United States Patent [19]

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[11] **3,836,340**

[45] **Sept. 17, 1974**

[54] **VANADIUM BASED RESISTOR COMPOSITIONS**

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[22] Filed: **Jan. 3, 1972**

[21] Appl. No.: **214,648**

[52] **U.S. Cl.**..... **29/182.5,** 29/182.7, 106/47, 252/512, 338/22 R, 338/20

[51] **Int. Cl.**..... **B22g 1/00**

[58] **Field of Search**..... 338/22 R, 20; 252/512; 106/47; 29/182.7, 182.5

[56] **References Cited**

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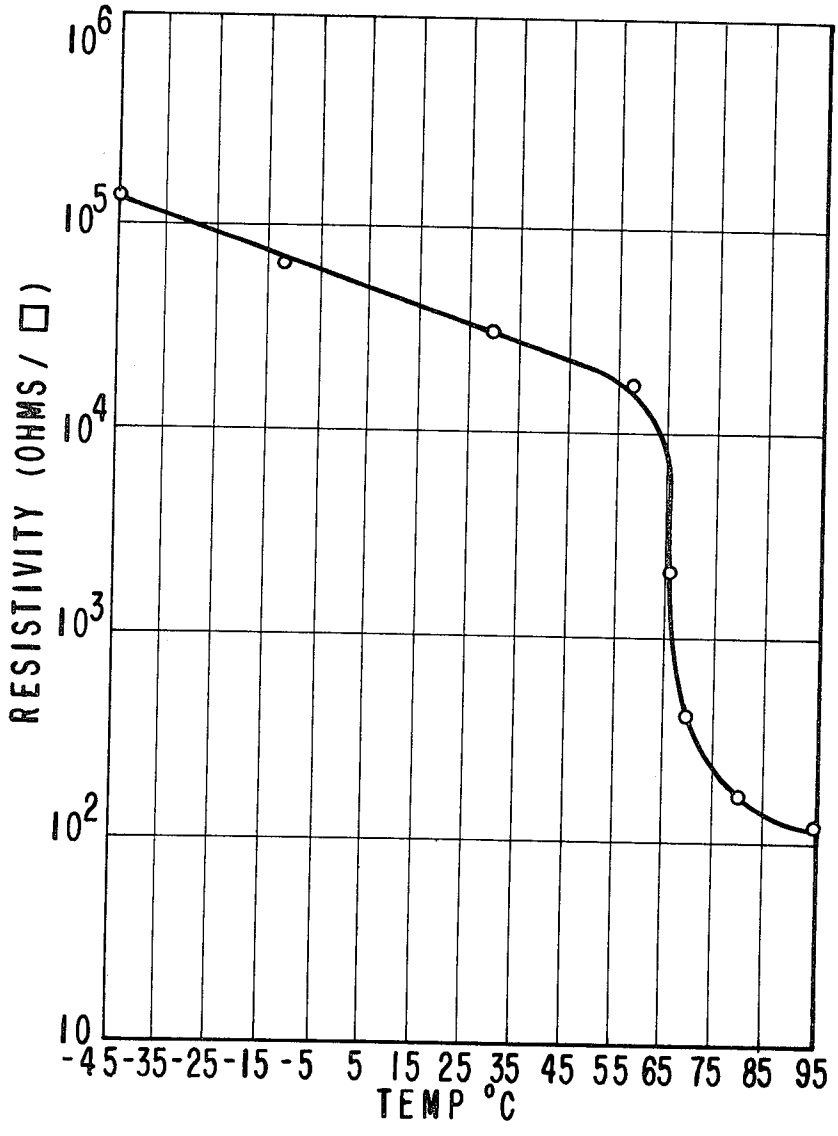
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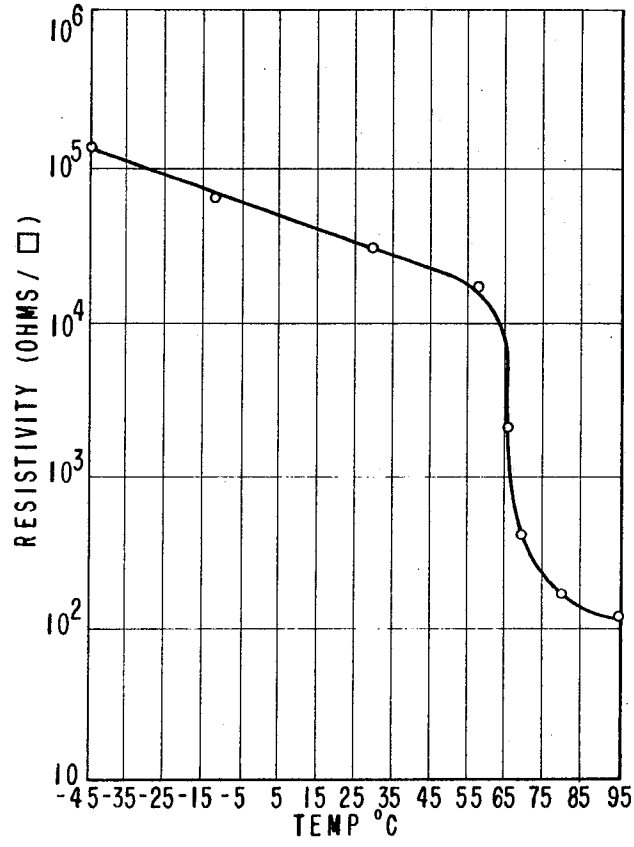
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[57] **ABSTRACT**

Screen printable, air fireable compositions comprising a vanadium glass, boron, and as optional components, noble metal and/or a low melting inorganic binder, wherein the vanadium glass contains 5–55 percent vanadium metal and from a small but effective amount up to 10 percent of fluorine and, sulfur. Various electronic devices are readily made from these compositions. A unique feature of the devices is their sensitivity to voltage as well as temperature. Consequently, the fired compositions are particularly useful whenever switching devices are needed, e.g., as transient suppressors in electronic equipment.

3 Claims, 1 Drawing Figure




RESISTIVITY (OHMS / □)
10^6
10^5
10^4
10^3
10^2
10
-45 -35 -25 -15 -5 5 15 25 35 45 55 65 75 85 95
TEMP °C

VANADIUM BASED RESISTOR COMPOSITIONS

BACKGROUND OF THE INVENTION

Vanadium dioxide (VO_2 or V_2O_4) has a phase transition temperature at about 68°C. where the monoclinic structure of the low temperature phase changes to a high temperature phase having tetragonal rutile structure. This transition is best described as a first order semiconductor to metal transition. The change in electrical resistance observed between the two states is approximately three orders of magnitude.

U.S. Pat. No. 3,402,131 describes a resistor having an abruptly changing negative temperature coefficient based on vanadium dioxide. The process described in this patent requires three different firing steps: (1) vanadium pentoxide is fused with other oxides in air at a temperature between 670°–1000°C.; (2) the fused product is fired in a reducing atmosphere of ammonia at a temperature within the range of 350°–400°C. in order to transform V_2O_5 into V_2O_4; and (3) this product is sintered at 1,000°C. in an inert or reducing atmosphere to finally shape the product as beads, rods, discs or flakes. This patent does not relate to or describe printable, air fireable compositions which can be used to form various electrical devices.

Attempts have been made to make thin film switching elements of VO_2. K. van Steensel et al. have described such switching elements in Philips Research Reports 22, pages 170–177 (1967). However, a thin film cannot carry large quantities of power in comparison to thick films, and thin film processing is exacting and time consuming.

Recently, vanadium based, thick film, air fireable compositions have been disclosed by Amin and Hoffman in assignee's U.S. Pat. No. 3,622,523, issued Nov. 23, 1971. However, devices made from these compositions do not switch properly at low temperatures due to their large increase in resistance at low temperatures. It is an object of this invention to produce vanadium based, thick film, air fireable compositions which yield devices that exhibit small changes in resistance at low temperatures (i.e., exhibit a very low negative temperature coefficient of resistance in the high resistance state).

SUMMARY OF THE INVENTION

This invention relates to screen printable, air fireable compositions comprising, on a weight basis, (1) 35–99 percent of a finely divided vanadium glass, wherein said glass comprises 5–55 percent vanadium and from a small amount effective to minimize the thermal coefficient of resistance (TCR), such as about 0.0001 up to 10 percent of a material from the group consisting of fluorine, sulfur, and mixtures thereof; (2) 1–15 percent of boron; (3) 0–50 percent of finely divided noble metal; and (4) 0–20 percent of a finely divided sintering promotor. In addition, various electrical devices made by firing the above-described compositions onto a substrate are part of this invention.

A glass batch containing oxides of vanadium and other required constituents is melted in air at a suitable temperature and the molten glass is quickly cooled to prevent crystallization. This vanadium glass is finely ground, mixed with the necessary amount of finely divided boron, and, optionally, finely divided noble metal and/or inorganic binder and dispersed in a liquid vehicle to make a printable paste. An electrical element resulting from the printing and firing of the paste is a sintered product having a VO_2 component which imparts a large useful change in resistance over a short temperature range. Additionally, the VO_2 component also exhibits a very low negative TCR in the high resistance state. Devices based on these printed elements have been found to be excellent transient suppressors. Most electronic instruments comprising delicate components such as transistors, require protection against overvoltage surges. The devices of this invention, when arranged in parallel circuit with such instruments, will allow normal operation of the instruments at a rated voltage while any overvoltage surge will internally heat the device and transform the device to a low resistance metallic state, even at very low temperatures (e.g., −45°C.). Consequently, most of the overvoltage surge will pass through the device rather than through the delicate electronic component. In general, the screen printed, air fired devices of this invention can be used wherever switching devices are needed.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a graphical representation of the temperature-resistance characteristics of electrical elements according to this invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The particular glasses utilized in the compositions of this invention contain different ingredients in varying proportions, but all of the glasses require the presence of 5–55 percent vanadium metal, preferably in the form of an oxide. When the glass is ultimately fired as a component of the novel compositions, VO_2 (V_2O_4) is formed in place. The amount of VO_2 formed is mainly determined by the amount of vanadium metal present in the glass. For this reason, the glass is defined on the basis of vanadium metal content. Although 35–99 percent of these glasses can be used in compositions of the invention, 74–96 percent glass is preferred for certain applications.

In preparing the glass, vanadium metal or any oxide of vanadium may be used as one of the batch constituents. Vanadium pentoxide is the most convenient to utilize because it has the lowest melting point and is the least expensive. The low melting point of V_2O_5 (690°C.) makes it much easier to melt a variety of the common glass constituents in air.

The important discovery of this invention resides in the incorporation of ionic species of fluorine, sulfur, and mixtures thereof, in the vanadium glass. The presence of these components in the vanadium glass produces screen printable, air fireable compositions which, when fired, yield devices which switch properly at low temperatures. These devices exhibit changes in resistance as low as a factor of 2 between room temperature and −45°C., which permits proper switching. The amount of the ionic species which can be present in the vanadium glass can range from 0.0001–10 percent by weight of the glass, with preferred ranges being about 0.01 or 0.1 to 5 percent or 10 percent. Sulfur may be incorporated in the glass from the elemental form or from compounds. Fluorine is most easily incorporated in the form of a compound. Any compounds of fluorine and, sulfur may be utilized; but simple salts are preferred. Suitable compounds include lead fluoride, barium fluoride, and lead sulfide.

Other components of the vanadium glass can be any of the normal glass constituents which are well known in the art. Some of the common glass constituents other than vanadium oxide include: CaO, MgO, BaO, SrO, PbO, CdO, ZnO, Na_2O, K_2O, Li_2O, Al_2O_3, Ga_2O_3, Cr_2O_3, B_2O_3, P_2O_5, Ta_2O_5, RuO_2, TiO_2, SiO_2, GeO_2, WO_3 and MoO_3.

The vanadium glass can be produced by melting suitable batch compositions yielding the prescribed metallic oxides and proportions thereof. The melting of the glass batch can be carried out in a variety of furnaces, such as gas or electric. A suitable container, such as a refractory crucible, can be utilized to melt the glass batch. The melting temperature of the glass batch will, of course, vary depending upon the composition of the batch. When a homogeneous molten liquid is obtained, the liquid is quickly cooled to retain the glassy structure of the composition. Glass frits are generally prepared by melting the glass batch composed of the desired metal oxides, or compounds which will produce the glass during melting, and pouring the melt into water. The coarse frit is then milled to a powder of the desired fineness.

The compositions of this invention must also contain 1–15 percent, or preferably 3–6 percent, of finely divided boron. While this invention is not based on any particular theory, it is believed that the boron acts as a reducing agent for the oxides of vanadium, which may be present in the glass, to form VO_2 in place by reduction. At least 1% boron must be present to produce VO_2-based devices which exhibit a transition from semiconductor to metal. At the other extreme, excessive amounts of boron, i.e., more than 15 percent, react with VO_2 and other oxide components during the firing operation. This produces a moisture-sensitive fired element while not leading to any large useful change in resistance on heating. Therefore, the amount of boron in the screen printable, air fireable compositions of this invention should conform with the above described limits, plus or minus a few percent.

It has also been discovered that a noble metal powder can, optionally, be included in the compositions of this invention. The noble metals include gold, silver, platinum, palladium, osmium, iridium, ruthenium, rhodium, alloys thereof and mixtures thereof. The noble metal lowers the resistance of the VO_2-containing element in both the state that is above and below the transition temperature of VO_2. A lower resistance above the transition temperature of the VO_2-containing element allows larger currents to pass through the fired elements without burning up the elements. Thus, the noble metal additions increase power-carrying capacity of the VO_2-containing elements in the "switched on" condition. The amount of noble metal may range between 0–50 percent with small amounts (i.e., 1–20 percent) producing very effective results. The use of more than 50 percent noble metal does not provide any additional power-carrying capacity while increasing the cost of the elements.

Another optional component is a sintering promotor. It has been found desirable, although not necessary, to include a sintering-promoting component in the compositions of this invention. A suitable promotor is an inorganic binder having a melting point below the melting point of the vanadium glass. Low melting binders such as lead borates, lead borosilicates, lead silicates, alkali-lead borosilicates, lead alumina borosilicates, etc. may be used. Other sintering promotors may also be used. The promotor can be present in amounts ranging from 0–20 percent, or preferably 1–15 percent.

The compositions of the invention will usually, although not necessarily, be dispersed in an inert liquid vehicle to form a paint or paste for application to various substrates. The proportion of vehicle to composition may vary considerably depending upon the manner in which the paint or paste is to be applied and the kind of vehicle utilized. Generally, from 1–20 parts by weight of solids composition (vanadium glass, boron, noble metal) per part by weight of vehicle will be used to produce a paint or paste of the desired consistency. Preferably, 3–10 parts per part of vehicle will be used.

Any liquid, preferably inert, may be employed as the vehicle. Water or any one of various organic liquids, with or without thickening and/or stabilizing agents, and/or other common additives, may be utilized as the vehicle. Examples of organic liquids that can be used are the higher alcohols; esters of such alcohols, for example, the acetates and propionates; the terpenes such as pine oil, alpha- and beta-terpineol and the like; and solutions of resins such as the polymethacrylates of lower alcohols, or solutions of ethyl cellulose, in solvents such as pine oil and the monobutyl ether of ethylene glycol monoacetate. The vehicle may contain or be composed of volatile liquids to promote fast setting after application; or it may contain waxes, thermoplastic resins or the like materials which are thermofluid so that the vehicle-containing composition may be applied at an elevated temperature to a relatively cold ceramic body upon which the composition sets immediately.

The compositions are conventionally made by admixing the components in their respective proportions. Additionally, one part of vehicle for every 1–20 parts of solids mentioned above may be admixed. The compositions are then applied to a dielectric body and fired to form stable electrical devices.

Application of the compositions in paint or paste form to the substrate may be effected in any desired manner. It will generally be desired, however, to effect the application in precise pattern form, which can be readily done by applying well-known screen stencil techniques or methods. The resulting print pattern will then be fired in the usual manner at a temperature from about 600° – 900°C. for a time within the range of 1–20 minutes. It has been found that excessively long firing times and high firing temperatures will oxidize the vanadium components of the glass to vanadium pentoxide. It is well known that vanadium pentoxide does not exhibit a semi-conductor to metal transition stage and, therefore, is not acceptable for purposes of this invention. A preferred firing temperature and time is 650° – 800°C. for 2–10 minutes.

The invention is illustrated by the following examples. In the examples and elsewhere in the specification, all parts, ratios and percentages of materials or components are by weight. Various glass compositions were melted and fritted. Each of the constituents present in the glass batch and the proportions thereof are reported in Table I. The amounts of certain constituents in the fired glass were determined by analysis and are presented in Table I in parenthesis.

TABLE I

Glass No.	Wt. % COMPONENT IN VANADIUM GLASS BATCH 1	2	3	4	5	6	7
V_2O_5	60	75	65	75	75	75	75
(V)	(33.5)	(38.5)	(36.5)	(36.9)	(40.9)	(37.6)	(33.4)
B_2O_3	15	10	10	12	4	15	15
CdO	5	—	—	5	6.5	—	—
BaO	10	5	10	—	(9.5)	—	5
Bi_2O_3	—	—	—	5	—	5	—
GeO_2	—	5	2	—	3	—	—
PbO	5	2	3	—	—	—	5
PbF_2	5	—	10	—	—	5	—
BaF_2	—	3	—	3	—	—	—
(F)	(0.13)	(0.09)	(0.25)	(0.11)	—	(0.09)	
S	—	—	—	—	2(0.03)	—	—

In the following examples the glasses of Table I were utilized to prepare screen printable, air fireable compositions. The fritted glasses, boron powder, and optionally, noble metal were dispersed in an inert vehicle (8 percent ethyl cellulose and 92 percent beta-terpineol) at a ratio of about 4:1. The paste compositions were screen printed onto a 96 percent alumina substrate onto which platinum/gold electrodes had been previously printed and fired. The printed pastes were fired to produce electrical elements which exhibited a transition from semi-conductor to metallic behavior as temperature was increased.

EXAMPLE 1

A composition comprising 95 percent glass No. 6 and 5% boron powder was printed bridging two palladium-silver electrodes. After drying, the coated substrate was fired in air at 700°C. for 5 minutes to form an electrical element on the substrate. The finished device was tested by measuring its resistance as a function of temperature. It was observed that the transition temperature was at about 68°C. and the resistance changed approximately 2 orders of magnitude. The change in sheet resistivity from +25°C. to −45°C. was a factor of 3 (40,000 ohms/sq. to 130,000 ohms/sq.). The results are shown in FIG. 1.

A composition that was similar but outside the invention, comprising 95 percent of glass No. 7 and 5 percent boron powder was printed and fired as described above. It was observed that the transition temperature was about 68°C. and the resistance changed approximately 2.5 orders of magnitude. However, the change in sheet resistivity from +25°C. to −45°C. was a factor of 20 (50,000 ohms/sq. to 1 megohm/sq.).

EXAMPLE 2

The effect of the presence of the noble metal in the compositions of this invention is shown in Table II. A procedure similar to Example 1 was followed to prepare the devices. The results show that the addition of a noble metal such as gold to the vanadium glass-boron system aids in lowering the resistance at room temperature as well as at 100°C. Thus, by adding noble metals, one can obtain VO_2-based devices which have lower resistances in "on-and-off" states. This, in turn, provides a higher power carrying capacity to the device in an "on" state.

TABLE II

	(Weight %)			
Glass (No. 2)	95	90	86	76
Boron	4	4	4	4
Gold	1	6	10	20
Resistance (ohms) at −45°C.	1×10^5	2.5×10^4	8×10^3	4×10^3
Resistance (ohms) at 25°C.	3×10^4	8×10^3	4×10^3	2×10^3
Resistance (ohms) at 100°C.	50	32	12	6

In a D-C. circuit, such as that employed to operate a radio in an automobile, a battery is connected to the radio in parallel relation through the ignition switch which is in series relation. Also connected to the battery in parallel relation are various inductive loads (e.g., motors for operating the windshield wipers, the windows, the seats, etc.). In the absence of a transient suppressing device, the inductive loads discharge through the radio to ground when the ignition switch is opened because it is in the nature of an inductance for the current to lag behind the voltage. Large voltages (e.g., 200–300 volts) with pulse widths of 1–2 milliseconds have been observed in the arrangement described above. The voltage surge can be suppressed from the radio by connecting before the radio, a VO_2 device of this invention in series with a load resistor, both in parallel relation to the radio. The voltage transient, occurring when the ignition switch is opened, generates sufficient temperature in the VO_2 device to cause the device to change to lower resistance (semiconductor to metallic behavior). Thereafter the current from the 200-300 volt transient passes through the load resistor to ground, rather than going through the radio and destroying delicate solid state devices in the radio. The following example demonstrates this concept.

EXAMPLE 3

A composition comprising 51 percent glass No. 6, 4 percent boron powder, 35 percent silver powder and 10 percent sintering promotor (80 percent PbO, 11 percent B_2O_3, 9% SiO_2) was screen printed as a pad bridging two palladium-silver electrodes which had been previously fired onto an alumina chip. After drying, the coated substrate was fired at 760°C. for 5 min-

utes. This VO_2 device was connected in series relation with a 5 ohm load resistor; the device was also connected in parallel relation with a solid state radio, a 10 millihenry induction coil, and a 12 volt battery. The ambient temperature was −40°C. The battery switch was turned "on" and the current passed to the induction coil, the VO_2 device and the radio. When the switch was turned "off", the voltage surge was sufficient to heat the VO_2 device and change its resistance to a much lower value. The current from the voltage transient passed through the load resistor to ground. Consequently, the voltage transient did not harm any delicate solid state devices in the radio. In the absence of the VO_2 device, the solid state radio was damaged and could not be operated after a relatively short period of use.

For purposes of comparison, glass No. 7 was used in place of glass No. 6. Sufficient heat was not generated by the voltage surge to cause this VO_2 device to change to lower resistance. Thus, this glass (No. 7), which is not within the scope of this invention, did not function properly at low temperatures.

The compositions of this invention may also contain minor amounts of additional constituents which modify and/or improve the electrical properties of the fired elements. Due to the ability of the fired elements to transform from semiconductors to metallic behavior, widely diversified uses may be made of this invention. Consequently, it is possible to conveniently and easily apply the compositions of this invention through conventional thick film techniques to form elements which are utilized in temperature-controlling devices, temperature-alarming devices, fire-alarms, etc.

What is claimed is:

1. A screen-printable, air-fireable composition comprising, on a weight basis, (1) 35–39 percent of a finely divided vanadium glass, wherein said glass comprises vanadium oxide in an amount equal to 5–55 percent vanadium, calculated as vanadium metal, and 0.01–5 percent of fluoride ion; (2) 1–15 percent of boron; (3) 0–50 percent of finely divided noble metal; and (4) 0-20% of a finely divided sintering promotor.

2. A screen-printable air-fireable composition comprising, on a weight basis, (1) 35–99 percent of a finely divided vanadium glass, wherein said vanadium glass comprises vanadium oxide in an amount equal to 5–55 percent vanadium, calculated as vanadium metal, and from a small amount effective to minimize the temperature coefficient of resistance up to 10 percent of an ionic species selected from the group consisting of fluorine and sulfur and mixtures thereof; (2) 1–15 percent of boron; (3) 0–50 percent of finely divided noble metal; and (4) 0–20 percent of a finely divided sintering promotor.

3. A transient suppressor device comprising, on a weight basis, (1) 35–99 percent of a finely divided vanadium glass, wherein said vanadium glass comprises vanadium oxide in an amount equal to 5–55 percent vanadium, calculated as vanadium metal, and from a small amount effective to minimize the temperature coefficient of resistance up to 10 percent of an ionic species selected from the group consisting of fluorine and sulfur and mixtures thereof; (2) 1–15 percent of boron; (3) 0–50 percent of finely divided noble metal; and (4) 0–20 percent of a finely divided sintering promotor; the composition having been fired in air at a temperature from about 600° to 900°C. for a time within the range 1–20 minutes.

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