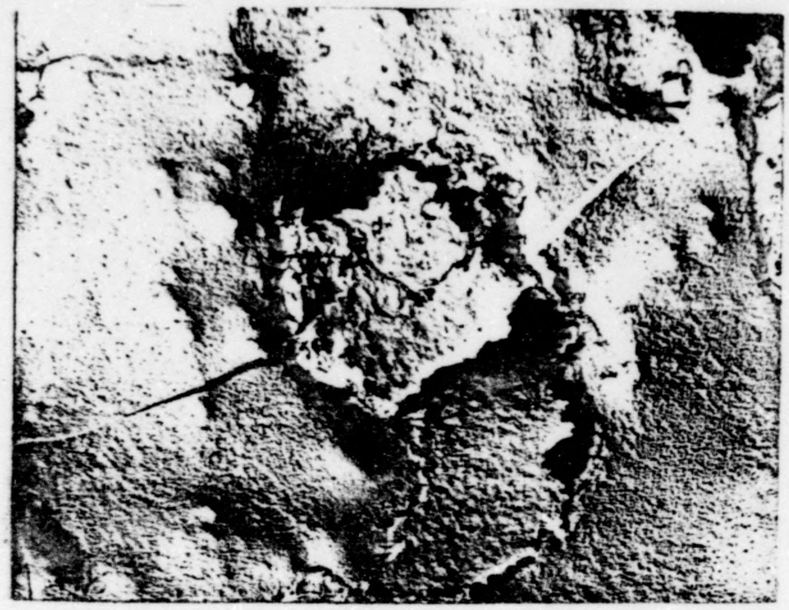

Fig. 37. - Good resistor (R25-1) surface after 541 hours of life test. Pitted area at 8465 magnification.

Fig. 38. - Bad resistor (R20-2) surface after 541 hours of life test. Grain structure at 8465 magnification.

Fig. 39. - Bad resistor (R20-2) surface after 541 hours of life test. Grain structure at 8465 magnification.

Fig. 40. - Bad resistor (R20-2) surface after 541 hours of life test. General appearance at 8465 magnification.

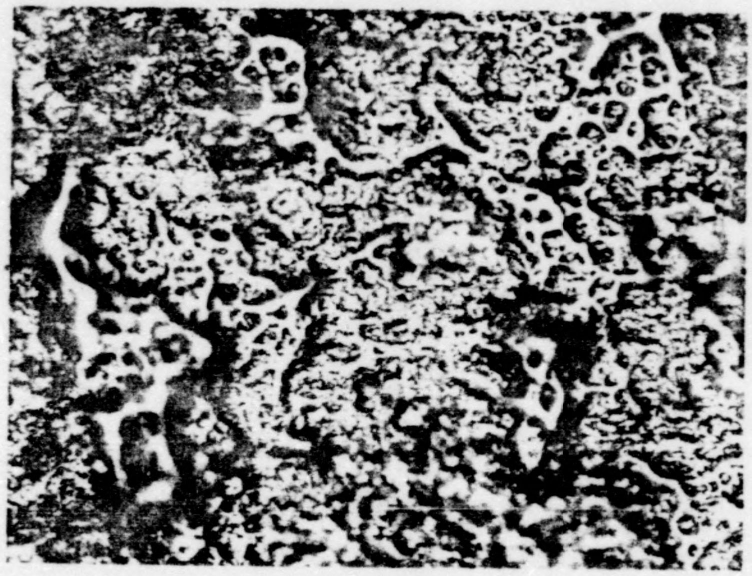

Fig. 41. - Good resistor (R25-1) surface at 700 magnification.

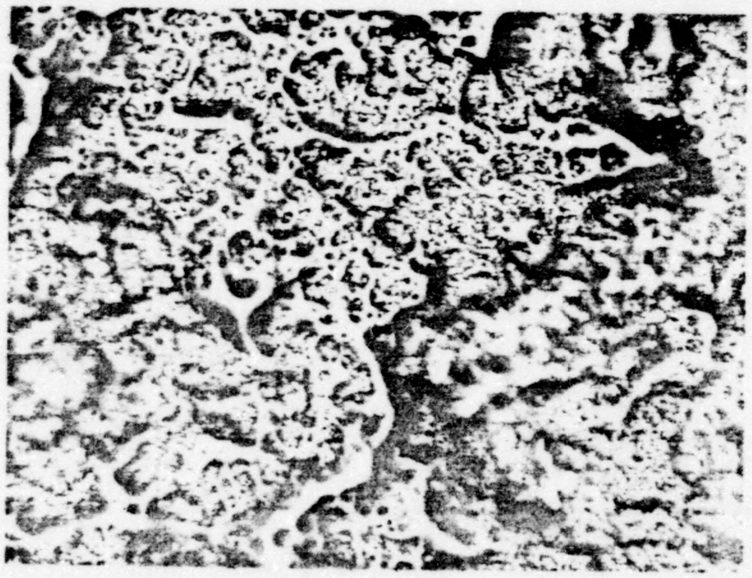

Fig. 42. - Bad resistor (R20-2) surface at 700 magnification.

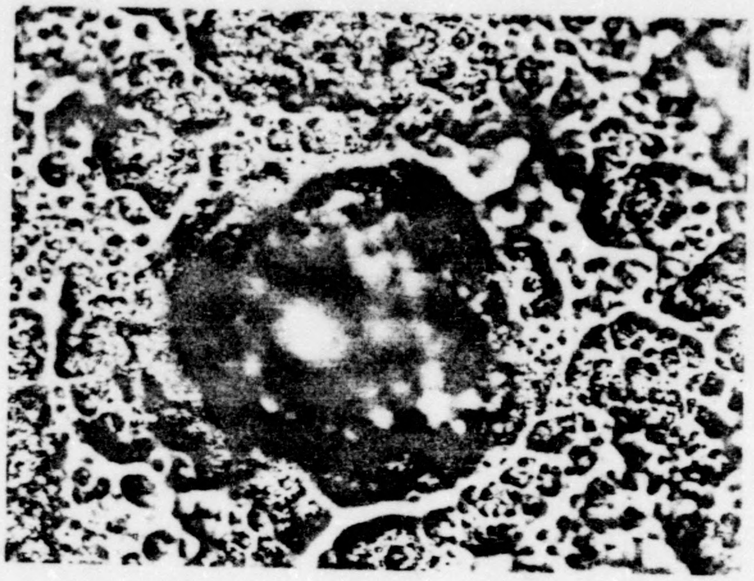

Fig. 43. - Bad resistor (R20-2) surface pit at 700 magnification.

Fig. 44. - Bad resistor (R20-2) surface pit at 700 magnification with the focus on the bottom of the pit.

giving the appearance of aggregate formation. The oxygen evolved is partially trapped in the glassy phase and the glaze resistor films contain a multitude of oxygen bubbles after firing. (6)

4. Plastic Cross Sections

The same resistor structure was observed in the vertical cross section of the good and bad resistors as shown in figures 45 and 46. Small white spherical particles are mixed in a grey mass. The bad resistor (R20-3) was thicker than the good resistor (R25-2). The large holes in both cross sections were pieces of resistor that pulled loose in the grinding operation.

A horizontal cross section of samples seemed to reveal an overall picture of the resistor structure. Figure 47 shows the good resistor at 600 magnification. A large white grain is obvious. The large black spots are pits. A look at an intermediate resistor in figure 48 also shows a large white grain. There is a sizeable white grain in the bad resistor shown in figure 49 but it is much smaller than the ones in the intermediate and good resistors.

An unusually narrow brownish band across the intermediate resistor was observed as shown in figure 50. Upon grinding the good resistor for the horizontal cross section, two such bands

Fig. 45. - Good resistor (R25-2)
vertical cross section at 700 magnification.

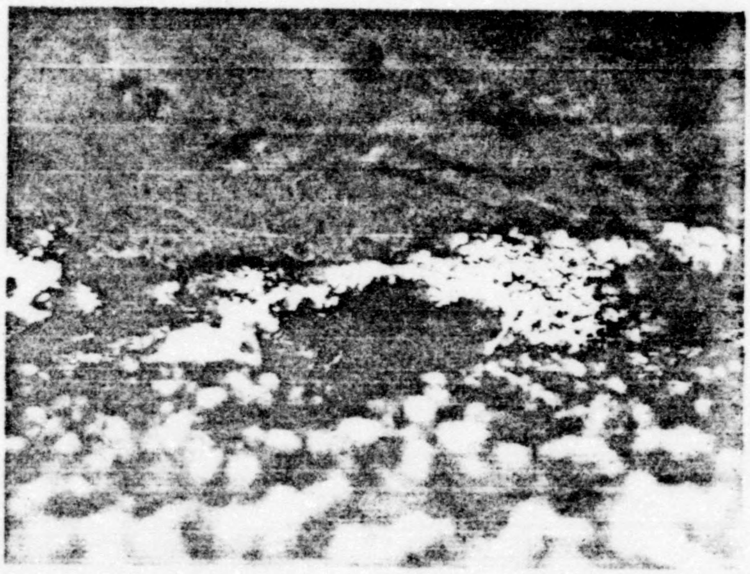

Fig. 46. - Bad resistor (R20-3)
vertical cross section at 700 magnification.

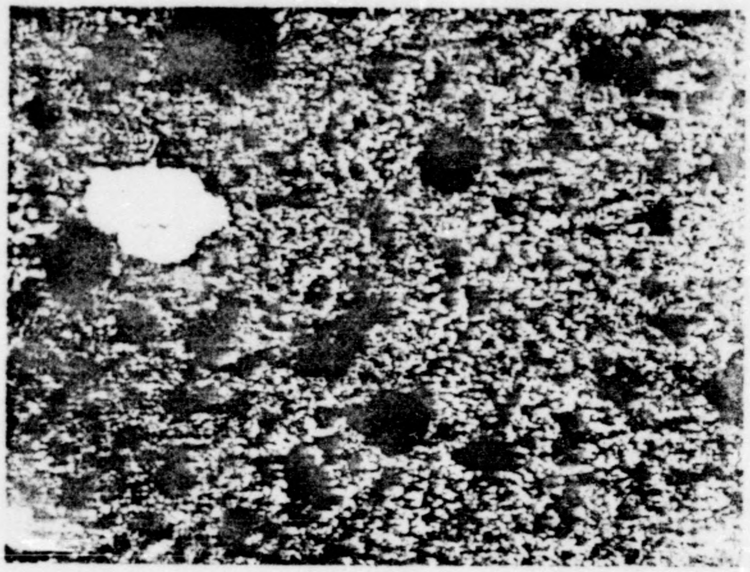

Fig. 47. - Good resistor (R25-1) horizontal cross section at 600 magnification.

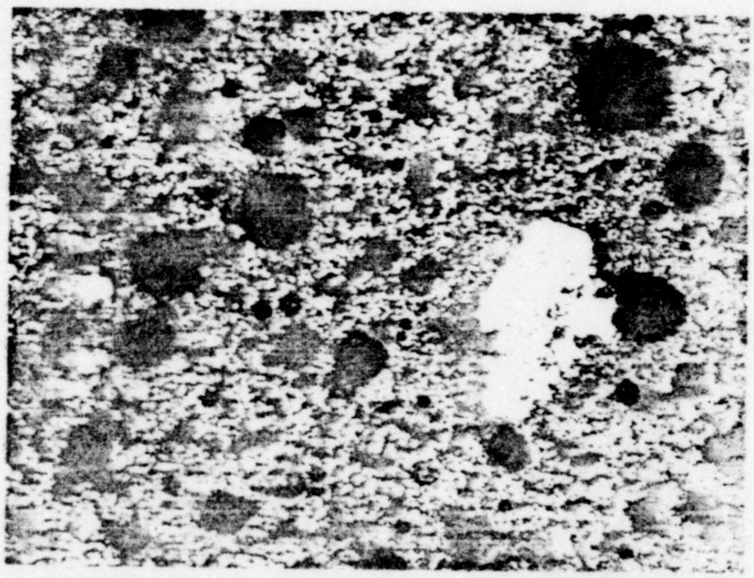

Fig. 48. - Intermediate resistor (R21-3) horizontal cross section at 600 magnification.

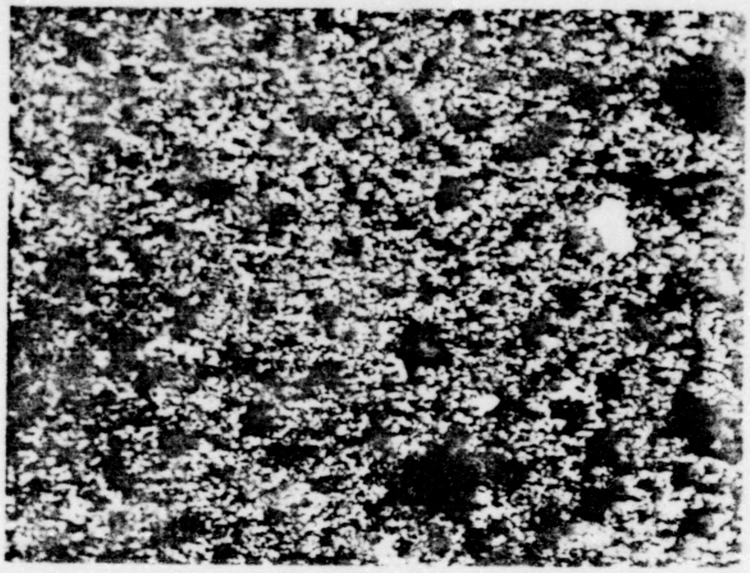

Fig. 49. - Bad resistor (R20-2) horizontal cross section at 600 magnification.

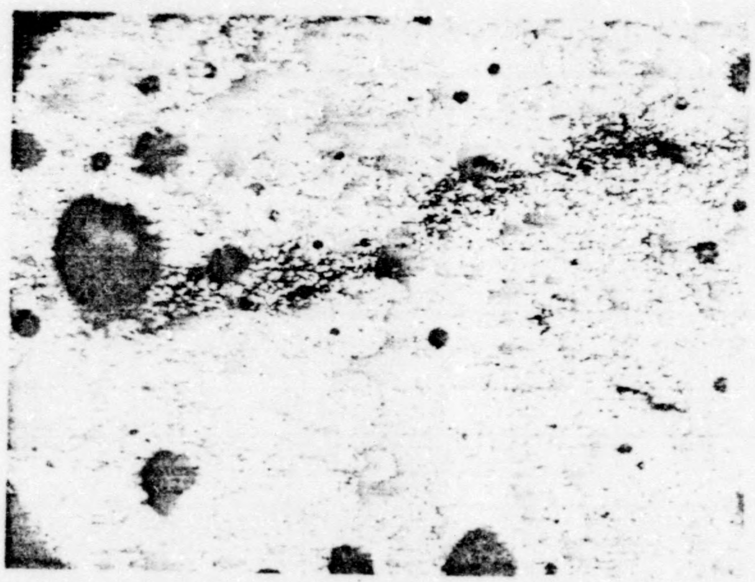

Fig. 50. - Intermediate resistor (R21-3) horizontal cross section at 600 magnification.

were observed in the good resistor. Grinding of the bad resistor did not reveal a band as described above. More research will be required to explain the observed band.

Additional good, intermediate and bad resistors were encapsulated in plastic and cross sections made in an attempt to identify the reasons for resistor failure. Pictures of a horizontal cross section of the good resistor (R25-3) at 600 magnification are shown in figures 51 and 52. There is a good distribution of the white and grey areas with many small isolated areas of each. It resembles a finely divided matrix network with very few large concentrated areas of either white or grey. The horizontal cross section of the intermediate resistor (R21) in figure 53 shows the formation of larger areas of concentration of both white and grey masses. The formation of large areas of centration is even more pronounced in the pictures of the bad resistor (R20) as shown in figures 54 and 55. Since there is an obvious, visual change in the good to bad resistor, identification of the materials shown in the horizontal cross sections become a vital necessity.

A sample of .001" thick palladium-silver conductor film was used for identification of the palladium-silver alloy. The composition of the

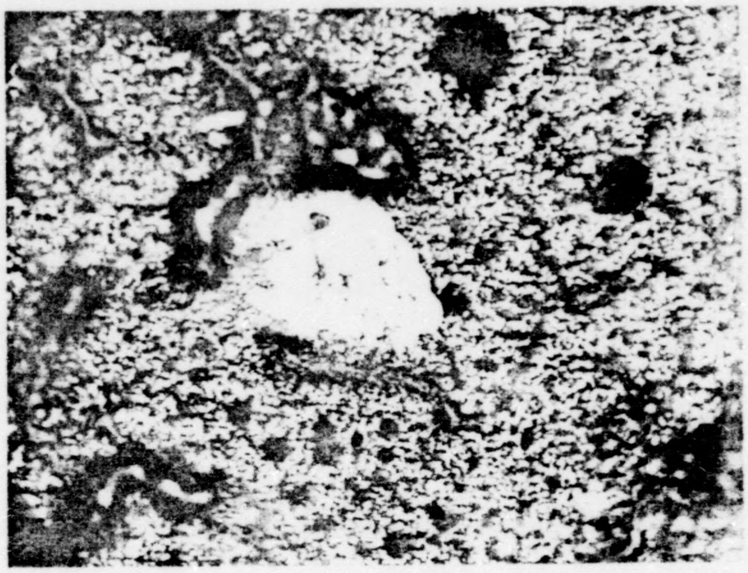

Fig. 51. - Good resistor (R25-3) horizontal cross section at 600 magnification.

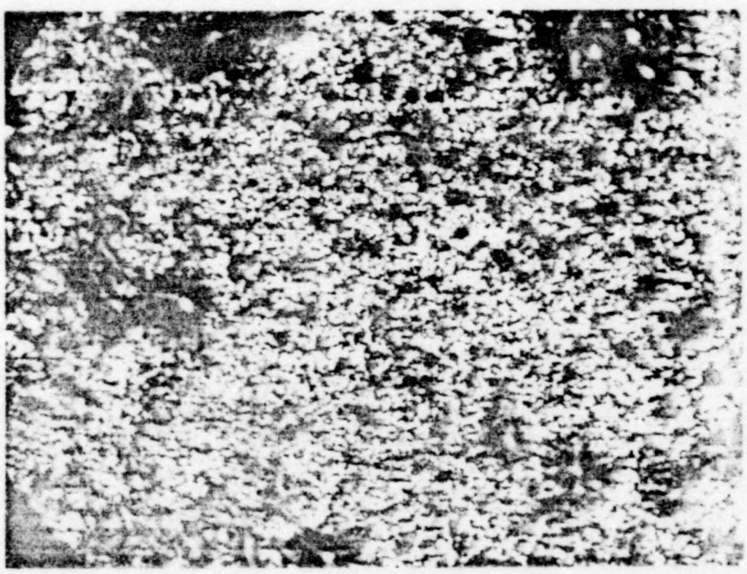

Fig. 52. - General appearance of good resistor (R25-3) horizontal cross section at 600 magnification.

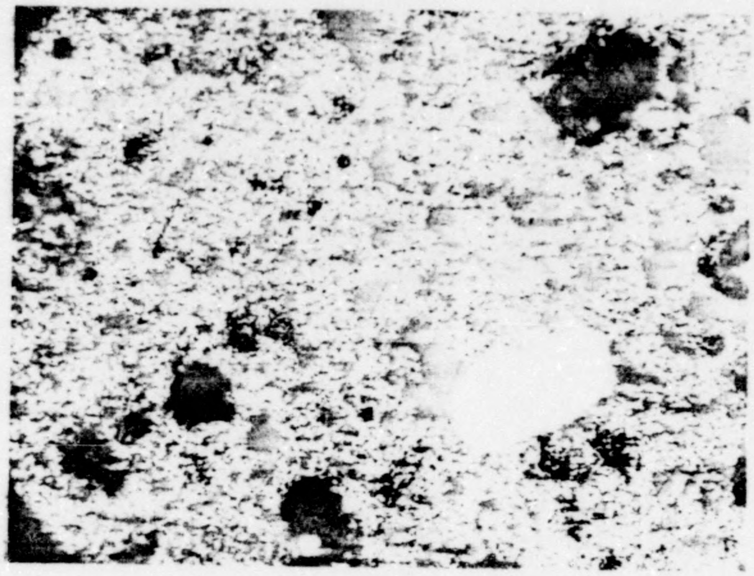

Fig. 53. - Intermediate resistor (R21) horizontal cross section at 600 magnification.

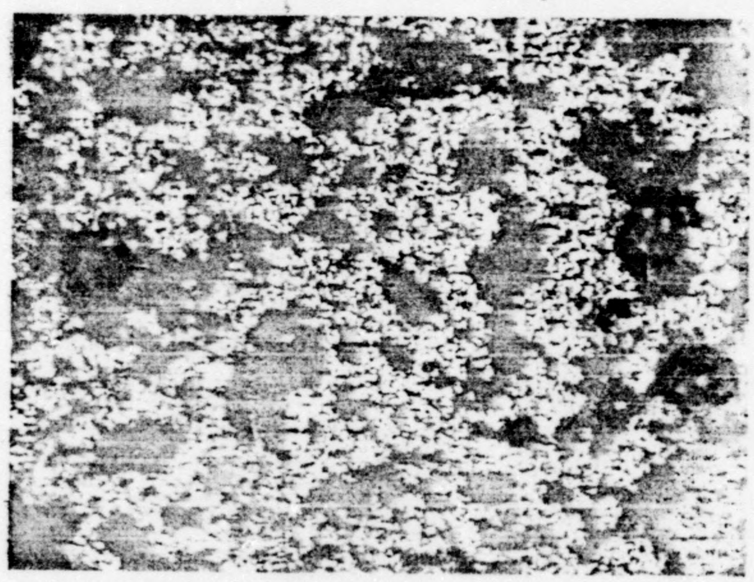

Fig. 54. - Bad resistor (R20) horizontal cross section at 600 magnification.

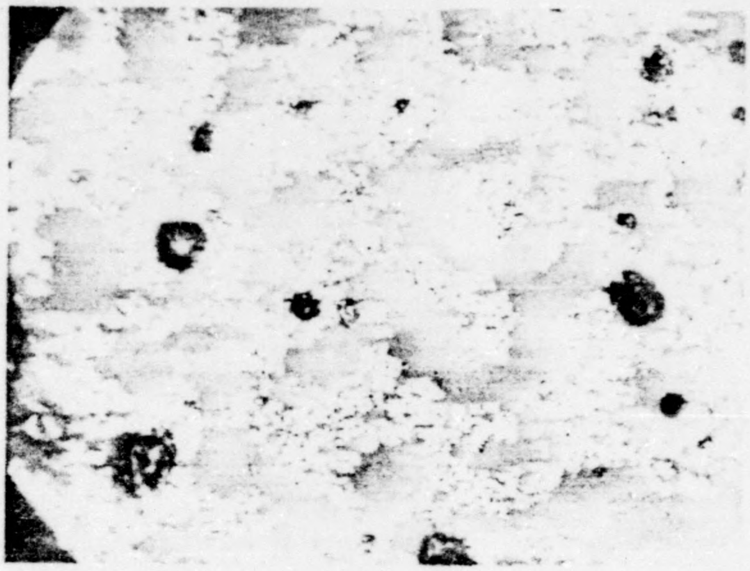

Fig. 55. - Bad resistor (R20) horizontal cross section at 600 magnification.

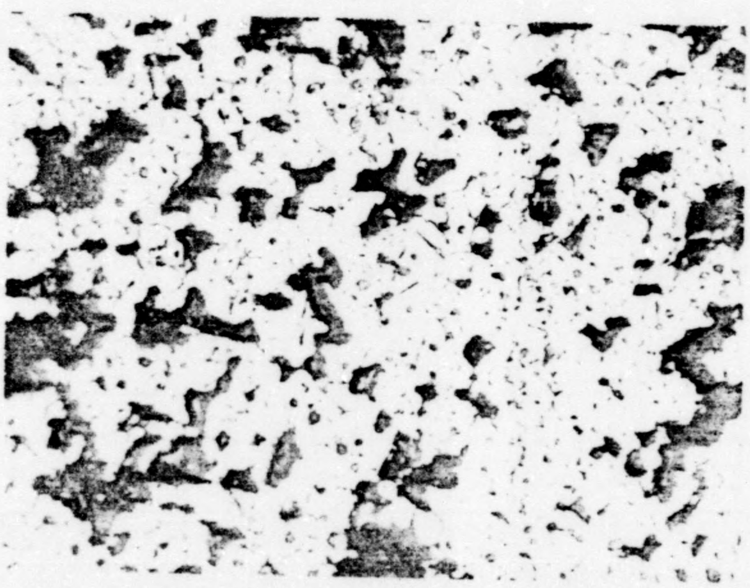

Fig. 56. - Palladium-silver conductor horizontal cross section at 600 magnification.

du Pont paste #8157 is palladium-silver with a very small amount of glass frit (silicon, boron, bismuth). Since the conductor paste does not have any PdO content initially and low glass frit content, the palladium-silver alloy should be identified easily. A horizontal cross section at 600 magnification is shown in figure 56. Metallographic etching (15) of the palladium-silver alloy was performed with Jewell-Wise etch (10% KCN, 10% $NH_4S_2O_8$). The etched grain structure of figure 56 is therefore the white palladium-silver alloy. The scattered dark areas are the glass frit.

Further identification of the resistor constituents in the horizontal cross sections was obtained by etching an as screened resistor. Hydrofluoric acid etchant was used on one-half of the resistor. This etchant very clearly worked on the dark colored glass frit as shown in figure 57. Large mounds of palladium-silver alloy were very prominent when the glass surface was removed. The palladium-silver alloy looked like a sponge when viewed through an optical microscope at 600 magnification. The use of the 10% KCN and 10% $NH_4S_2O_8$ etchant on the other half of the resistor removed the white shiny palladium-silver alloy from the surface as shown in figure 58. This is further evidence that the palladium-silver alloy is the

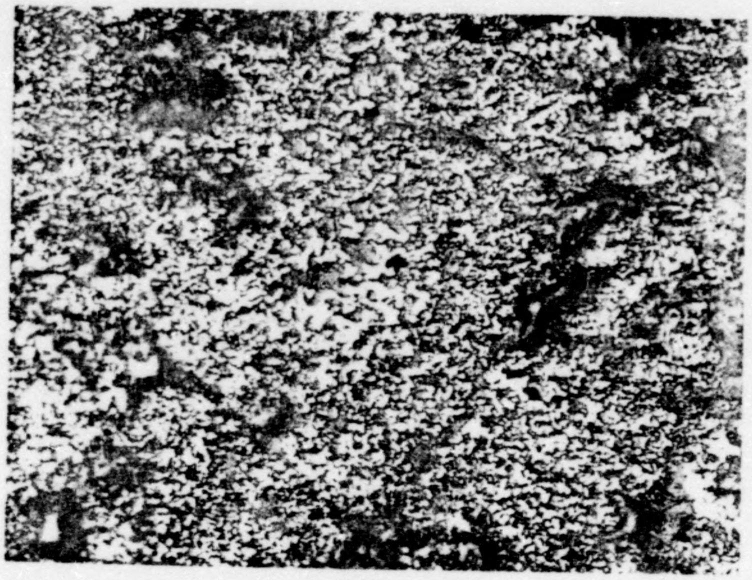

Fig. 57. - Horizontal cross section of R1 at 600 magnification. Resistor as screened with 730°C firing. Glass etched with Hf etchant.

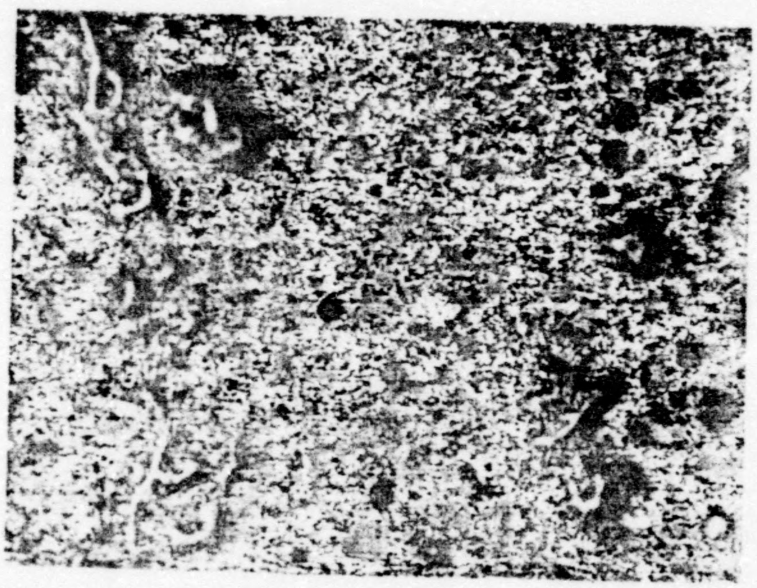

Fig. 58. - Horizontal cross section of R1 at 600 magnification. Resistor as screened with 730°C firing. Pd-Ag etched with 10% KCN and 10% $NH_4S_2O_8$.

white shiny area in the cross sections. This includes the large white areas observed in the pictures which looked like one single grain. These large, very scattered areas are palladium-silver alloy.

Another observation was made on all the horizontal cross sections. One can focus through the grey areas and see the white shiny structure below the grey areas. The grey area is very definitely the glass frit.

The only resistor constituent that was not identified in the horizontal cross section pictures was the PdO. Du Pont is chemically, pre-oxidizing the palladium to obtain PdO. (10) The previously discussed x-ray data of this thesis indicated the presence of PdO in the as received mix. Palladium is superficially oxidized when heated to a temperature of 700°C. (16) Others have reported the oxidation of palladium at temperatures as low as 250 to 330°C. (7)(13) The oxide (PdO), which is formed, decomposes at temperatures above 875°C. (16)(17)

There are two sources of PdO in the resistor. One is the chemically pre-oxidized PdO and the other is the thermally oxidized PdO. The resistor material, after silk screen printing, is fired at 730°C for several minutes with the glass frit melting at about 580 to 650°C. As the glass frit chills, the oxidation of the palladium is inhibited by the solidified glass structure. Hoffman (6) noted there is a difference between the thermally formed PdO and the electrolytically formed PdO. However, the PdO was not positively identified in the cross sections reported in this thesis.

Emission spectrography data obtained at the General Electric plant in Owensboro, Kentucky on du Pont resistor paste #7826 showed the constituents to be palladium, silver, silicon, boron, lead, aluminum, copper and strontium. The previous discussion of palladium-silver-lead borosilicate glass on pages 13-18 would apply to the resistor paste #7826 used in all the experiments reported in this thesis. The copper, aluminum and strontium were trace elements.

The remaining questions are how does the palladium-silver-glass resistor work and how did it fail in the experiments? An attempt will be made to answer both of these questions.

The palladium and silver form a continuous series of solid solutions (15) in the resistor. The palladium-silver alloy is the conductor of current in the resistor. These alloy conductors look like a sponge with a large number of tiny connecting links. The sponge is filled with an insulating glass frit. The PdO is used as a doping agent to obtain the resistance properties. Without the PdO, the resistor would be a good conductor of electricity. The PdO, however, must be a part of the palladium-silver connecting link system to impede the flow of current through the conductor. The molten glass frit helps make the palladium-silver alloy connecting links very small. The isolation effect of the glass frit and the small conductors also impede the flow of current.

The chemically formed PdO may be completely or partially surrounded by the palladium-silver alloy. The thermally formed PdO is probably formed at the grain boundaries of the palladium-silver close to the surface of the resistor. Longer firing schedules for the resistor at 730°C will increase the resistance value.

Some impedance to current flow can be attributed to the craters or holes in the resistor due to decomposition of the PdO during firing and the release of oxygen bubbles. These voids will certainly reduce the number of conduction paths available to the flow of current.

Another aspect of the palladium-silver resistor is the relationship of the palladium-silver alloy and palladium oxide resistivities with respect to temperature. The electrical resistivity data for various palladium-silver alloys is available. (18)

Very little information about palladium oxide has been reported in the literature. Du Pont has performed the basic research on palladium oxide over the past two years, (19) but information on palladium oxide resistivity, conductivity, etc. has not been published. Palladium oxide is a semiconductor. (19) As the temperature of the resistor increases the palladium-silver alloy resistance increases and the palladium oxide resistance decreases. More information will be needed to better describe the interactions of the palladium-silver resistor model elements.

How did the resistor fail? The resistors did not open. The reported failures were due to an excessive decrease (greater than 10%) in resistance value. The pictures of figures 49, 50, 51, 52 and 53 clearly show the bad resistor has evolved to a series of larger conducting paths and a combination of the glass frit into large areas so as to decrease the impedance to current flow. The previously discussed x-ray analysis also indicated a reduction in PdO content in both the good and the bad resistors as the resistors were processed. There is probably a migration of PdO between the palladium-silver alloy grain boundaries such that the impedance within the alloy is lower. More research will be required to reveal all the conduction and failure mechanisms of the palladium-silver-glass resistor.

FABRICATION

I. Screen Process and Printing

The use of the silk screen printing process is not new in the electronics industry. The technique has been used for 25 years to produce miniature circuits. (20)(21) However, during the last five years the fabrication of thick film resistors has made extensive use of the screen printing process.

It is extremely important in the fabrication of resistors that the resistor film thickness be maintained. Changes in film thickness alter the resistance values since resistance is a function of resistor dimensions. Differences in application thickness also lead to variations in texture of fired resistors which cause wide variations in resistance. The best control of print thickness, which can be expected with silk screen printing, is ± 10%. (23) The ideal printed film thickness is 0.9 to 1.1 mil. Experience has shown this thickness range will result in the least change in film thickness during firing and provide reproducible film texture. (20)(21)

A micrometer can be used to monitor application thickness of the dried but unfired film. Weighing may be used to measure thickness but this requires a balance sensitive to the fourth decimal place. A 1/8" x 3/8" print, for example, weighs only 2.5 mg. (20)(22)

One important factor in maintaining constant print thickness is controlling the viscosity of the paste. (23) When a jar is opened, the paste is thoroughly mixed before use to give a homogeneous mixture from top to bottom in the container. The jar is then kept tightly closed except when paste is being transferred to the screen. Best results have been obtained by measuring the viscosity of the resistor composition periodically and making up solvent losses by adding butyl Carbitol acetate. While the paste on the screen is being used, its viscosity will increase because of solvent evaporation. The increase in viscosity will result in thicker prints with lower resistance values. (20) The solvent losses during printing have been minimized by doing the printing in an air conditioned room.

To minimize variation in print thickness, the screen was set as far from the substrate as possible while still obtaining prints with a taut 4' x 4" screen. (20) The bottom of the screen was 0.040" from the top of the substrate before printing. When the squeegee blade pressed down on the screen and forced the paste through the openings, the 0.040" gap was closed and the screen contacted the substrate. As the screen was moved closer to the substrate, the prints became thicker and the variation in thickness increased. The first one or two prints made from a stencil, just after it was charged with composition, differed considerable in thickness from those which followed. The first prints were discarded in order to maintain high standards of reproducibility.

After printing, the resistors were allowed to dry in air for a controlled length of time before forced drying. Levelling of the print begins right after printing and has the effect of raising the resistance value. (20) Therefore, an air drying period greatly improves the reproducibility.

Firing the resistor is the most important and most critical step of the process. The highly complex chemical reaction that occurs does not reach equilibrium, but rather is arrested, and the point at which it is arrested depends upon the temperature/time cycle of the firing process. Reproducibility of electrical characteristics depends upon how carefully this firing procedure is controlled.

II. <u>Adjustment</u>

The adjustment of resistors can be made with a diamond cutting wheel or by abrading away a portion of the print on the flat substrates. (20)(22)

One approach would be to choose a composition of resistivity which provides optimum electrical properties and then adjust to the desired value by changing the geometry of the film after firing. Control of the resistor processing should eliminate later adjusting of resistance except in complex circuits.

There were no adjustments of resistors in any of the tests recorded in this paper.

III. Encapsulation

Encapsulation plays an important part in the characteristics of the resistor since they will be in close contact during actual use. It is important to evaluate the proposed encapsulation material thoroughly to insure that no adverse effects will result during resistor operation. (20) It is important that the cover coat does not react with the resistor composition to form reaction products which could result in excessive change in resistance. It is most important to remove dirt, moisture, and salts, such as fingerprints, before encapsulating. Trapping moisture under an encapsulating film is just as deleterious as using an encapsulating material which allows it to permeate. (20)

Data reported in this thesis has shown encapsulation does change the initial resistor value. The encapsulation did form a protective coat and prevent moisture and gases from reaching the resistor film.

IV. Substrates

The base material has a marked effect on the properties of the resistor. First of all, only materials capable of withstanding a firing temperature of at least 1350°F (732°C) are suitable for use with the screen printed resistors. This eliminates many glass substrate materials and leaves ceramic materials as the best choice. It is important that the substrate be flat, smooth, and free of camber in order to provide the best possible reproducibility of resistor film thickness. Also, the coefficient of thermal expansion of the substrate will affect the temperature coefficient of resistance (TCR) and drift of the resistor by causing changes in particle-to-particle pressure when the resistor and substrate are heated.

Experience has shown that a 96% alumina ceramic substrate, such as American Lava's "AlSiMag" 614, has the inherently high thermal conductivity needed for microcircuits and provides good electrical characteristics with du Pont resistor compositions.(20)(22)

Other high alumina bodies are also used. In choosing the type of alumina, consideration should be given to the chemical composition. There have been instances where some alumina compositions resulted in extremely rough resistor and conductor films because of some minor, seemingly innocuous, ingredient in the ceramic reacting with the resistor composition. Table 22 illustrates the effect of the substrate on some resistor properties. (22)

The substrates used for all tests reported in this thesis were 96% alumina ceramic substrates.

TABLE 22. - Effect of substrate on resistor properties (22)

Substrate	TCR at 25-105°C ppm/°C	Resistance (ohms/sq/mil)	Percent Drift*, after 16 hr. at 150°C
Aluminum oxide, 96%	+175	250	+0.75
Aluminum oxide, thin sheets	+175	250	+0.75
Barium titanate, high "K"	+200	500	+1.5
Forsterite, high expansion	+240	150	+2.8
Steatite, high expansion	+200	350	+1.8
Steatite, low expansion	+180	50	+1.3
Titanium dioxide	+220	500	+0.8
Zircon porcelain	-800	100	+5.0

* Permanent change in resistance on heating.

V. Equipment

The resistors were made on equipment made by Precision Systems Company (PRESCO) of Bound Brook, New Jersey. PRESCO printers were the first production laboratory machines offered to the industry which were specifically designed for electronic ceramic substrate and cermet printing requirements. They permit screen application of various patterns of silver, gold-platinum, resistor compositions and glazes, to flat ceramic substrates, discs, wafers or modules, in the production and development of resistor networks, r-c networks, integrated circuits, capacitors, etc. (24)

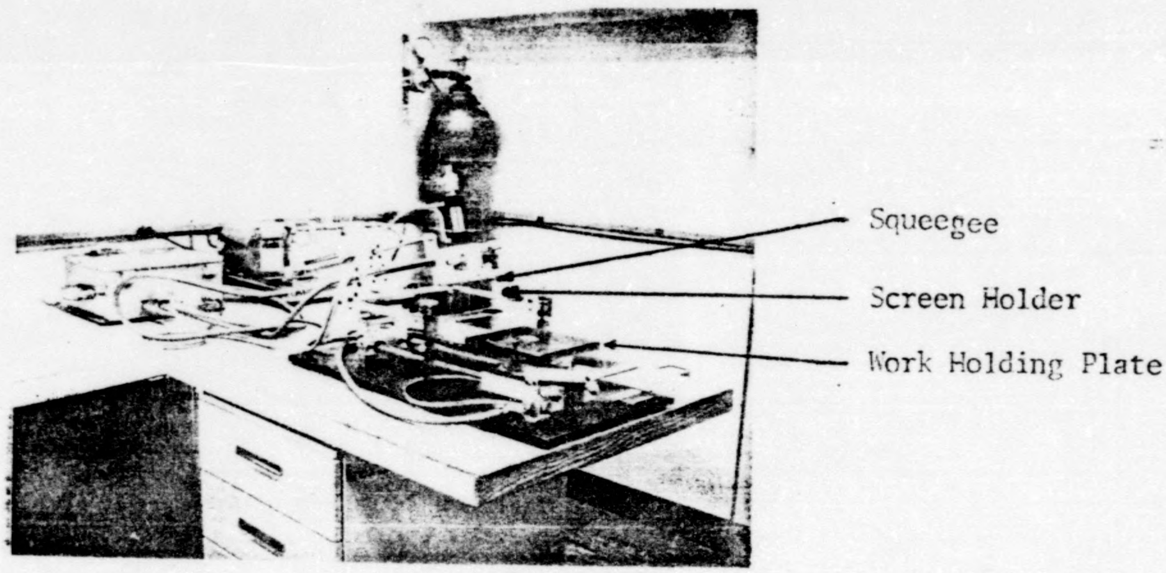

Fig. 59. - Model 100C PRESCO printer

The model 100C PRESCO printer, shown in figure 59, has a hand-operated carriage with time squeegee action which simplifies the machine for lab use. The part to be printed is oriented on the work holding plate and held by vacuum. The carriage is then pushed under the screen mounting where it automatically latches and simultaneously trips a switch to initiate squeegee cycle. The squeegee comes down, makes a timed pass at constant pressure and raises before the end of the cylinder stroke to hop over the metalizing to be returned on next cycle. By pressing the carriage release, the carriage can then be withdrawn to load position. A separate, compact control box for time and valve mounting was located on the same table with the printer. The printer was located in a clean room where the air, temperature and humidity were controlled.

VI. Interconnection

Contact to the glaze resistor can be made either by printing a high temperature silver or solderable platinum-gold terminal composition under the resistor and co-firing the two prints, or by printing a low temperature silver composition over the fired resistor film and using a second firing cycle. (6) Leads can then be soldered to the contacts after the resistor and contacts are fired.

Platinum gold conductor compositions offer a simple, reliable means of interconnecting components in hybrid microcircuitry. Optimum adhesion is only obtained by careful control of firing temperature and time. Adhesion is degraded by high temperature and high humidity through continued reaction with eutectic solder, but useful life even at 150°C is of the order of 1,000 hours. (25) Silver conductors which exhibit more rapid degradation than platinum gold conductors have, nevertheless, found wide utility. Soldered silver and soldered platinum gold patterns are both insensitive to thermal cycling. (25)

All resistors reported in this thesis used the platinum gold conductor. The resistor and conductor were co-fired. A metal pin was connected to the platinum gold conductor by pressure. The pin was then used for external connections.

SUMMARY

AND

CONCLUSIONS

The complex environment of the vacuum electron devices can affect the performance of an unencapsulated palladium-silver-glass resistor. The preliminary tests have shown that seven major variables can affect the resistor in the exhaust cycle. The median resistance change was -30%. Life test accentuated the variables that decreased the resistance value from the initial reading. Resistors which decreased by less than 10% an exhaust processing had less than 10% decrease due to life test. A large decrease in resistance on exhaust processing was indicative of a large decrease on life test. The resistor operation on life test did not affect the operation of the 17BF11 tube.

Several tests have shown the presence of hydrogen from the forming gas or degasing of the metal parts during exhaust is not detrimental. Hydrogen has a very small effect on the resistor (less than 1%). Tests of preconverted and unconverted alclad plates indicated that water may be a source of trouble in vacuum tube processing. The unencapsulated resistor had a very small change in its resistance value when placed in a vacuum of approximately 10^{-6} torr (less than .5%).

Drying time and firing temperature were the most critical prior processing variables. The reheating of the resistor (400-450°C) in the tube sealing cycle can be neglected. The visible sublimation in all of the tests did not cover the resistors and did not affect the values of the resistances. However, sublimation is a potential source of problems.

Using the information from the preliminary tests, a promising combination of processing variables was selected. Apparently, the right combination was chosen because most of the unencapsulated resistors had less than $\pm$ 1% change due to tube processing. A substrate height of 9 mm was included in this test. The height of the substrate above the source of heat is an important variable (substrate ambient temperature).

After analyzing several selected resistors, a model of the palladium-silver-glass resistor was developed. The palladium-silver alloy is the conductor of current in the resistor. These alloy conductors look like a sponge with a large number of tiny connecting links. The sponge is filled with an insulating glass frit. The PdO is used as a doping agent to obtain the resistor properties. The PdO, however, must be a part of the palladium-silver connecting link system to impede the flow of current through the conductor. The very small palladium-silver alloy connnecting links also impede the flow of current.

The resistor failures reported in this thesis were due to an excessive decrease (greater than 10%) in resistance value. The bad resistors had evolved to a series of larger conducting paths and a combining of the glass frit into large areas so as to decrease the impedance to current flow.

A proper choice of tube materials and processing schedule, relatively low (170°C) substrate ambient temperature, and operation within dissipation ratings (tube and resistor) will yield a very satisfactory thick film, palladium-silver-glass resistor system within a high vacuum environment (vacuum receiving tube). However, more research will be required to reveal all of the conduction and failure mechanisms of the palladium-silver-glass resistor.

APPENDIXES

I. Random Balance Test Data

TABLE 23. - Random balance test data (Resistance values in ohms)

	Before Exhaust	After Exhaust	After Aging	% Change from Initial	Test Run % Median
R1-1	1 903	1 890	1 914	+ .58%	
R1-2	2 205	2 191	2 212	+ .32	+ .32
R1-3	1 924	1 805	1 812	- 5.82	
R2-1	1 666	1 246	1 300	-21.9	
R2-2	1 829	1 315	1 376	-24.6	-21.9
R2-3	1 797	1 576	1 593	-11.4	
R3-1	1 789	1 353	1 386	-22.5	
R3-2	1 872	1 244	1 297	-30.7	-22.5
R3-3	1 765	1 434	1 478	-16.2	
R4-1	1 848	1 667	1 662	-10.1	
R4-2	1 922	1 738	1 735	- 9.75	- 9.75
R4-3	1 831	1 707	1 704	- 6.93	
R5-1	1 797	1 036	1 130	-36.9	
R5-2	1 770	1 350	1 368	-22.7	-29.7
R5-3	1 926	1 186	1 353	-29.7	
R6-1	1 719	1 617	1 610	- 6.35	
R6-2	1 915	1 639	1 628	-15.0	- 7.9
R6-3	1 886	1 746	1 737	- 7.9	
R7-1	2 137	1 697	1 705	-20.2	
R7-2	2 324	2 035	2 037	-12.4	-12.4
R7-3	1 791	1 684	1 685	- 5.9	
R8-1	1 773	1 287	1 321	-25.5	
R8-3	1 794	1 313	1 373	-23.5	-25.5
R8-4	1 677	1 129	1 220	-27.3	
R9-1	2 070	1 261	1 316	-36.3	
R9-2	2 068	1 188	1 272	-38.3	-36.3
R9-3	1 951	1 197	1 260	-35.4	
R10-1	2 063	1 885	1 880	- 8.9	
R10-2	1 718	1 436	1 430	-16.8	-15.7
R10-3	1 824	1 531	1 538	-15.7	
R11-2	2 075	1 402	1 500	-27.7	-27.1
R11-4	1 785	1 251	1 311	-26.5	

TABLE 23. - Continued

	Before Exhaust	After Exhaust	After Aging	% Change from Initial	Test Run % Median
R12-1	2 004	1 620	1 616	-19.3	
R12-2	2 038	1 521	1 526	-25.2	-22.8
R12-3	2 066	1 593	1 594	-22.8	
R13-1	2 285	2 269	2 205	- 3.5	
R13-2	1 813	1 696	1 691	- 6.72	- 6.72
R13-4	1 889	1 183	1 177	-37.7	
R14-2	1 967	1 104	1 349	-31.4	
R14-3	1 980	1 040	1 277	-35.6	-31.4
R14-4	1 777	1 060	1 312	-26.2	
R15-1	2 395	2 317	2 313	- 3.42	
R15-2	1 806	1 665	1 659	- 8.12	- 8.08
R15-3	1 423	1 311	1 308	- 8.08	
R16-1	1 869	1 073	1 226	-34.4	
R16-2	1 872	1 106	1 173	-37.3	-35.1
R16-3	1 818	1 084	1 180	-35.1	
R17-2	2 184	2 140	2 133	- 2.34	- 8.55
R17-3	2 350	2 019	2 004	-14.75	
R18-2	1 731	1 602	1 592	- 8.0	- 7.45
R18-3	2 180	2 026	2 030	- 6.9	
R19-2	2 179	1 353	1 423	-34.6	-35.7
R19-3	1 690	1 008	1 068	-36.8	
R20-1	1 964	1 129	1 424	-27.5	
R20-2	2 292	1 176	1 373	-40.1	-36.6
R20-3	2 185	1 120	1 386	-36.6	
R21-1	1 808	1 364	1 387	-23.2	
R21-2	2 153	1 759	1 765	-18.0	-21.3
R21-3	1 993	1 554	1 569	-21.3	
R22-1	1 794	1 500	1 508	-16.0	
R22-2	1 680	1 682	1 682	+ .12	- 7.55
R22-3	1 735	1 606	1 604	- 7.55	
R23-1	1 791	1 098	1 138	-36.4	
R23-2	1 901	1 448	1 495	-21.4	-36.4
R23-3	2 057	1 212	1 266	-38.3	

TABLE 23. - Continued

	Before Exhaust	After Exhaust	After Aging	% Change from Initial	Test Run % Median
R24-1	1 974	1 847	1 855	- 6.05	
R24-2	1 853	1 710	1 711	- 7.68	- 7.68
R24-3	1 982	1 786	1 786	- 9.8	
R25-1	1 846	1 782	1 783	- 3.40	
R25-2	1 801	1 680	1 672	- 7.15	- 5.6
R25-3	1 676	1 562	1 562	- 5.60	
R26-1	1 927	1 870	1 861	- 3.42	
R26-2	1 898	1 835	1 831	- 3.54	- 3.42
R26-3	1 630	1 600	1 595	- 2.14	
R27-1	2 203	2 200	2 201	- .09	
R27-2	2 064	1 759	1 778	-13.9	-13.9
R27-3	2 027	1 661	1 668	-17.6	
R28-2	1 855	1 413	1 454	-21.6	-26.6
R28-3	1 753	1 179	1 198	-31.6	
R29-1	1 705	1 075	1 150	-32.5	
R29-2	1 931	1 180	1 245	-35.5	-32.5
R29-4	1 835	1 206	1 290	-29.7	
R30-1	1 961	1 749	1 862	- 5.05	
R30-2	1 882	1 054	1 257	-33.1	-33.1
R30-3	1 951	1 092	1 224	-37.2	

II. Substrate Temperature Measurements

TABLE 24. - Substrate 9 mm above 17BF11 top mica

Test Point	Tube #	Position	Heater Power (Watts)	Plate Power (Watts)	Grid #2 Power (Watts)	Substrate Temperature (°C)
1	101	1	3.35			95
2	101	1	7.65			137
3	101	1	7.65	3.22	.79	164 1/2
4	101	1	7.65	5.88	.60	176
5	101	1	7.65	9.1	.50	187
1	102	2	3.33			96
2	102	2	7.64			137
3	102	2	7.64	3.24	.55	163
4	102	2	7.64	5.82	.35	174
5	102	2	7.64	9.1	.24	187

TABLE 25. - Substrate 7 mm above 17BF11 top mica

Test Point	Tube #	Position	Heater Power (Watts)	Plate Power (Watts)	Grid #2 Power (Watts)	Substrate Temperature (°C)
1	103	1	3.33			101 1/2
2	103	1	7.64			144
3	103	1	7.64	3.21	.64	170
4	103	1	7.64	5.88	.45	182
5	103	1	7.64	9.15	.35	195
1	104	2	3.34			98 1/2
2	104	2	7.64			138 1/2
3	104	2	7.64	3.22	.75	165
4	104	2	7.64	5.41	.55	177 1/2
5	104	2	7.64	9.16	.46	188
1	105	3	3.4			106
2	105	3	7.64			150 1/2
3	105	3	7.64	3.22	.67	176
4	105	3	7.64	5.97	.46	190
5	105	3	7.64	9.17	.37	202
1	106	4	3.7			110 1/2
2	106	4	7.68			158
3	106	4	7.68	3.22	.65	185 1/2
4	106	4	7.68	5.97	.46	200 1/2
5	106	4	7.68	9.5	.36	219

TABLE 26. - Substrate 5 mm above 17BF11 top mica

Test Point	Tube #	Position	Heater Power (Watts)	Plate Power (Watts)	Grid #2 Power (Watts)	Substrate Temperature (°C)
1	107	4	3.3			114
2	107	4	7.61			164
3	107	4	7.61	3.22	.61	194
4	107	4	7.61	5.88	.5	207
5	107	4	7.61	9.1	.24	222 1/2
1	108	2	3.33			112
2	108	2	7.59			162
3	108	2	7.59	3.22	.59	189
4	108	2	7.59	5.88	.43	202
5	108	2	7.59	9.1	.31	214 1/2
1	109*	4	3.32			106
2	109	4	7.61			155 1/2
3	109	4	7.61	3.22	.55	186
4	109	4	7.61	5.88	.32	200
5	109	4	7.61	9.1	.22	216
1	110	2	3.28			100
2	110	2	7.62			145
3	110	2	7.62	3.22	.48	168
4	110	2	7.62	5.88	.28	181
5	110	2	7.62	9.1	.19	193

* Tube heater loop positioned below cage.

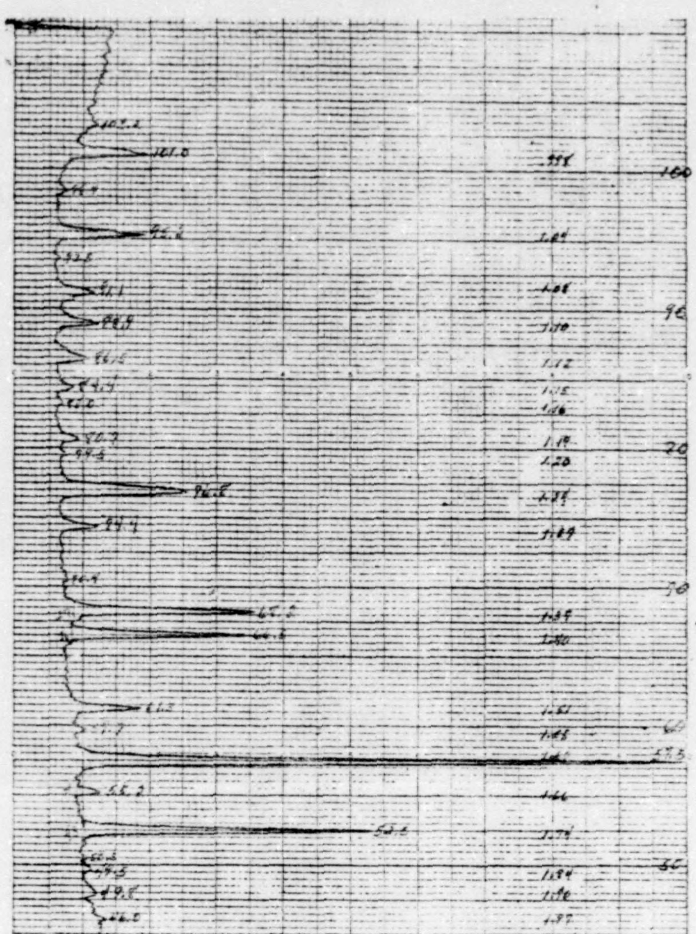

Fig. 60. - X-ray diffraction data for ceramic substrate

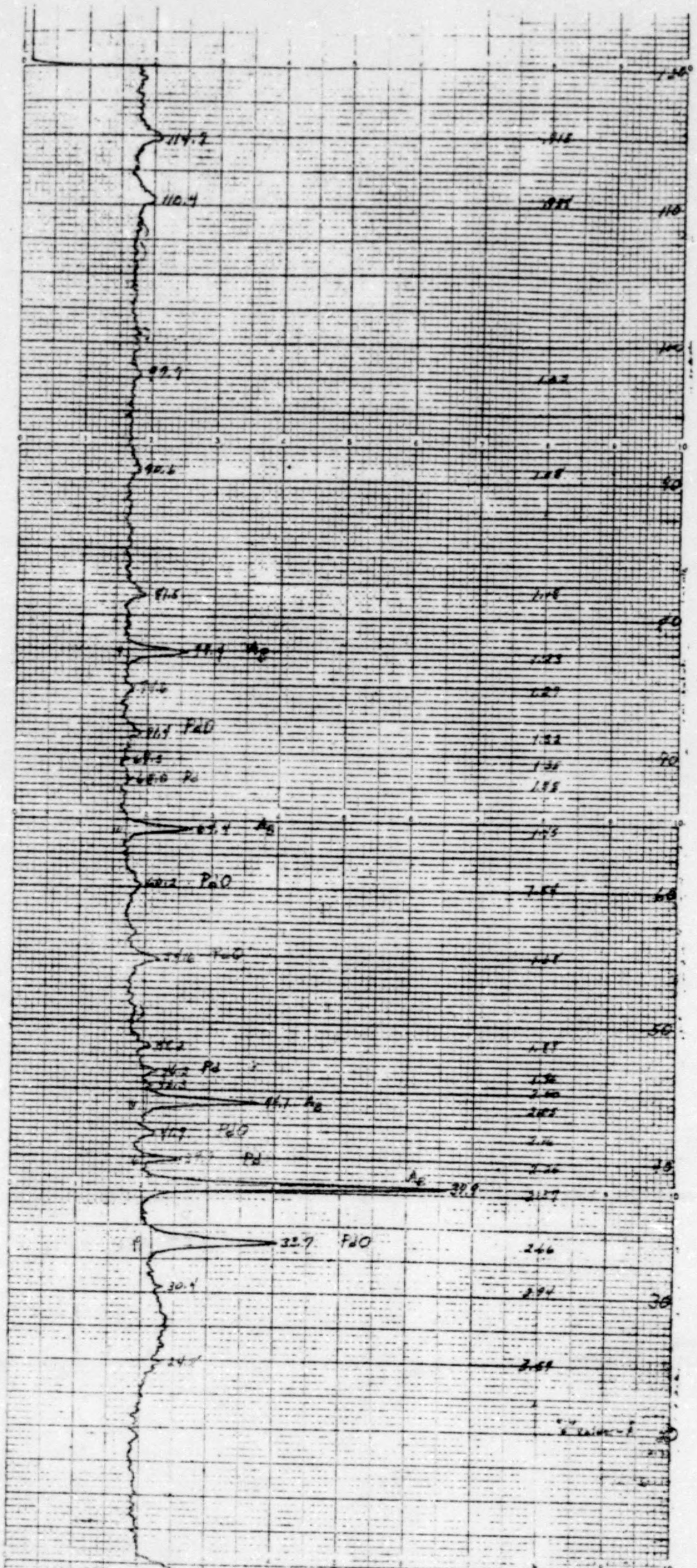

Fig. 61. - X-ray diffraction data for du Pont resistor paste #7826 as received

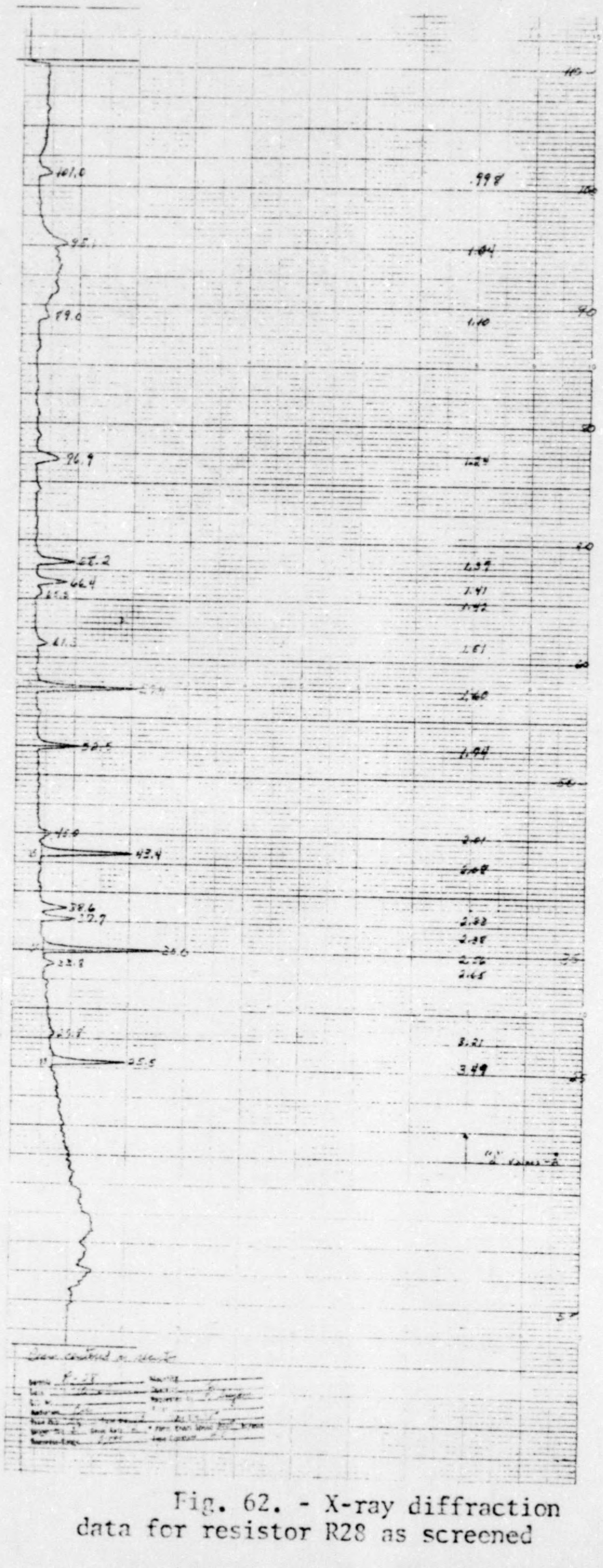

Fig. 62. - X-ray diffraction
data for resistor R28 as screened

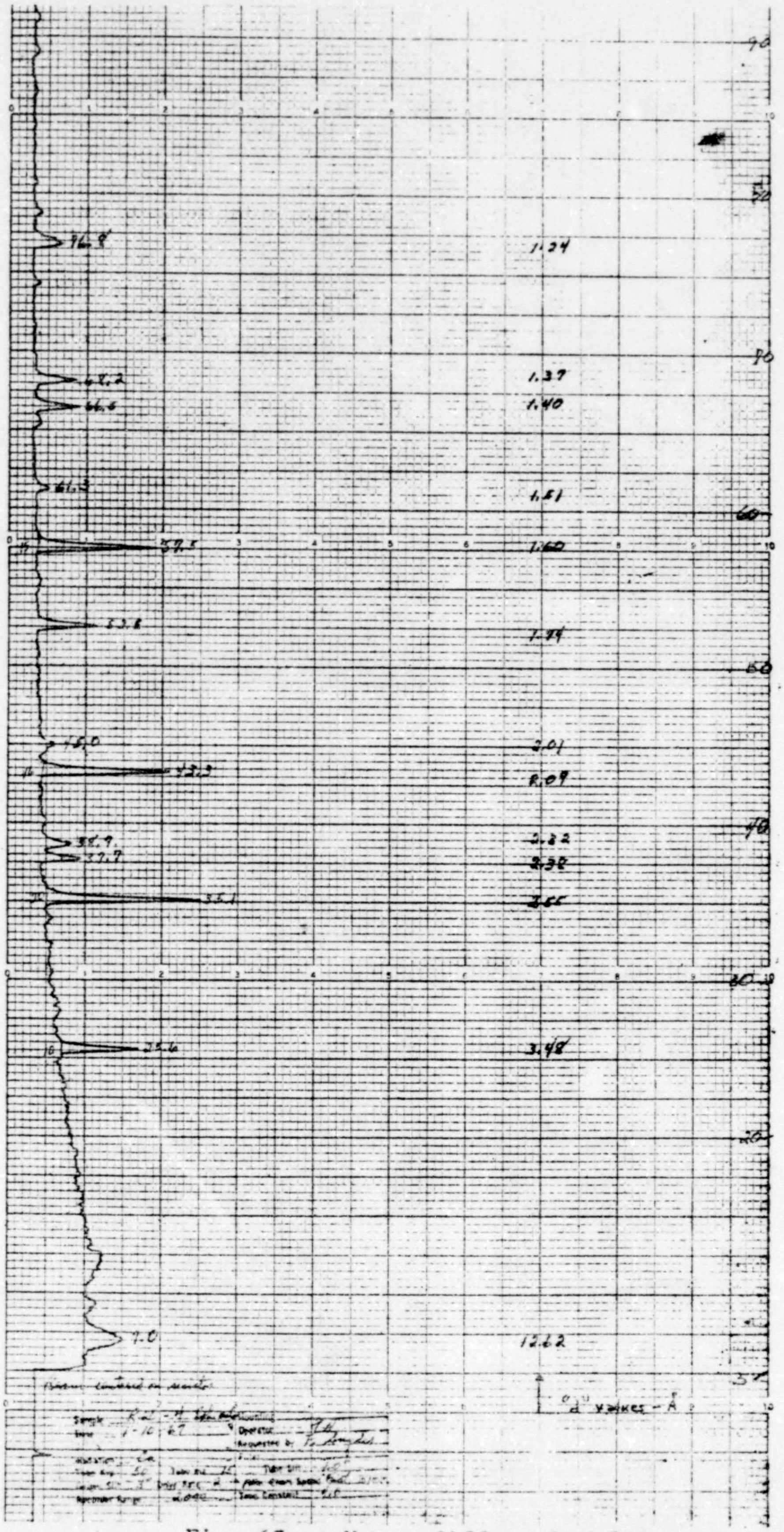

Fig. 63. - X-ray diffraction data
for resistor R20-4, 1° beam, exhaust only

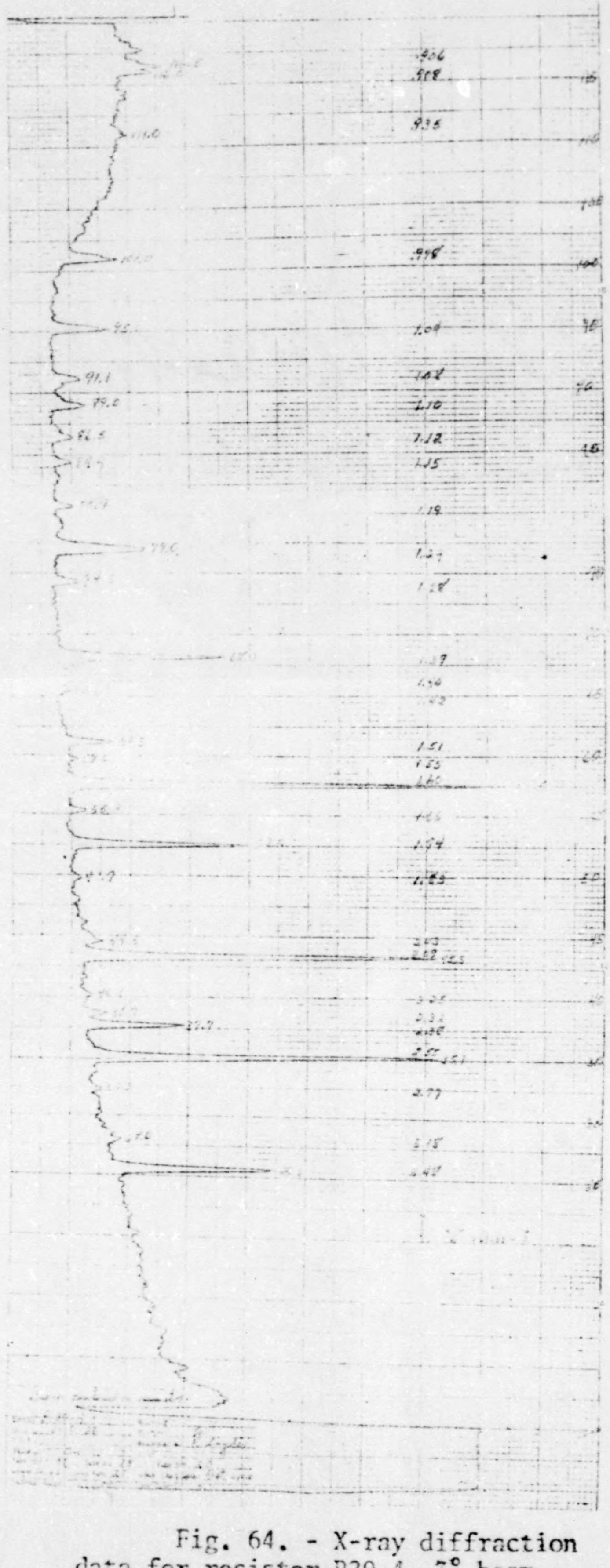

Fig. 64. - X-ray diffraction data for resistor R20-4, 3° beam, exhaust only

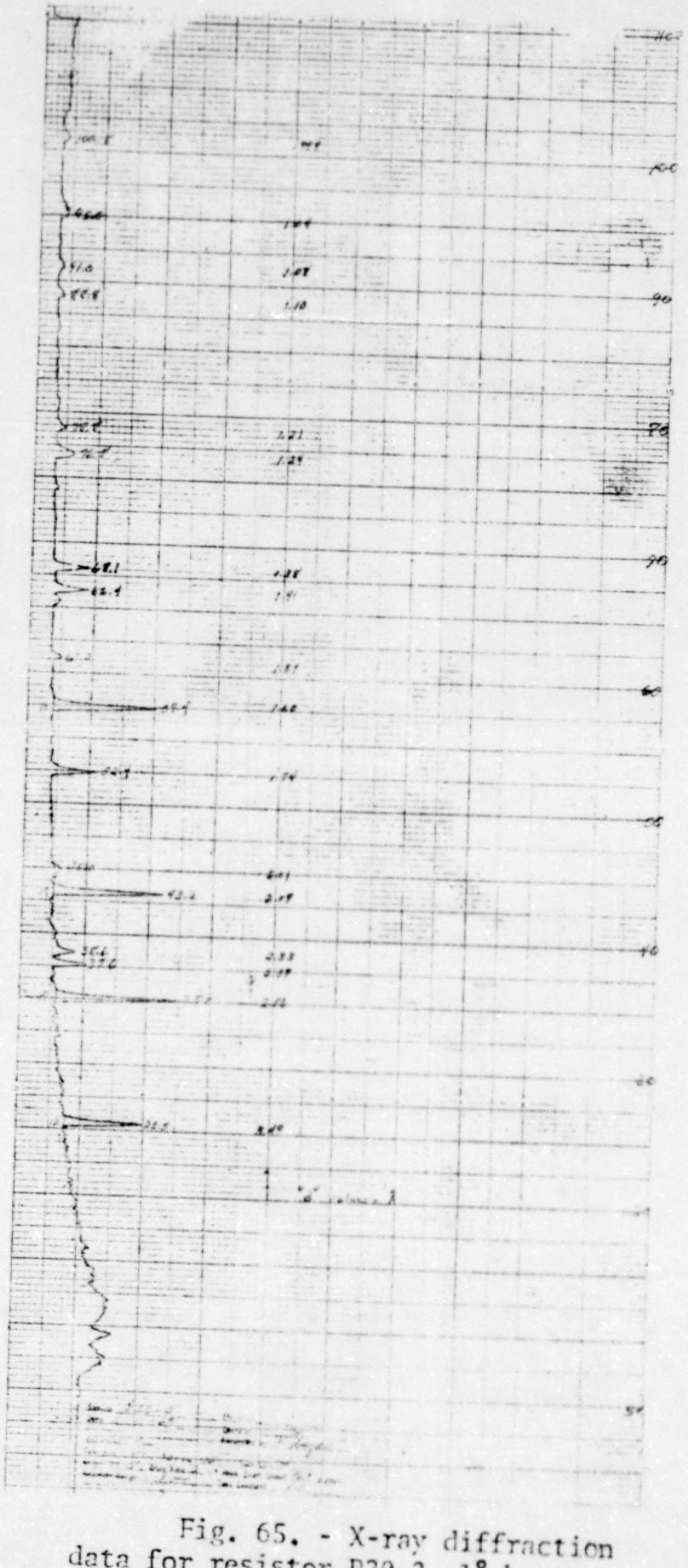

Fig. 65. - X-ray diffraction data for resistor R20-2, 1° beam, 541 hours of life

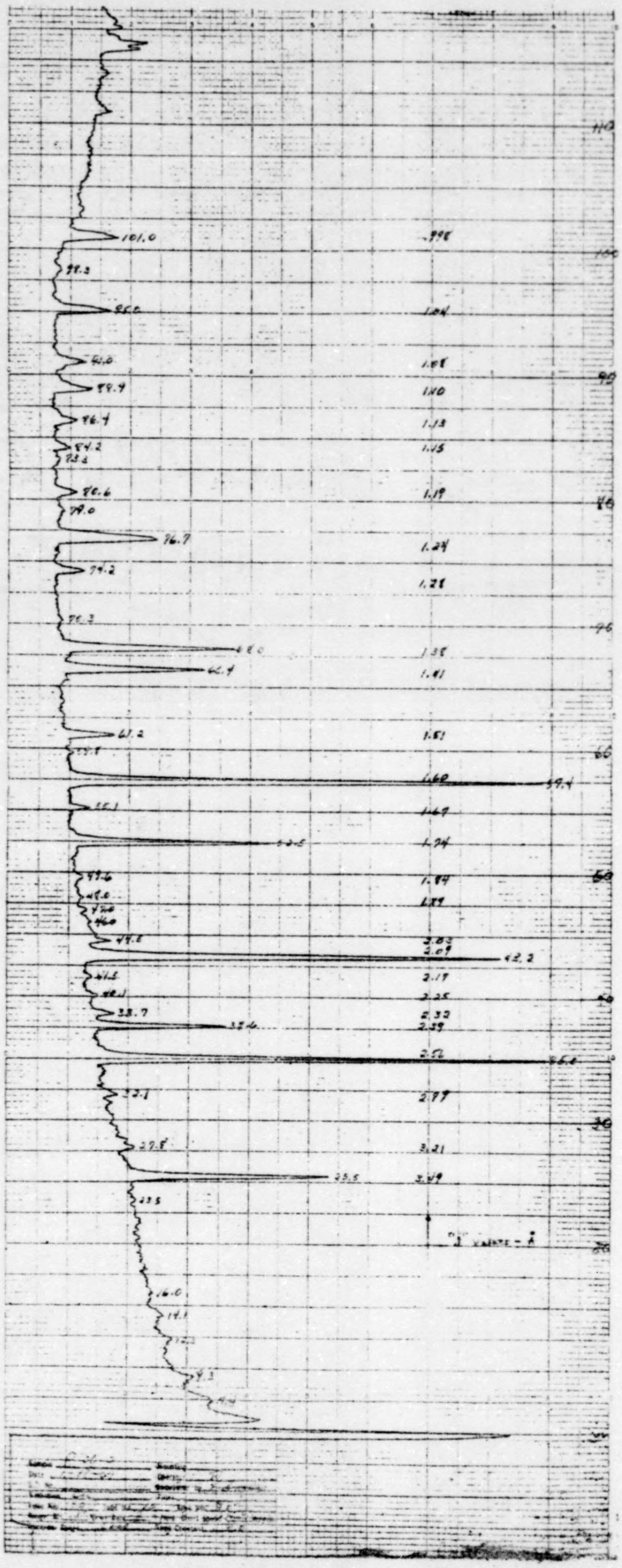

Fig. 66. - X-ray diffraction data for resistor R20-2, 3° beam, 541 hours of life

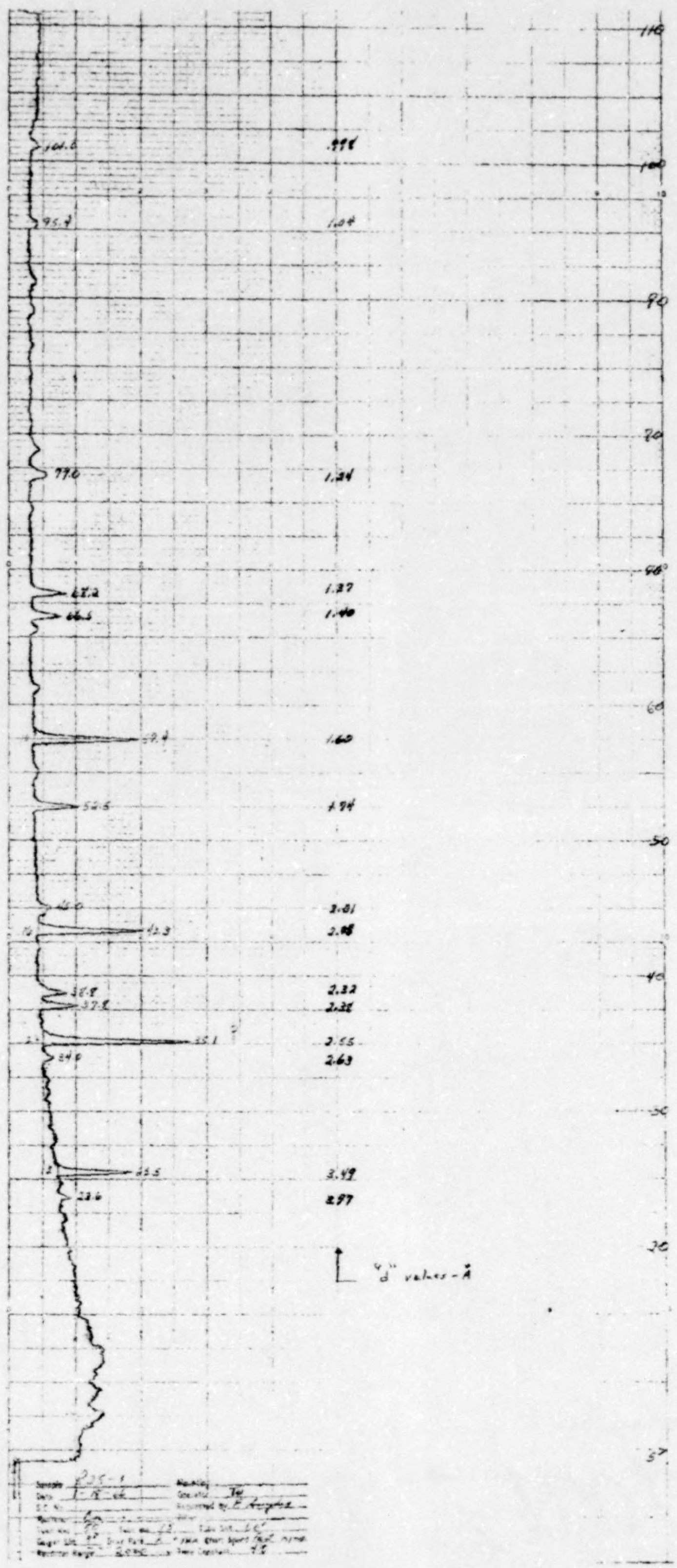

Fig. 67. - X-ray diffraction data for resistor R25-1, 541 hours of life

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