(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 704 864 A2

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
03.04.1996 Bulletin 1996/14

(51) Int. Cl.[6]: H01C 17/02, H01C 17/065

(21) Application number: 95115134.9

(22) Date of filing: 26.09.1995

(84) Designated Contracting States:
DE FR GB

(30) Priority: 28.09.1994 JP 233365/94
09.03.1995 JP 49723/95

(71) Applicant: SUMITOMO METAL CERAMICS INC.
Yamaguchi (JP)

(72) Inventor: Fukaya, Masashi,
c/o Sumitomo Metal Ceramics Inc.
Mine-shi, Yamaguchi (JP)

(74) Representative: Sandmair, Kurt, Dr. Dr.
Patentanwälte
Schwabe, Sandmair, Marx
Stuntzstrasse 16
D-81677 München (DE)

(54) Resistor on a ceramic circuit board

(57) A ceramic circuit board having an external resistor prepared by co-firing a low-bubbling resistor and a glass overcoat in which Ag is used in an amount of 0 to less than 1% by weight with a glass having a deformation temperature not higher than that of the glass of the overcoat in the low-bubbling resistor and a glass of CaO-Al_2O_3-SiO_2-B_2O_3 system is used in the overcoat. Also, in the low-bubbling resistor, Ag may be contained in an amount of at least 1% by weight in combination with a glass having such a deformation temperature that this deformation temperature minus 10 °C is not higher than that of the glass of the overcoat. Addition of Ag to the resistor can render the deformation temperature of the glass of the resistance paste substantially equal to or less than that of the glass of the overcoat, thereby enabling further reduction of the amount of bubbles remaining in the resistor after firing. The low-bubbling resistor not only enables accurate adjustment of the resistivity by laser trimming but also enables stable maintenance of the resistance value after the trimming.

EP 0 704 864 A2

Printed by Rank Xerox (UK) Business Services
2.9.16/3.4

Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a ceramic circuit board having on its surface an external resistor covered with a glass overcoat. More particularly, the present invention is concerned with a ceramic circuit board having an external resistor which stably maintains an accurate resistance value obtained by trimming.

2. Description of the Prior Art

Besides the internal resistor disposed between the layers of a multilayer circuit board, a ceramic circuit board for use in integral circuits is provided with a circuit comprising an external resistor and a conductor pattern printed on the surface of the ceramic circuit board, which contributes toward imparting an advanced function to the ceramic circuit board and reducing the production cost.

In the formation of a resistor on a substrate surface, generally, a conductive substance is added to a glass composition, rendered pasty, printed and sintered into the desired resistor. In the formation of the resistor, occasionally, printing is effected so as to cover the resistor with a glass material and fired to thereby form an overcoat in order to protect the resistor from climatic changes or other environmental influences. The obtained resistor has its resistance value finely adjusted by laser trimming.

Generally, a resistor used in a ceramic circuit board is formed by firing a resistor at 800 to 900°C, printing an overcoat paste comprising a low-melting-point glass thereon, and firing at 500 to 600°C. In accordance with the miniaturisation of electronic appliances and the higher-density packaging therein, there is the tendency that the ceramic substrate is also provided in multilayer form to comply with higher-density packaging. Further, there is the tendency that use is made of substrate materials which have a low coefficient of thermal expansion in conformity with that of silicon chips to be mounted thereon. Under such circumstance, low-temperature firable substrates are used for circuit boards.

In most of the substrates fired at low temperatures, Ag or Cu is used for the formation of internal conductors in the inner layers. However, the coefficient of thermal expansion of the ceramic substrate is different from that of the internal conductors, and such a difference will generate strain when the ceramic substrate undergoes repeated firing steps, thereby resulting in an electrical disconnection. In order to obtain a circuit board of high reliability, the number of firing steps should be minimized. Further, for conformity with the thermal expansion of the circuit board, a glass of a low coefficient of thermal expansion should be used in the overcoat as well. Still further, for forming the overcoat by firing at low temperatures, it is preferred that a low-melting-point glass be employed in the overcoat. However, the low-melting-point glass has a drawback in weather resistance, so that it is required to use a glass having a melting point as high as about the temperature employed for firing the resistor.

It is therefore apparent that a resistor capable of being co-fired with the overcoat is desirably employed in a multilayer structure or a ceramic circuit board of a low thermal expansion coefficient. Such a co-firing leads to a reduction in the production steps and in the plant and equipment investment. However, such a co-firing of the resistor and the overcoat brings about the tendency that the glass of the overcoat confines the bubbles generated from the resistor in the external resistor, thereby causing the bubbles to remain within the fired resistor. When the bubbles remain as confined in the resistor, the problem occurs such that a very close access of a trimming edge to the bubble at the time of laser trimming produces cracks therebetween, resulting in the formation of a resistor lacking in the stability in resistance values.

The above situation will be described with reference to the drawings. Fig. 1 is a plan of one form of a conventional external resistor disposed on a substrate of a ceramic circuit board, and Fig. 2 is a sectional view thereof. A wiring material such as a metal paste is printed on a ceramic substrate surface 1, thereby forming a conductor pattern 2 on the surface. Part thereof constitutes an electrode for a resistor 3. The resistor 3 is composed of glass components having a conductive material such as a metal added thereto. The upper part thereof is covered with an overcoat 4 composed of glass materials. The resistor 3 and the overcoat 4 constitute an external resistor 7. The overcoat 4 may either cover each individual resistor 3 a little wider than the same or uniformly cover a wide area of not only a plurality of resistors 3 but also a conductor pattern 2.

The co-firing of the overcoat 4 and the resistor 3 prevents the bubbles 6 generated in the resistor from escaping outside because of the presence of the overcoat 4, thus causing them to remain as confined in the resistor 3. Laser trimming of such an external resistor 7 leads to formation of a trimming channel 5 as shown in the figures which extends through the overcoat 4 and the resistor 3.

Although laser trimming is generally conducted while measuring the resistance value exhibited by the resistor, the presence of the bubbles 6 not only interferes with such precision trimming but also generates microcracks upon access of the trimming channel tip to the bubbles 6. Also, even if there is no occurrence of cracks during trimming, cracks may occur because of the bubbles during the use as a part. Thus, the presence of bubbles in the resistor renders the resistance value exhibited by the resistor inaccurate and renders its resistance value after trimming instable.

SUMMARY OF THE INVENTION

An object of the present invention is to resolve the above drawbacks of the prior art and specifically to provide a ceramic circuit board having an external resistor obtained by the co-firing of a resistor and an overcoat which does not permit bubbles to remain in the resistor to thereby resolve the cracking during laser trimming or thereafter attributed to the bubbles remaining in the resistor.

The inventors have made intensive studies to find out that the above objects can be attained by using a overcoat glass satisfying specific requirements described in detail hereinafter.

The present invention has been arrived at on the basis of the above finding.

Accordingly, the present invention provides ceramic circuit boards with the following constructions (1) to (5).

(1) A ceramic circuit board having an external resistor prepared by co-firing a resistor and a glass overcoat, the resistor of the external resistor is a low-bubbling resistor.

(2) The ceramic circuit board as recited in item (1) above, wherein the resistor contains Ag in an amount of 0 to less than 1% by weight and the glass of the resistor has a deformation temperature which is not higher than that of the glass of the overcoat.

(3) The ceramic circuit board as recited in item (1) above, wherein the resistor contains Ag in an amount of at least 1% by weight and the glass of the resistor has such a deformation temperature that this deformation temperature minus 10 °C is not higher than that of the glass of the overcoat.

(4) The ceramic circuit board as recited in item (1) above, wherein a glass of the resistor is $CaO\text{-}Al_2O_3\text{-}SiO_2\text{-}B_2O_3$ system glass.

(5) The ceramic circuit board as recited in item (1), wherein a glass of the overcoat comprises 60 to 90% by weight of $CaO\text{-}Al_2O_3\text{-}SiO_2\text{-}Cr_2O_3\text{-}B_2O_3$ system glass and 10 to 40% by weight of alumina, the glass having a deformation temperature of 720 to 740°C.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a view illustrating a conventional external resistor.

Fig. 2 is a sectional view of the resistor of Fig. 1.

Fig. 3-10 show the change in resistivity versus the difference in deformation temperature between the glass used in a resistor and the glass used in an overcoat.

Fig. 11-18 show the change in resistivity versus the number of bubbles remaining in resistors.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

According to the present invention, the deformation temperature of the glass of the resistor of the external resistor is rendered equal to or lower than that of the glass of the overcoat to provide a more excellent low-bubbling resistor even if the glass overcoat and the resistor are co-fired. This is because the glass of the resistor is caused to have a deformation temperature equal to or lower than that of the overcoat by adding 0 to less than 1% of an Ag component to the resistor, so that the sintering of the resistor is accelerated to thereby allow the generated bubbles to escape to the side of the glass overcoat, or because, in addition to an electric resistance component such as RuO_2-based or $Bi_2Ru_2O_7$-based component, Ag is positively added in an amount of at least 1% to the resistor, so that Ag is combined with the resistor materials to thereby promote the sintering with the same result that the sintering of the resistor is accelerated to thereby allow generated bubbles to escape from the side of the glass overcoat.

The term "deformation temperature" as used in the present invention refers to the softening temperature of a glass material at which the thermal expansion thereof, which has been increasing linearly as the glass material is heated, comes to stop and then begins to decrease. The method of measuring the thermal expansion itself is stipulated in the Japanese Industrial Standards.

The ceramic circuit board of the present invention may have any of the monolayer and multilayer constructions as long as a ceramic is used as an insulator. A multilayer ceramic circuit board can be produced by, for example, the green sheet lamination process or the printing lamination process. A circuit may be provided only on one side of the substrate or both sides thereof.

The ceramic material composing the ceramic substrate for use in the present invention is not particularly limited, examples thereof including alumina (Al_2O_3), aluminum nitride (AlN), silicon carbide (SiC) and various ceramics composed mainly thereof. A low-temperature firing ceramic can be used which is a mixture of alumina powder with glass powder. The conductor material used in the inner layers is varied depending on the substrate material. When the substrate material is alumina or aluminum nitride, use is made of a high-melting-point metal such as molybdenum or tungsten. When the substrate material can be fired at relatively low temperatures, use is made of a metal such as gold, silver, silver-palladium alloy, copper or nickel.

A ceramic circuit board in which W or Mo is used as a wiring conductor on a substrate of alumina, aluminum nitride or the like and of which the co-firing is conducted in a reducing atmosphere for preventing the oxidation of the conductor is known as an example of the co-fired ceramic circuit boards produced by co-firing a ceramic green sheet and a wiring conductor paste. However, this encounters the problem that conductor oxidation cannot be avoided in the formation of RuO_2-type or $Bi_2Ru_2O_7$-type resistor of high reliability which must be fired in the air.

On the other hand, a low-temperature firable multilayer ceramic circuit board in which use is made of an Ag-based conductor which has a low circuit resistance and can be fired in the air, such as Ag, Ag-Pd, Ag-Pt or Ag-Pd-Pt, and in which a ceramic material capable of be fired at temperatures not higher than the melting point of the above conductor material (900 to 1200°C) is used as an insulator has been developed, which is especially preferred as the ceramic circuit board of the present invention. Generally, a ceramic board to be fired at about 1200°C or below is called "low-temperature firable ceramic board", in which, for example, an Ag-based, Au-based or Cu-based conductor is used as conductors on inner layers and surface layers.

A ceramic material which can be fired at temperatures lower than the melting point of, for example, inserted Ag conductor material is preferably employed as the low-temperature firable ceramic insulator material. When use is made of an Ag conductor or an Ag alloy conductor in which the contents of Pd and Pt are low, because the melting point of such a metal formed in multiple layers is as low as about 900 to 1200°C, it is necessary to employ a material which can be fired at 800 to 1100°C. Representative examples of such materials include a mixture of the powder of a glass such as borosilicate glass or glass further containing some oxides (e.g., MgO, CaO, Al_2O_3, PbO, K_2O, Na_2O, ZnO, Li_2O, etc.) with the powder of a ceramic such as alumina or quartz, and a crystallizable glass powder which undergoes cordierite or α-spodumene crystallization.

The above material can be used not only in the monolayer form as mentioned above but also in the multilayer form. The multilayer substrate can be produced according to the green sheet lamination process in which a plurality of green sheets are employed. For example, a powdery ceramic insulator material is mixed with additives, such as a solvent, resin, etc., and molded according to the doctor blade method into green sheets of about 0.1 to 0.5 mm in thickness. A paste of a conductor material such as Ag, Ag-Pd, Ag-Pt or Ag-Pd-Pt is screen printed on one of the green sheets to thereby give a desired wiring pattern. Through holes each of about 0.1 to 2.0 mm in diameter are formed in the green sheet by means of blanking dies or a punching machine so as to enable connection to another conductor layer. Also, wiring via holes are formed and filled with an Ag conductor material. In the same manner, wiring patterns are printed on other green sheets as many as required for forming the desired circuit. These green sheets are accurately laminated one upon another with the use of tooling holes respectively formed in the green sheets and unified by thermocompression bonding effected at 80 to 150°C under 10 to 250 kg/cm^2.

When the circuit includes an inner resistor or resistors, an RuO_2 system, or $Bi_2Ru_2O_7$ system resistor is formed which is fired in the air. In that case, it is printed together with terminals therefor on the green sheet for forming an inner layer.

The obtained structure is co-fired in the air, thereby providing a ceramic multilayer board with built-in conductors.

The present invention has been described with the low-temperature firable ceramic as an example. Although it is a preferred embodiment of the present invention, the present invention is not limited thereto.

The resistors use in the present invention include those composed of an RuO_2-based or $Bi_2Ru_2O_7$-based electric resistance component and a glass component and, generally, printed in the form of a paste on a ceramic substrate surface according to the thick-film process. Further, an overcoat composition comprising, for example, a $CaO\text{-}Al_2O_3\text{-}SiO_2\text{-}Cr_2O_3\text{-}B_2O_3$ system glass is printed on the printed resistor generally by the thick film process. In the present invention, these resistor and glass overcoat are co-fired. The firing is conducted in the air.

The present invention will now be described in greater detail with reference to the following Examples and Comparative Examples.

EXAMPLES

A ceramic circuit board was prepared with the use of a low-temperature firable ceramic prepared according to the following procedure. 60% by weight of glass powder composed of, in weight percentages, 27% of CaO, 5% of Al_2O_3, 59% of SiO_2 and 9% of B_2O_3 was mixed with 40% by weight of Al_2O_3 powder having an average particle size of 1.0 μm to prepare a powder component.

The above powder component was mixed with, in weight percentage, 10% of acrylic resin, 30% of toluene, 10% of isopropanol and 5% of dibutyl phthalate with respect to 100% by weight of the powder component in a ball mill and formed into a green sheet of 0.4 mm in thickness according to the doctor blade process. This green sheet was punched at given positions by means of dies and an Ag paste was screen printed to fill the holes therewith. The sheet was dried, and further the Ag paste was screen printed on the sheet to thereby form a wiring pattern. In the same manner, other green sheets having printed wiring patterns were prepared. A given number of obtained sheets were laminated one upon another and caused to undergo thermocompression bonding. The resultant laminate was fired by holding it at 900°C for 20 min. Thus, a ceramic circuit substrate was obtained.

Each of the resistor compositions having the chemical compositions specified in Table 1 was printed on the ceramic substrate so as to form a resistor of 1 mm in width and 2 mm in length. The overcoat was formed by printing on the above resistor each overcoat composition including each of the glass compositions A to H of Table 2 having respective deformation temperatures indicated in the table, with which Al_2O_3 powder was mixed.

Table 1

Chemical Composition of Resistor and Deformation Temperature

Resistor No.	Chemical composition of glass of resistor (%) CaO	Al_2O_3	SiO_2	B_2O_3	impurities	Deformation temperature of glass of resistor (°C)	Content of RuO_2 in resistor material (%)	Content of Ag in resistor material (%)
1	33.3	4.2	43.4	16.1	3.0	727	20	0
2	33.3	4.2	43.4	16.1	3.0	727	40	0
3	30.4	3.7	41.2	22.4	2.3	723	20	0
4	30.4	3.7	41.2	22.4	2.3	723	40	0
5	28.1	3.4	38.6	28.3	1.6	720	20	0
6	28.1	3.4	38.6	28.3	1.6	720	40	0
7	26.2	3.1	36.2	32.9	1.6	690	20	0
8	26.2	3.1	36.2	32.9	1.6	690	40	0
9	25.0	4.2	53.2	16.7	0.9	727	20	0
10	25.0	4.2	53.2	16.7	0.9	727	40	0
11	23.0	3.7	49.7	22.7	0.9	725	20	0
12	23.0	3.7	49.7	22.7	0.9	725	40	0

Table 1 (continued)

Chemical Composition of Resistor and Deformation Temperature

Resistor No.	Chemical composition of glass of resistor (%) CaO	Al_2O_3	SiO_2	B_2O_3	impurities	Deformation temperature of glass of resistor (°C)	Content of RuO_2 in resistor material (%)	Content of Ag in resistor material (%)
13	21.2	3.5	45.8	27.9	1.6	718	20	0
14	21.2	3.5	45.8	27.9	1.6	718	40	0
15	27.3	4.5	58.1	9.1	1.0	731	40	5.0
16	27.3	4.5	58.1	9.1	1.0	731	40	0
17	25.0	4.2	53.2	16.7	0.9	727	40	3.0
18	36.4	4.5	48.9	9.0	1.2	733	40	0
19	36.4	4.5	48.9	9.0	1.2	733	40	4.0
20	27.3	4.5	58.1	9.1	1.0	731	20	3.0
21	27.3	4.5	58.1	9.1	1.0	731	20	0
22	36.4	4.5	48.9	9.0	1.2	733	20	3.0
23	36.4	4.5	48.9	9.0	1.2	733	20	0
24	25.0	4.2	53.2	16.7	0.9	727	40	1.2

Table 2

Chemical Composition of Glass Overcoat and Deformation Temperature									
Designation of glass overcoat		A	B	C	D	E	F	G	H
Chemical composition of glass (%)	SiO_2	43.9	41.8	55.0	53.1	49.6	60.1	53.2	45.2
	Al_2O_3	4.7	4.0	4.5	4.3	13.1	14.1	4.2	4.3
	CaO	33.9	30.6	25.5	24.2	27.3	20.7	25.0	39.6
	B_2O_3	16.2	22.4	12.3	16.6	9.1	4.6	16.7	9.0
	Cr_2O_3	0.0	0.0	1.8	0.9	0.0	0.0	0.0	0.0
	impurities	1.3	1.2	0.9	0.9	0.9	0.5	0.9	1.9
	deformation temp. (°C)	727	723	730	725	726	737	727	720
Chemical composition of glass overcoat(%)	glass content	80	70	90	60	80	70	70	60
	Al_2O_3 content	20	30	10	40	20	30	30	40

With respect to each of various combinations of these resistors with glass overcoats, a simultaneous firing was performed in the air at 890°C for 10 min.

Each resultant resistor was laser-trimmed so that the resistivity was increased to twice its initial resistivity. The initial resistivities are shown in Table 3.

The RuO_2 content in the resistor material indicated in Table 1 means the weight % based on the total weight of the resistor including Ag and glass components. Likewise, the Ag content means the weight % based on the total weight of the resistor including glass components, RuO_2 and Ag. The load test indicated in Table 4 means the maximum of the percentage of change in resistivity with respect to the laser-trimmed resistivity, after observed at the 1000-hr continuous application of 1/32 W load.

Figs. 3-10 show the relationship between the percentage of the change in resistivity and the difference in deformation temperature between the glasses used in the resistors and the overcoats. The difference was obtained by subtracting the deformation temperature of a glass used in a resistor from the deformation temperature of a glass used in an overcoat (i.e., the deformation temperature of a glass used in an overcoat minus the deformation temperature of a glass used in a resistor). In figures, concerning resistors without the addition of Ag, the test results are indicated by the solid circle symbol (●) and region A (hatched with thin lines) is an acceptable range. While, concerning resistors with the addition of Ag, the test results are indicated by the open circle symbol (o) and region B (hatched with thick lines) is an acceptable range. In Fig. 8, the change in resistivity was relatively large because the yield point of the glass used in the overcoat was high and a sufficient sintering was not performed at the firing temperature of 890°C.

Table 3

Resistivity before Laser Trimming

Resistor No. \ Glass over-coat	A	B	C	D	E	F	G	H
1	81kΩ	103kΩ	82kΩ	101kΩ	100kΩ	86kΩ	82kΩ	125kΩ
2	550 Ω	622 Ω	533 Ω	610 Ω	613 Ω	542 Ω	537 Ω	613 Ω
3	73kΩ	76kΩ	76kΩ	78kΩ	74kΩ	69kΩ	70kΩ	89kΩ
4	420 Ω	433 Ω	435 Ω	436 Ω	415 Ω	431 Ω	416 Ω	486 Ω
5	65kΩ	66kΩ	65kΩ	61kΩ	63kΩ	75kΩ	68kΩ	73kΩ
6	373 Ω	370 Ω	370 Ω	380 Ω	368 Ω	385 Ω	367 Ω	393 Ω
7	37kΩ	38kΩ	35kΩ	37kΩ	36kΩ	39kΩ	36kΩ	39kΩ
8	286 Ω	277 Ω	293 Ω	286 Ω	278 Ω	272 Ω	274 Ω	292 Ω
9	85kΩ	101kΩ	86kΩ	113kΩ	99kΩ	94kΩ	87kΩ	118kΩ
10	567 Ω	586 Ω	570 Ω	579 Ω	589 Ω	578 Ω	563 Ω	631 Ω
11	78kΩ	96kΩ	76kΩ	89kΩ	88kΩ	89kΩ	81kΩ	107kΩ
12	549 Ω	666 Ω	540 Ω	578 Ω	610 Ω	643 Ω	584 Ω	690 Ω
13	71kΩ	72kΩ	73kΩ	72kΩ	77kΩ	82kΩ	72kΩ	79kΩ
14	404 Ω	407 Ω	406 Ω	421 Ω	393 Ω	431 Ω	416 Ω	425 Ω
15	543 Ω	572 Ω	554 Ω	541 Ω	580 Ω	560 Ω	537 Ω	628 Ω
16	606 Ω	622 Ω	630 Ω	611 Ω	614 Ω	583 Ω	635 Ω	680 Ω
17	534 Ω	589 Ω	544 Ω	594 Ω	548 Ω	590 Ω	559 Ω	606 Ω
18	652 Ω	663 Ω	645 Ω	676 Ω	652 Ω	621 Ω	706 Ω	712 Ω
19	596 Ω	601 Ω	588 Ω	605 Ω	604 Ω	612 Ω	595 Ω	628 Ω
20	573 Ω	585 Ω	573 Ω	592 Ω	597 Ω	584 Ω	566 Ω	603 Ω
21	106kΩ	106kΩ	103kΩ	111kΩ	127kΩ	94kΩ	124kΩ	126kΩ
22	98kΩ	102kΩ	99kΩ	105kΩ	118kΩ	109kΩ	99kΩ	121kΩ
23	113kΩ	117kΩ	108kΩ	129kΩ	132kΩ	96kΩ	128kΩ	127kΩ
24	534 Ω	558 Ω	528 Ω	546 Ω	536 Ω	545 Ω	533 Ω	560 Ω

Table 4

Percentage (%) of Change (Max.) in Load Test

Glass overcoat / Resistor	Designation	A	B	C	D	E	F	G	H
	Deformation temperature	727	723	730	725	726	737	727	720
Resistor No.	Deformation temperature								
1	727	0.3	1.3	0.1	1.1	1.2	0.5	0.3	2.1
2	727	0.3	1.4	0.2	1.1	1.1	0.3	0.4	2.3
3	723	0.2	0.3	0.1	0.3	0.1	0.3	0.1	1.5
4	723	0.2	0.3	0.1	0.2	0.1	0.4	0.2	1.4
5	720	0.2	0.2	0.2	0.3	0.2	0.5	0.2	0.6
6	720	0.1	0.2	0.2	0.2	0.1	0.5	0.1	0.6
7	690	0.1	0.2	0.1	0.2	0.1	0.4	0.1	0.5
8	690	0.1	0.2	0.1	0.2	0.1	0.4	0.1	0.7
9	727	0.3	1.3	0.2	1.2	1.1	0.5	0.3	1.9
10	727	0.3	1.2	0.3	1.1	1.1	0.5	0.4	1.9
11	725	0.2	1.1	0.2	0.5	0.4	0.7	0.1	1.6
12	725	0.2	1.1	0.1	0.6	0.3	0.8	0.2	1.6

Table 4 (continued)

Percentage (%) of Change (Max.) in Load Test

Resistor No. \ Glass overcoat: Designation		A	B	C	D	E	F	G	H
	Deformation temperature	727	723	730	725	726	737	727	720
Resistor No.	Deformation temperature								
13	718	0.2	0.1	0.2	0.2	0.2	0.7	0.1	0.6
14	718	0.1	0.2	0.1	0.2	0.2	0.5	0.1	0.6
15	731	0.1	0.6	0.1	0.5	0.5	0.5	0.1	1.3
16	731	1.2	1.6	1.2	1.4	1.4	0.6	1.6	2.7
17	727	0.1	0.5	0.1	0.6	0.2	0.6	0.1	0.8
18	733	1.6	2.0	1.3	1.7	1.3	0.7	2.6	2.9
19	733	0.2	0.7	0.1	0.7	0.6	0.5	0.2	1.2
20	731	0.2	0.6	0.2	0.7	0.5	0.6	0.1	1.2
21	731	1.1	1.5	1.2	1.5	1.3	0.7	2.2	2.8
22	733	0.1	0.7	0.1	0.7	0.5	0.8	0.1	1.3
23	733	1.3	2.1	1.4	1.8	1.4	0.8	2.8	1.5
24	727	0.1	0.7	0.1	0.8	0.4	0.4	0.1	0.7

With respect to each of various combinations of resistors 1 to 24 with glass overcoats A to H, Table 4 gives the load test results in terms of the maximum of the percentages of change of resistivity. Table 5 lists the number of bubbles of at least 5 µm in diameter contained in a section of 300 µm x 15 µm which was measured by an electron microscope observation of a section of each resistor.

Figs. 11-18 show the relationship between the percentage of the change in resistivity and the number of bubbles remaining in the resistor.

Table 5

Number of Bubbles

Resistor No. \ Glass overcoat	A	B	C	D	E	F	G	H
1	2	23	0	18	23	9	2	26
2	2	28	2	22	25	5	6	25
3	2	5	0	5	0	4	0	20
4	3	6	0	4	0	6	0	19
5	2	2	3	6	1	8	0	13
6	1	3	3	3	0	11	0	15
7	0	1	2	2	0	9	0	10
8	0	2	2	4	0	10	0	14
9	2	21	3	22	22	9	2	26
10	4	19	4	21	23	12	6	33
11	2	20	4	9	6	13	1	31
12	0	22	2	11	6	15	2	29
13	0	0	2	3	4	15	1	11
14	0	3	0	3	4	11	1	15
15	0	10	1	8	8	10	0	22
16	20	31	21	24	26	11	25	39
17	0	8	0	10	3	13	0	13
18	31	36	23	33	31	14	33	35
10	2	12	0	12	10	10	4	21
20	3	7	2	13	9	11	3	25
21	15	27	17	27	23	12	31	37
22	0	13	1	15	7	15	1	18
23	25	35	13	32	25	16	35	25
24	0	8	4	17	7	9	1	16

With respect to various combinations of resistors 1 to 24 with glass overcoats A to H as listed in Tables 4 and 5, the examples of the present invention in which the deformation temperature of the glass of the resistor is not higher than that of the overcoat glass are combinations of glass overcoat A with resistors 1 to 14, glass overcoat B with resistors 3 to 8, 13 and 14, glass overcoat C with resistors 1 to 14, glass overcoat D with resistors 3 to 8, 11 and 14, glass overcoat E with resistors 3 to 8 and 11 to 14, glass overcoat F with resistors 1 to 14, 16, 18, 21 and 23, glass overcoat G with resistors 1 to 14, and glass overcoat H with resistors 5 to 8, 13 and 14. The examples exerting the same effects as at the deformation temperature of the glass of the resistor minus 10°C by virtue of the addition of at least 1.0% of Ag are combinations of glass overcoat A with resistors 15, 17, 19, 20, 22 and 24, glass overcoat B with resistors 15, 17, 19, 20, 22 and 24, glass overcoat C with resistors 15, 17, 19, 20, 22 and 24, glass overcoat D with resistors 15, 17, 19, 20, 22 and 24, glass overcoat E with resistors 15, 17, 19, 20, 22 and 24, glass overcoat F with resistors 15, 17, 19, 20, 22 and 24, glass overcoat G with resistors 15, 17, 19, 20, 22 and 24, and glass overcoat H with resistors 17 and 24. The other combinations are comparative examples to the present invention.

It is apparent from Tables 4 and 5 that, when use is made of, for example, glass overcoat G, as demonstrated by the combinations with resistors 1 to 14, rendering the deformation temperature of the glass of the resistor equal to or lower than the deformation temperature of the overcoat glass causes the sintering of the resistor to precede that of the overcoat glass, so that the number of bubbles is markedly small with the excellent load test result that the rate of change is not greater than 1%. Generally, the reliability of the thick-film resistor is evaluated on whether the change in acceleration test is within ±1% as a rule of thumb. Further, for example, comparison of the combinations with resistors 15, 17, 19, 20, 22 and 24 to the combinations with resistors 16, 18, 21 and 23 as comparative examples shows that the addition of Ag promotes the sintering of the resistor, so that the number of generated bubbles is nil or extremely small, thereby ensuring excellent results in the load test.

It is apparent that the addition of Ag in an amount of at least 1.0% exerts the same effect as a temperature fall of 10°C from the deformation temperature in respect of the promotion of the sintering of the resistor. However, the addition of Ag in an amount greater than 10% causes Ag particles to precipitate, thereby lowering the resistance value.

As apparent from the foregoing, the present invention provides a ceramic circuit board having an external resistor formed by co-firing a resistor and an overcoat, prevents the cracking of the resistor at the time of trimming and thereafter, and realizes the exertion of resistance performance ensuring excellent weather resistance and stability.

Claims

1. A ceramic circuit board having an external resistor prepared by co-firing a resistor and a glass overcoat, the resistor of the external resistor being a low-bubbling resistor.

2. The ceramic circuit board as recited in Claim 1, wherein the resistor contains Ag in an amount of 0 to less than 1% by weight and the glass of the resistor has a deformation temperature which is not higher than that of the glass of the overcoat.

3. The ceramic circuit board as recited in Claim 1, wherein the resistor contains Ag in an amount of at least 1% by weight and the glass of the resistor has such a deformation temperature that the deformation temperature minus 10 °C is not higher than that of the glass of the overcoat.

4. The ceramic circuit board as recited in Claim 1, wherein a glass of the resistor is CaO-Al_2O_3-SiO_2-B_2O_3 system glass.

5. The ceramic circuit board as recited in Claim 1, wherein a glass of the overcoat comprises 60 to 90% by weight of CaO-Al_2O_3-SiO_2-Cr_2O_3-B_2O_3 system glass and 10 to 40% by weight of alumina, the glass having a deformation temperature of 720 to 740°C.

FIG.1 PRIOR ART

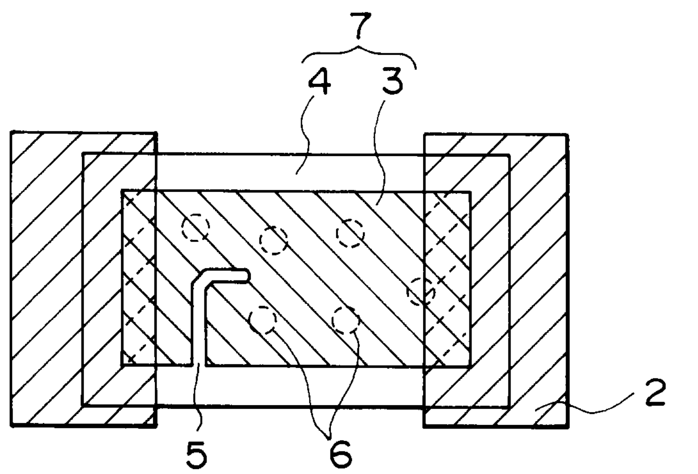


FIG.2 PRIOR ART

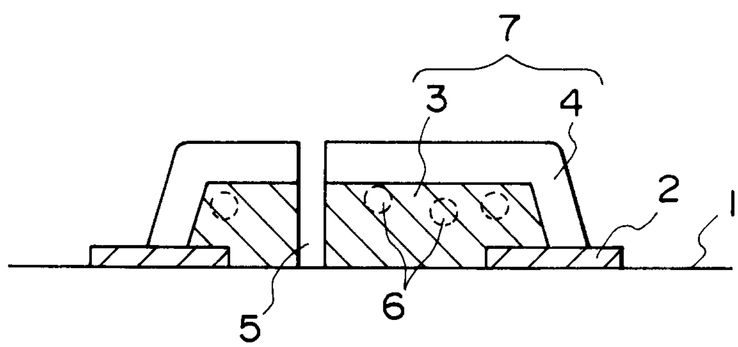


FIG. 3

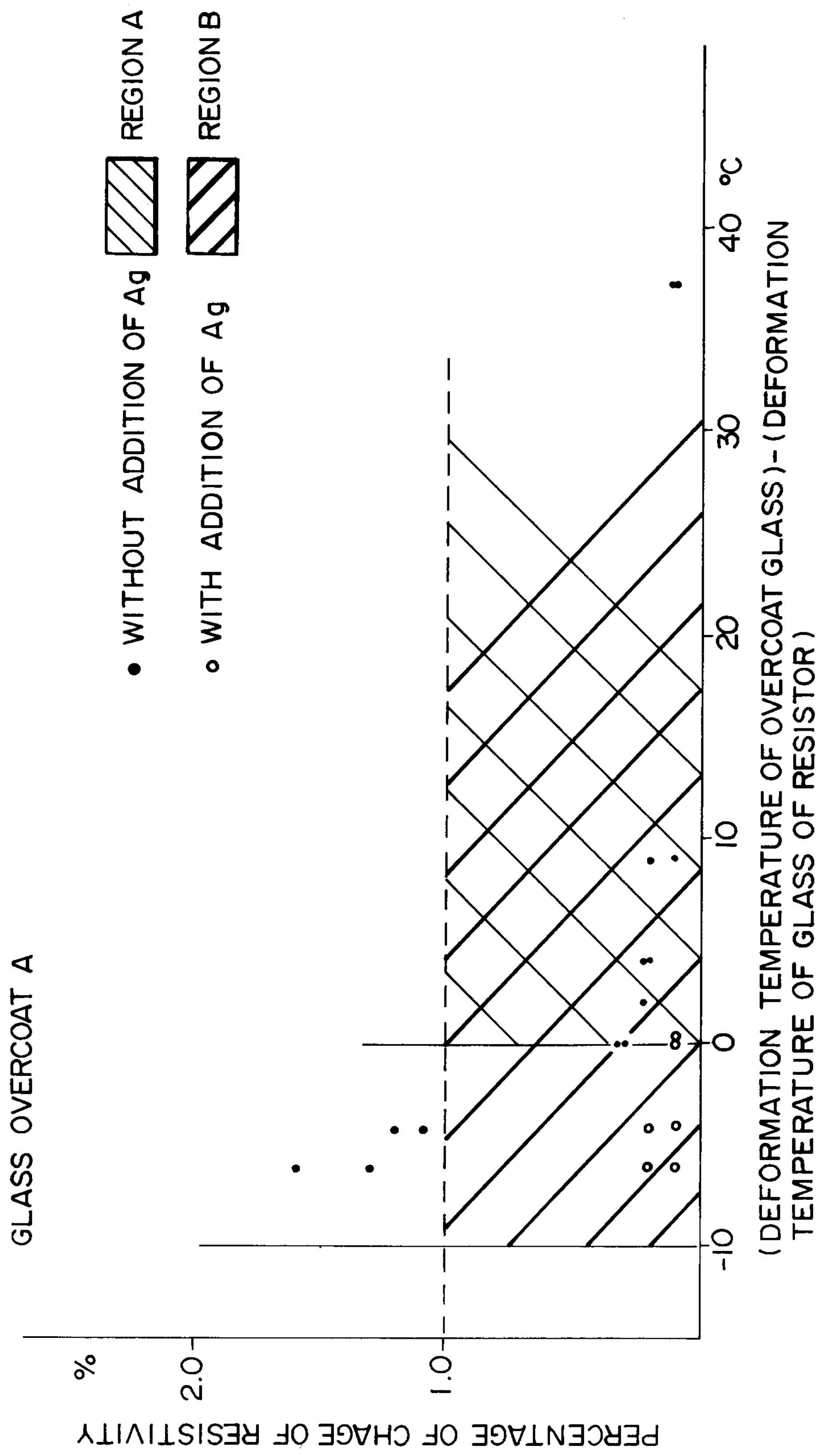

GLASS OVERCOAT A
• WITHOUT ADDITION OF Ag
REGION A
∘ WITH ADDITION OF Ag
REGION B
%
2.0
1.0
PERCENTAGE OF CHAGE OF RESISTIVITY
-10
0
10
20
30
40 °C
(DEFORMATION TEMPERATURE OF OVERCOAT GLASS)-(DEFORMATION TEMPERATURE OF GLASS OF RESISTOR)

FIG. 4

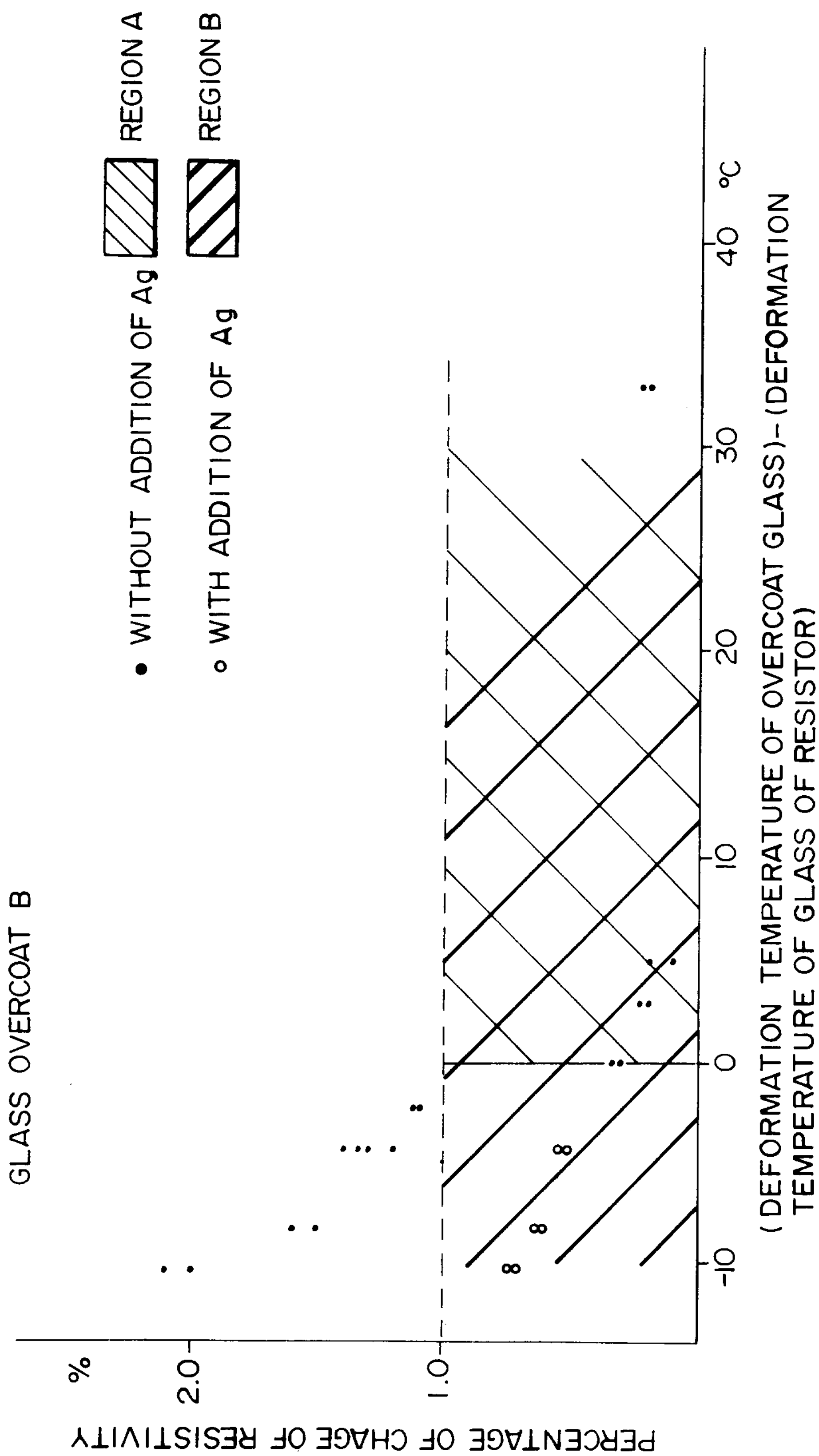

GLASS OVERCOAT B
• WITHOUT ADDITION OF Ag
REGION A
∘ WITH ADDITION OF Ag
REGION B
%
2.0
1.0
PERCENTAGE OF CHAGE OF RESISTIVITY
-10
0
10
20
30
40
°C
(DEFORMATION TEMPERATURE OF OVERCOAT GLASS)-(DEFORMATION TEMPERATURE OF GLASS OF RESISTOR)

FIG. 5

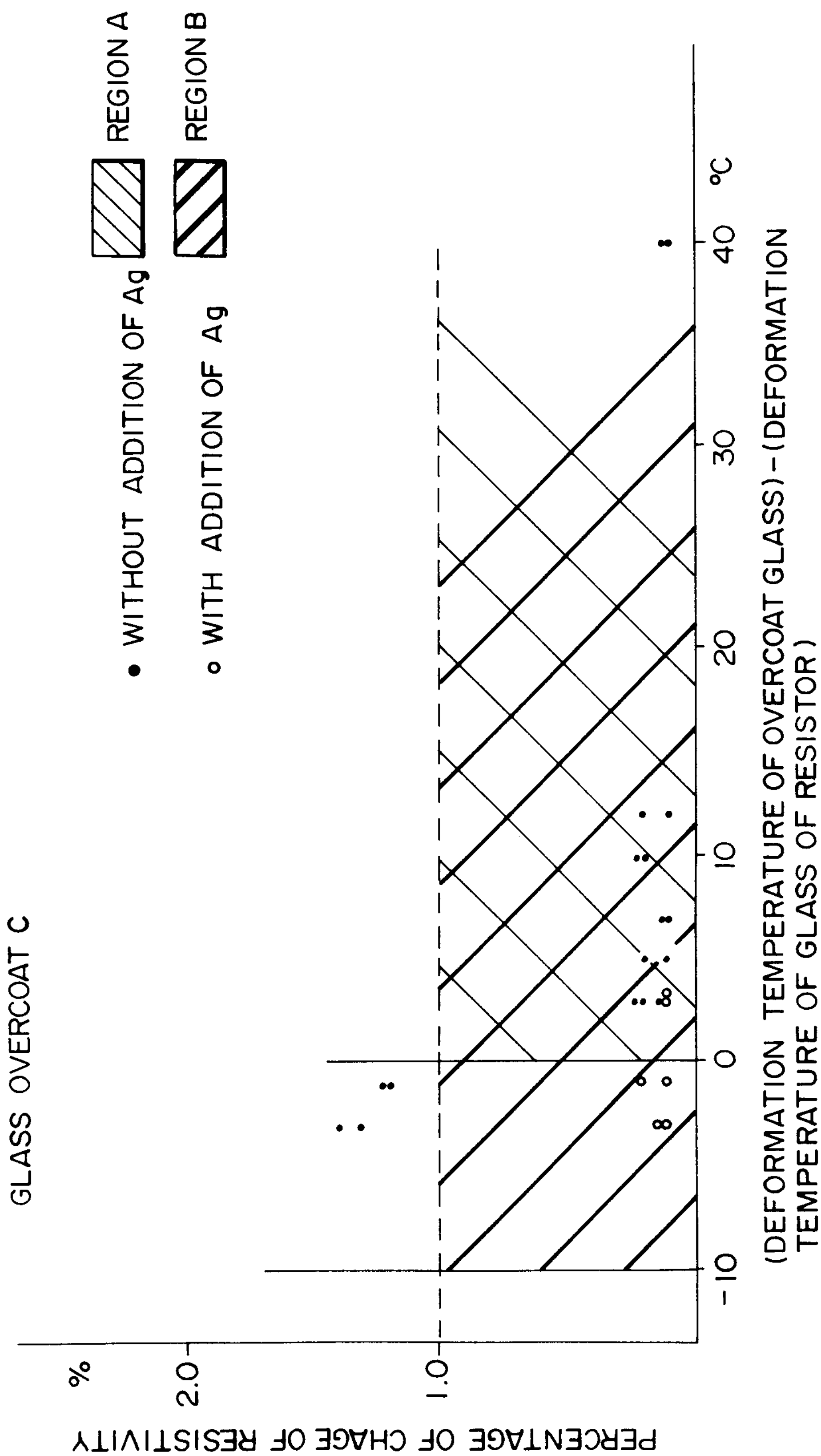

GLASS OVERCOAT C
• WITHOUT ADDITION OF Ag
REGION A
∘ WITH ADDITION OF Ag
REGION B
%
2.0
1.0
PERCENTAGE OF CHAGE OF RESISTIVITY
-10
0
10
20
30
40
°C
(DEFORMATION TEMPERATURE OF OVERCOAT GLASS)-(DEFORMATION TEMPERATURE OF GLASS OF RESISTOR)

FIG. 6

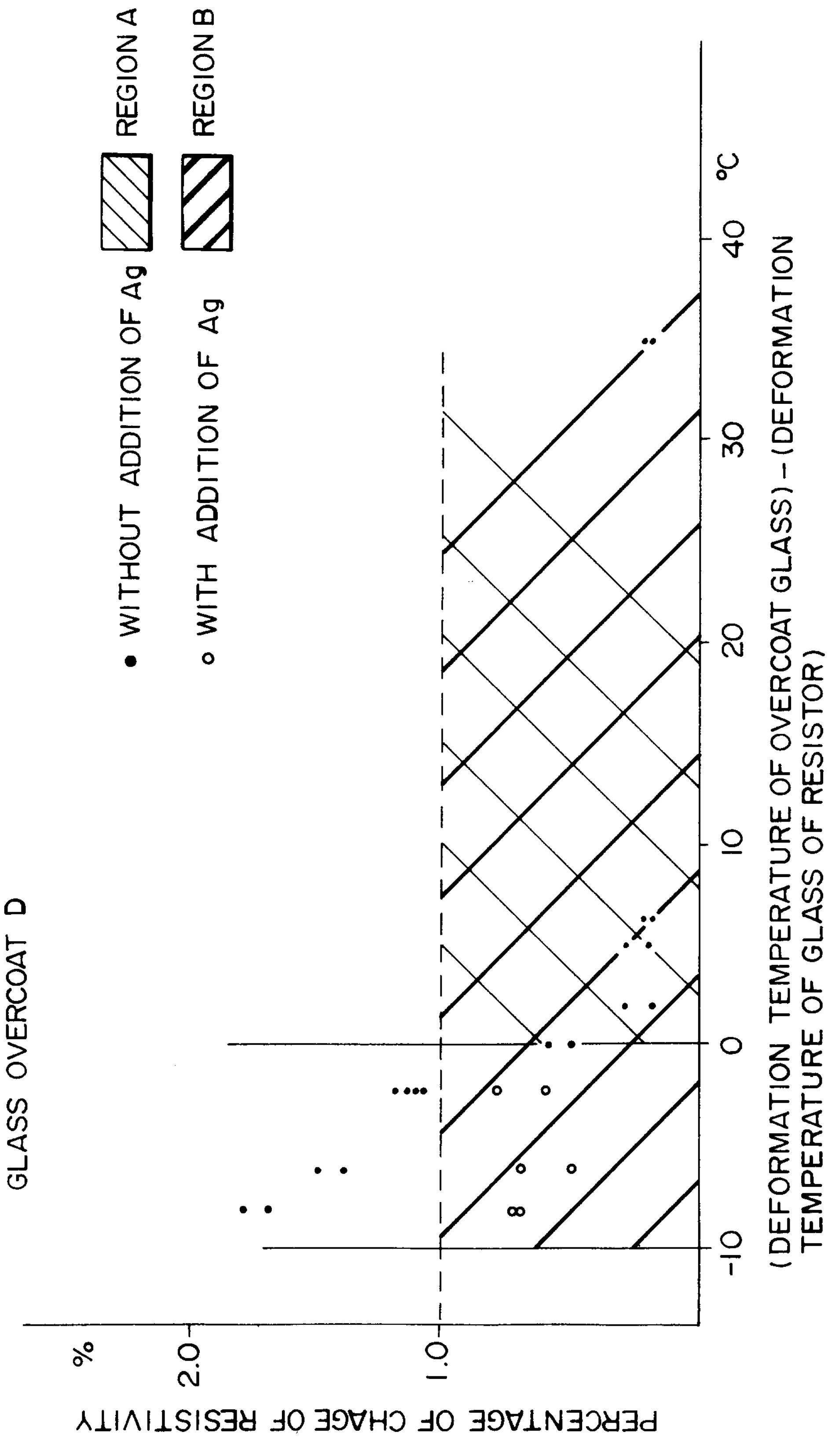

GLASS OVERCOAT D
• WITHOUT ADDITION OF Ag
REGION A
∘ WITH ADDITION OF Ag
REGION B
%
2.0
1.0
PERCENTAGE OF CHAGE OF RESISTIVITY
-10
0
10
20
30
40
°C
(DEFORMATION TEMPERATURE OF OVERCOAT GLASS) – (DEFORMATION TEMPERATURE OF GLASS OF RESISTOR)

FIG. 7

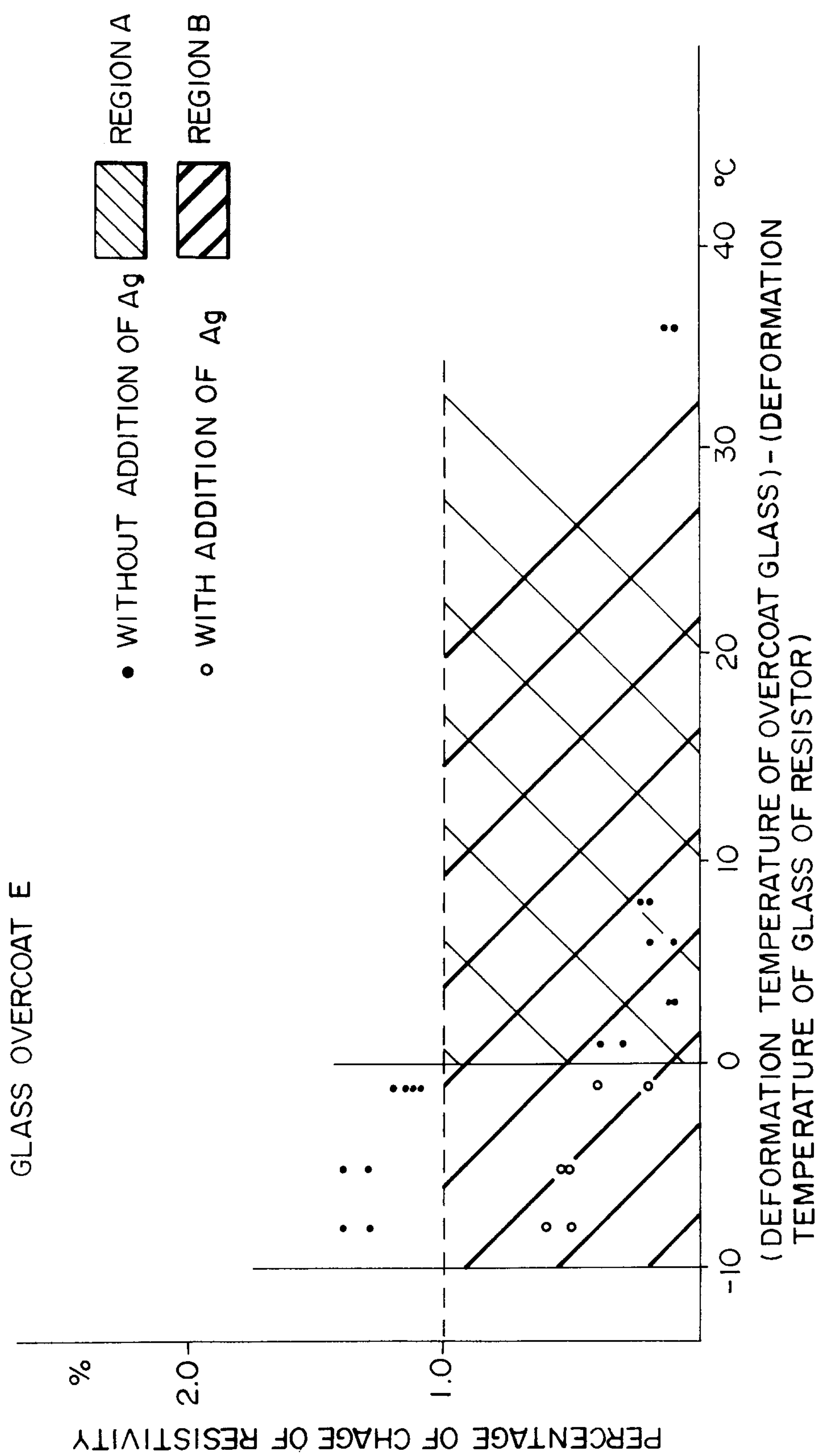

GLASS OVERCOAT E
• WITHOUT ADDITION OF Ag
REGION A
∘ WITH ADDITION OF Ag
REGION B
%
2.0
1.0
PERCENTAGE OF CHAGE OF RESISTIVITY
-10
0
10
20
30
40
°C
(DEFORMATION TEMPERATURE OF OVERCOAT GLASS)-(DEFORMATION TEMPERATURE OF GLASS OF RESISTOR)

FIG. 8

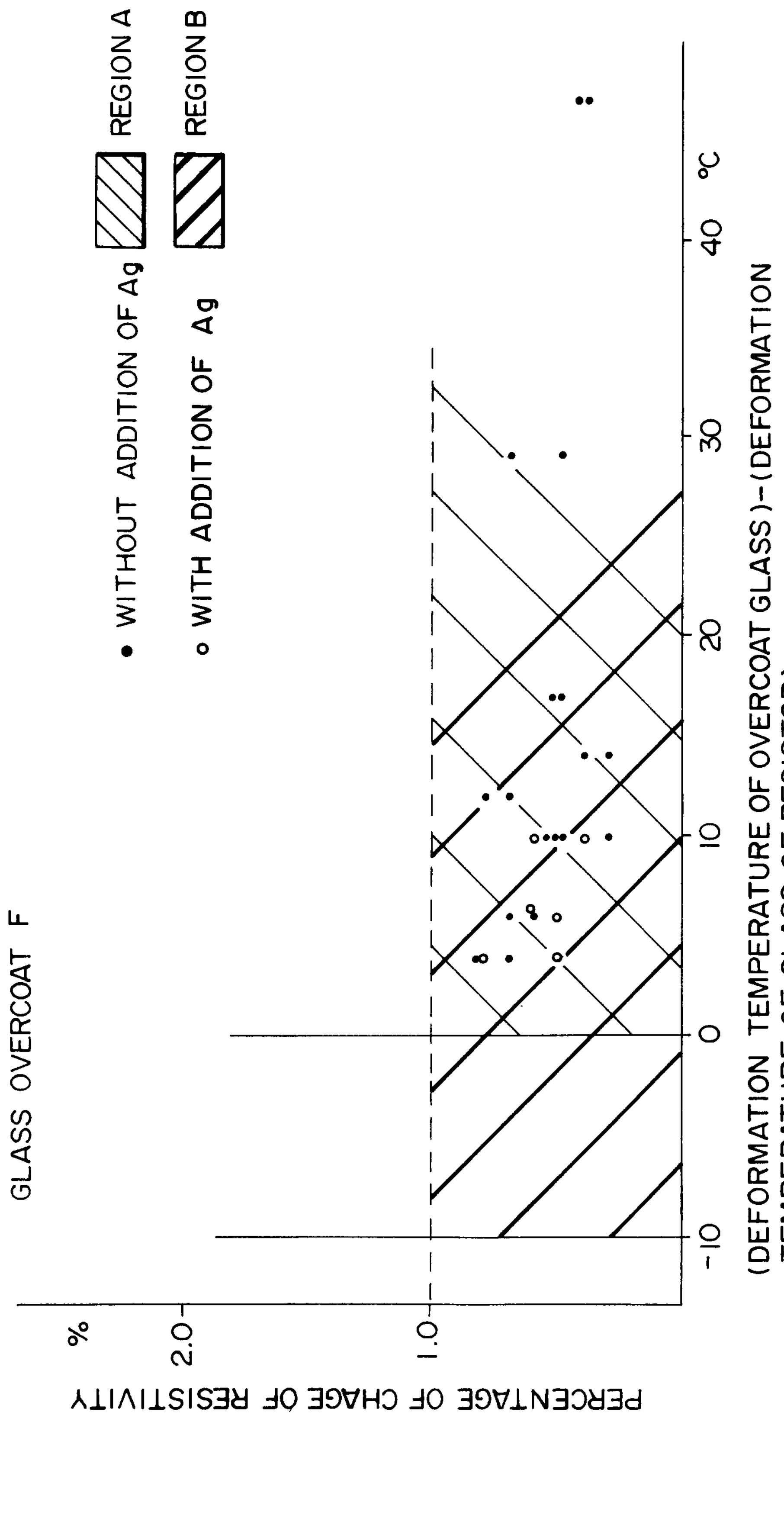

GLASS OVERCOAT F
• WITHOUT ADDITION OF Ag
REGION A
○ WITH ADDITION OF Ag
REGION B
%
2.0
1.0
PERCENTAGE OF CHAGE OF RESISTIVITY
-10
0
10
20
30
40
°C
(DEFORMATION TEMPERATURE OF OVERCOAT GLASS)-(DEFORMATION TEMPERATURE OF GLASS OF RESISTOR)

FIG. 9

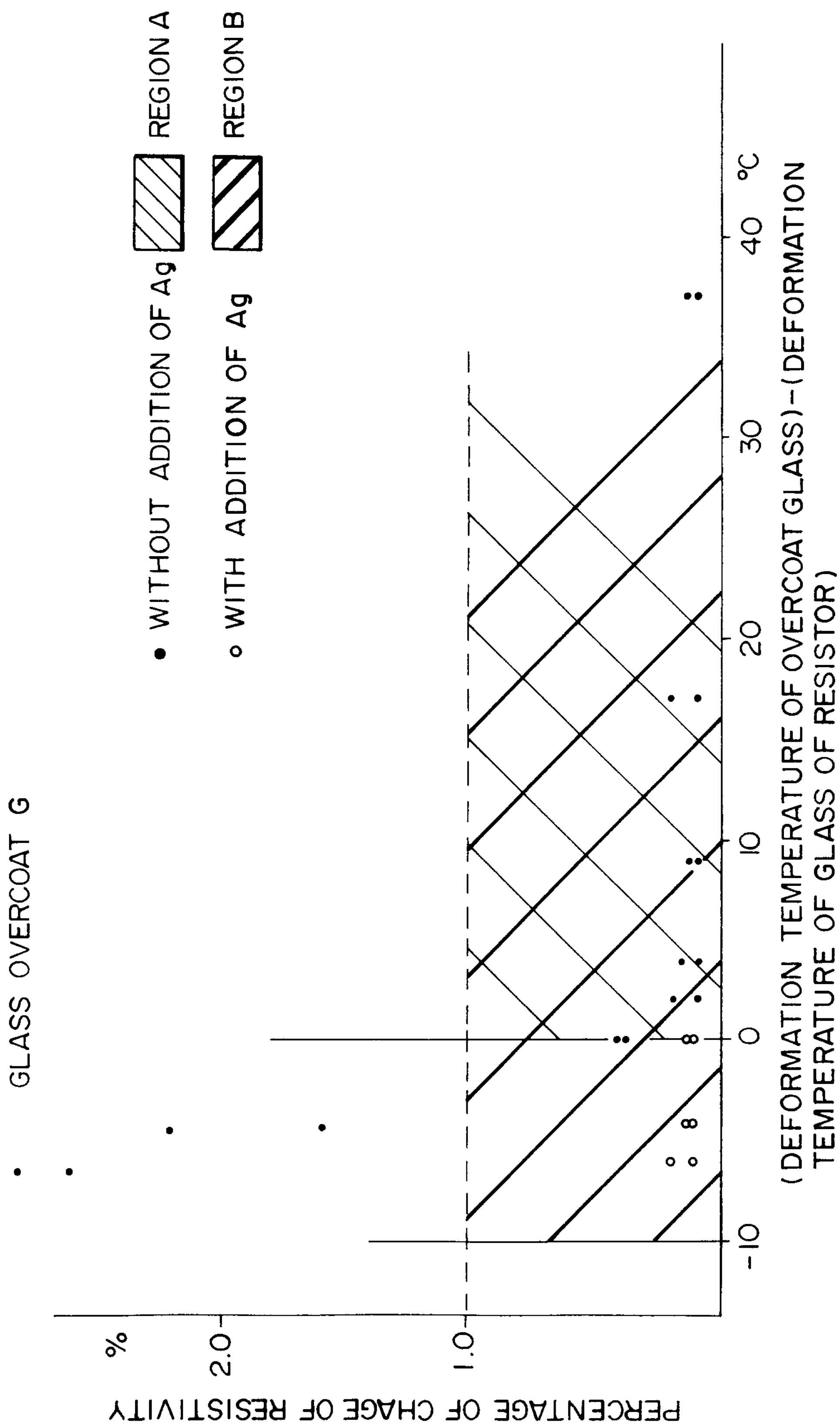

GLASS OVERCOAT G
• WITHOUT ADDITION OF Ag
REGION A
○ WITH ADDITION OF Ag
REGION B
%
2.0
1.0
PERCENTAGE OF CHAGE OF RESISTIVITY
-10
0
10
20
30
40
°C
(DEFORMATION TEMPERATURE OF OVERCOAT GLASS)-(DEFORMATION TEMPERATURE OF GLASS OF RESISTOR)

FIG. 10

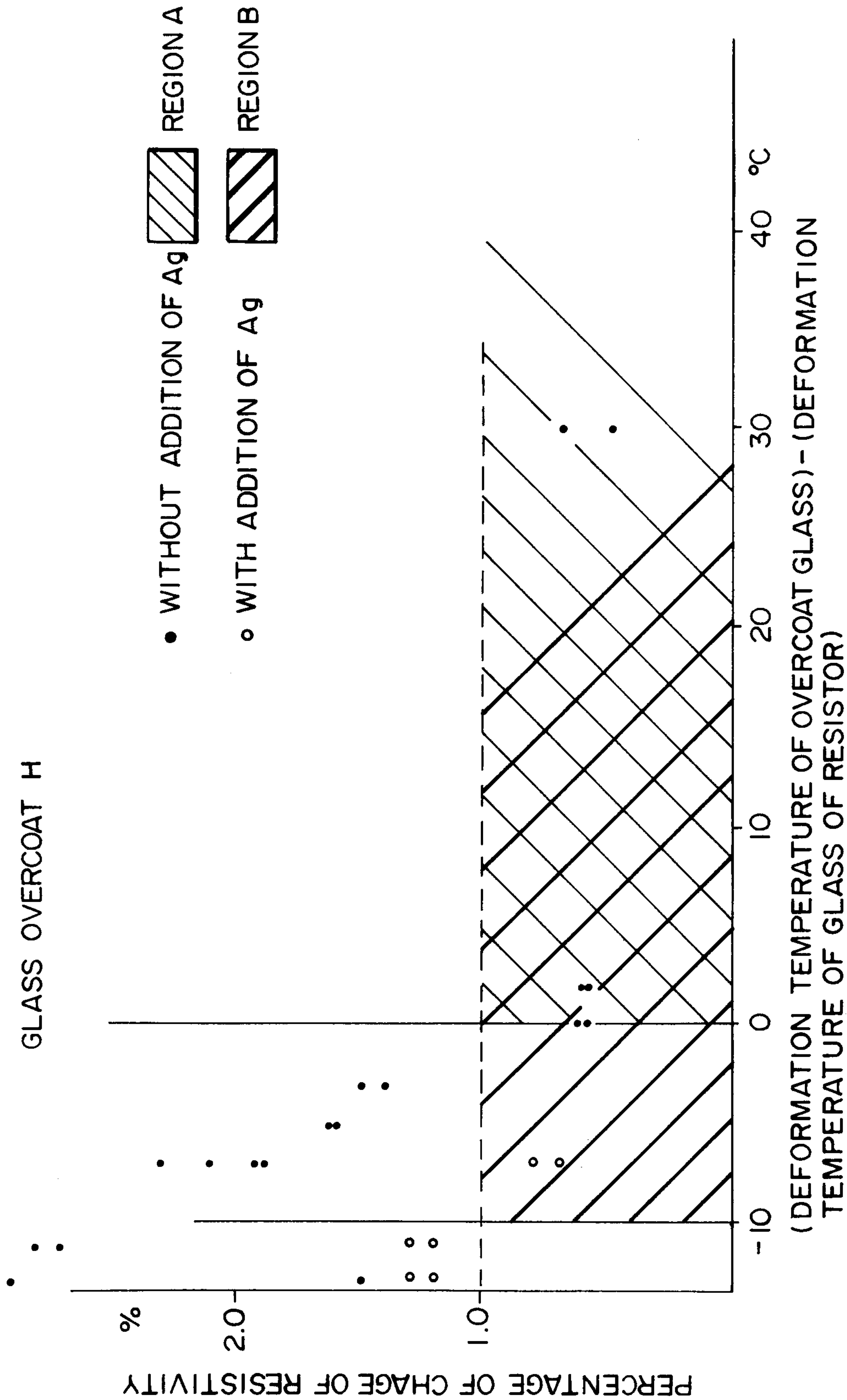

GLASS OVERCOAT H
• WITHOUT ADDITION OF Ag
REGION A
○ WITH ADDITION OF Ag
REGION B
%
2.0
1.0
-10
0
10
20
30
40
°C
(DEFORMATION TEMPERATURE OF OVERCOAT GLASS)-(DEFORMATION TEMPERATURE OF GLASS OF RESISTOR)
PERCENTAGE OF CHAGE OF RESISTIVITY

FIG. 11

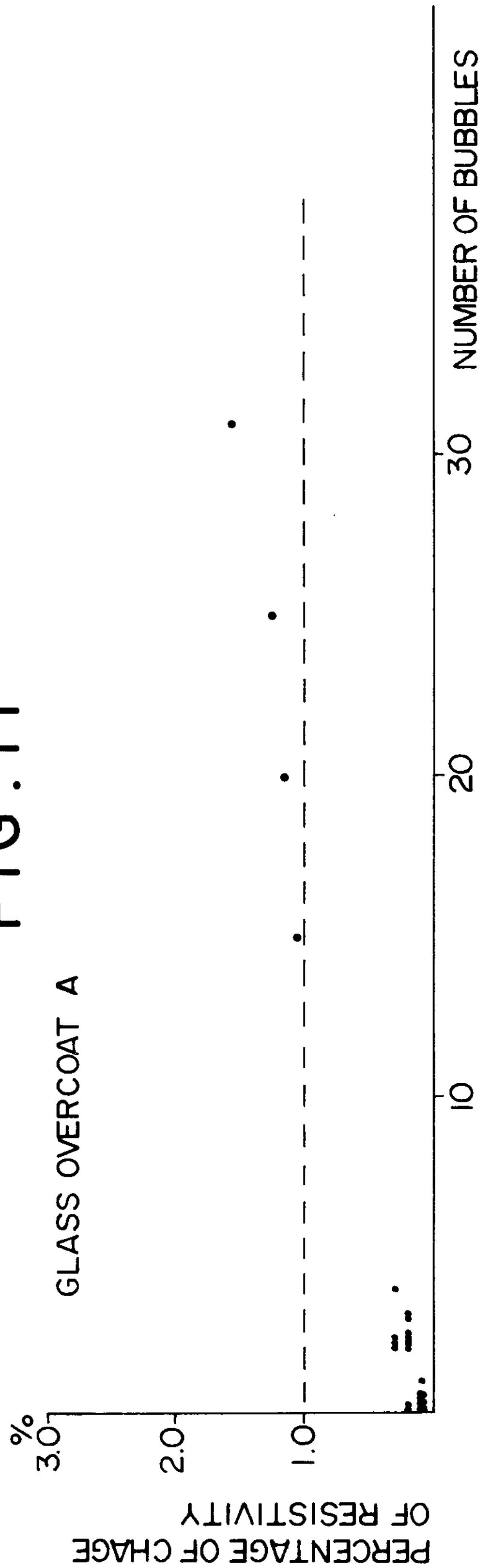

GLASS OVERCOAT A
NUMBER OF BUBBLES
10
20
30
%
3.0
2.0
1.0
PERCENTAGE OF CHAGE
OF RESISTIVITY

FIG. 12

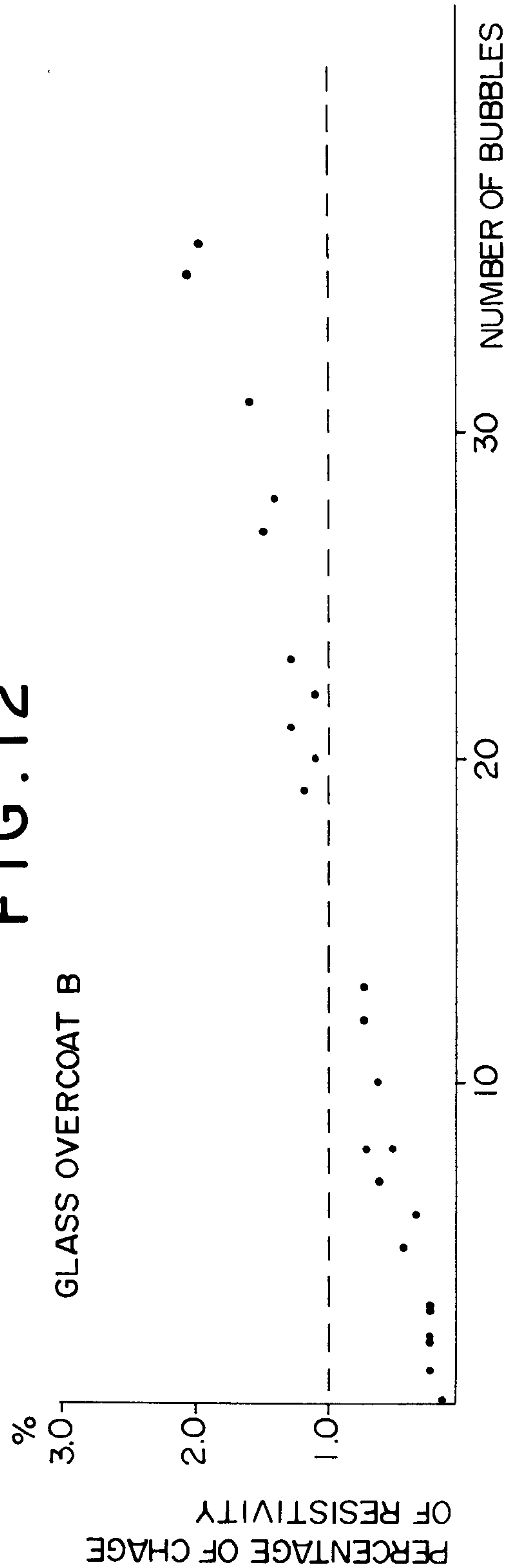

GLASS OVERCOAT B
NUMBER OF BUBBLES
10
20
30
%
3.0
2.0
1.0
PERCENTAGE OF CHAGE
OF RESISTIVITY

FIG.13

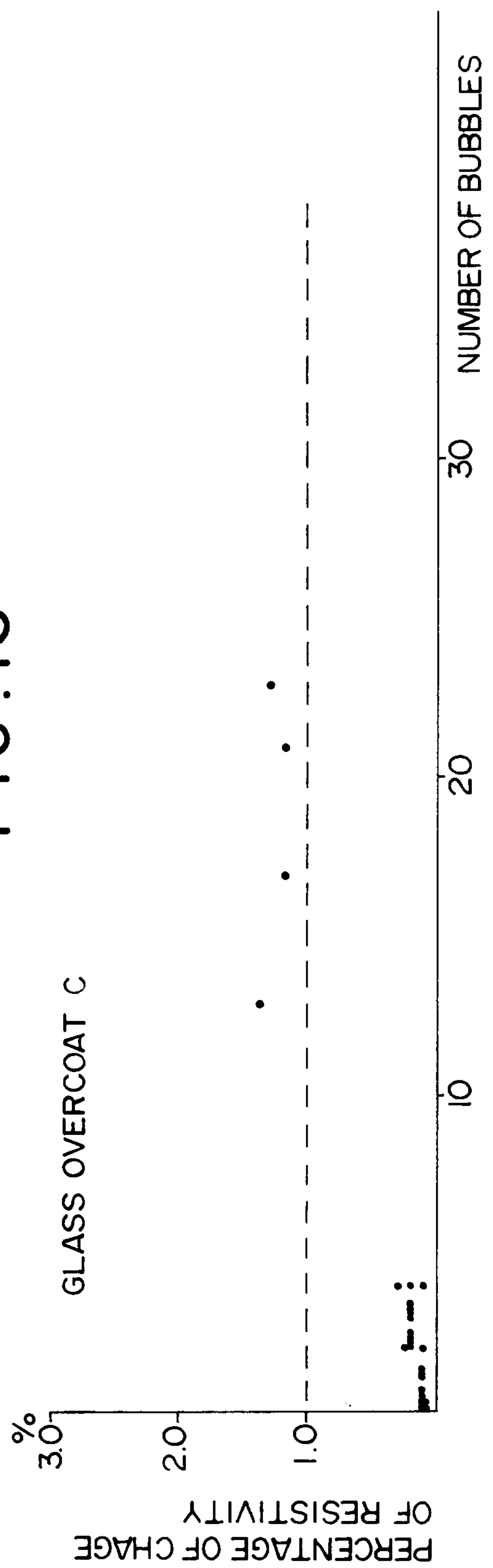

GLASS OVERCOAT C
%
3.0
2.0
1.0
10
20
30
NUMBER OF BUBBLES
PERCENTAGE OF CHAGE
OF RESISTIVITY

FIG.14

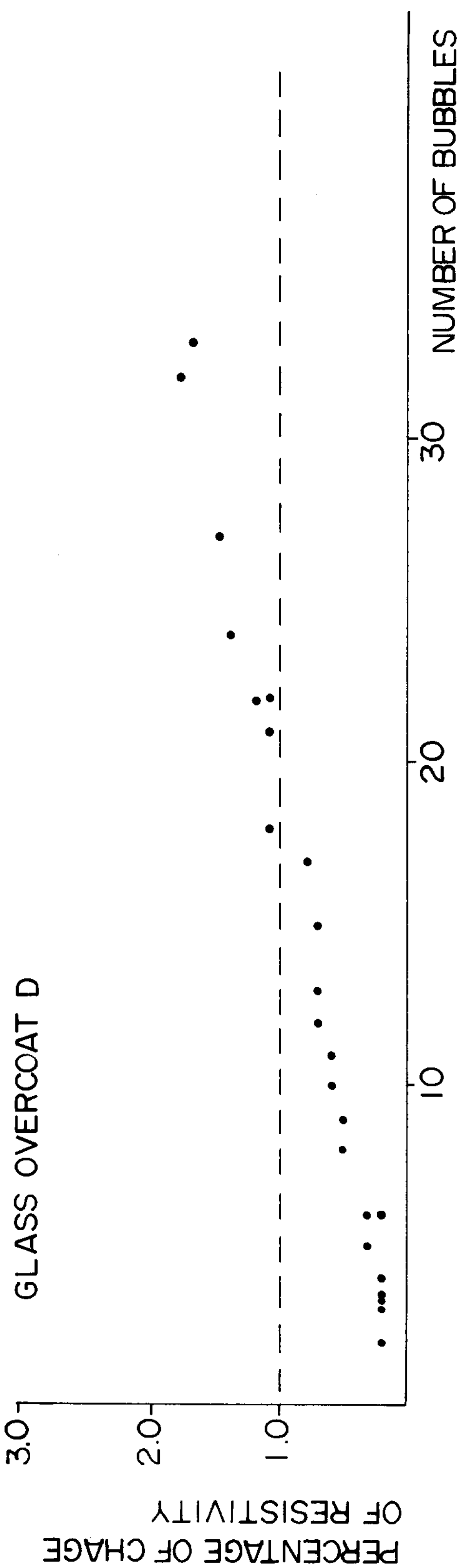

GLASS OVERCOAT D
%
3.0
2.0
1.0
10
20
30
NUMBER OF BUBBLES
PERCENTAGE OF CHAGE
OF RESISTIVITY

FIG. 15

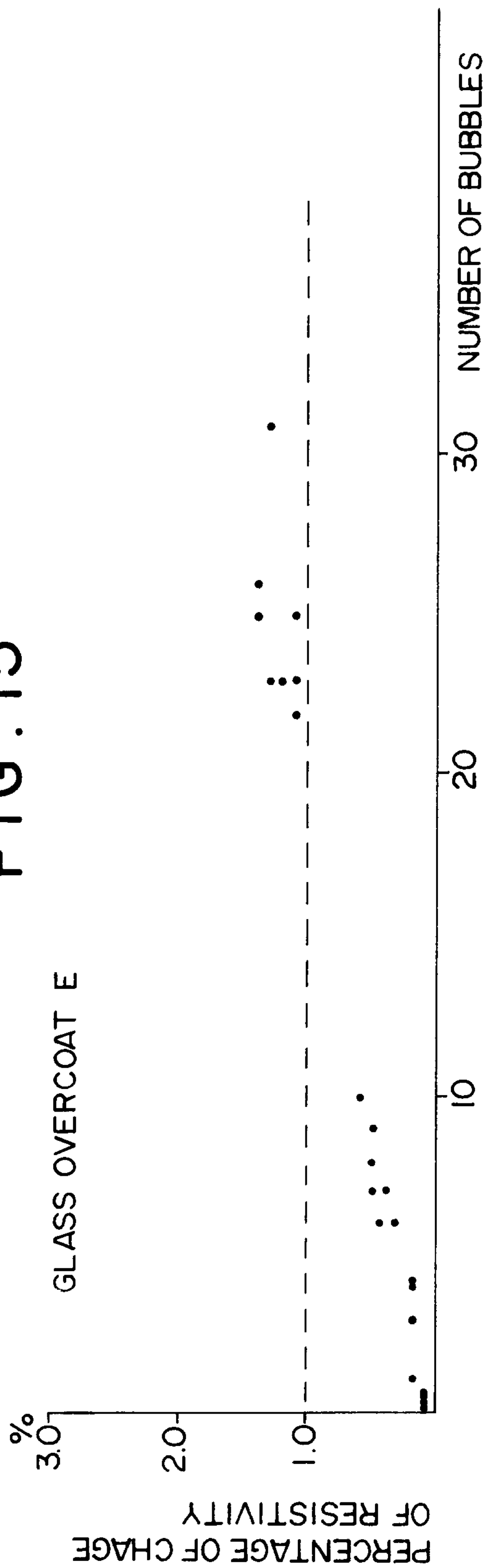
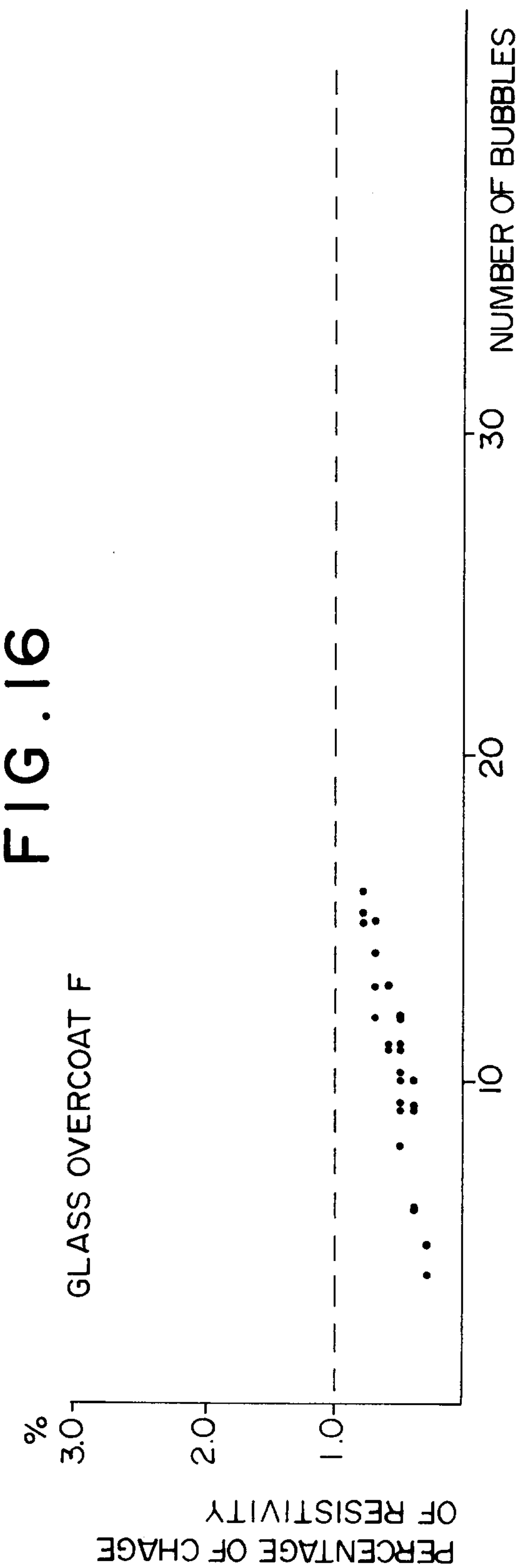

GLASS OVERCOAT E
PERCENTAGE OF CHAGE OF RESISTIVITY
%
3.0
2.0
1.0
10
20
30
NUMBER OF BUBBLES

FIG. 16


GLASS OVERCOAT F
PERCENTAGE OF CHAGE OF RESISTIVITY
%
3.0
2.0
1.0
10
20
30
NUMBER OF BUBBLES

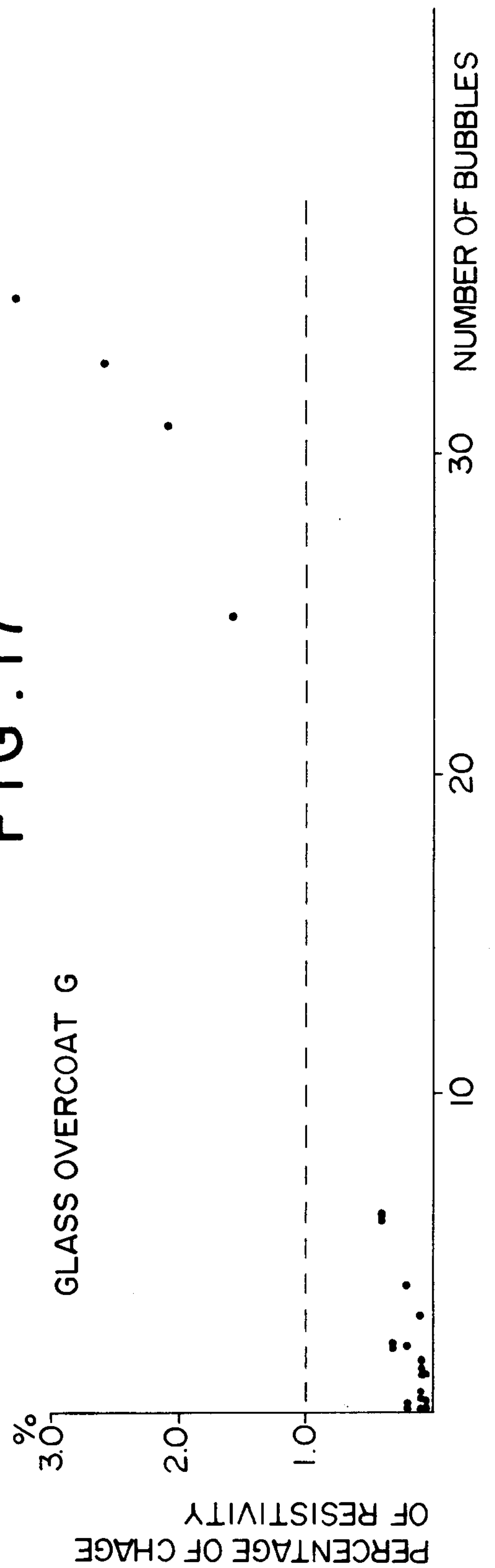

GLASS OVERCOAT G
NUMBER OF BUBBLES
10
20
30
%
3.0
2.0
1.0
PERCENTAGE OF CHAGE
OF RESISTIVITY

FIG. 17

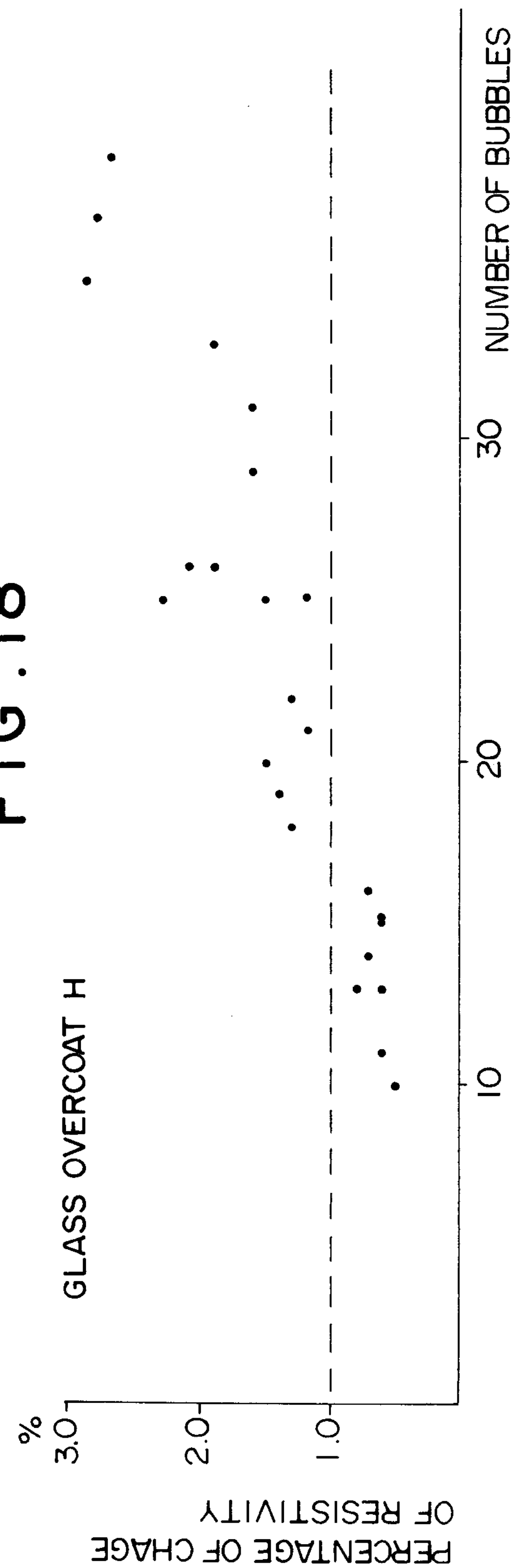

GLASS OVERCOAT H
NUMBER OF BUBBLES
10
20
30
%
3.0
2.0
1.0
PERCENTAGE OF CHAGE
OF RESISTIVITY

FIG. 18