

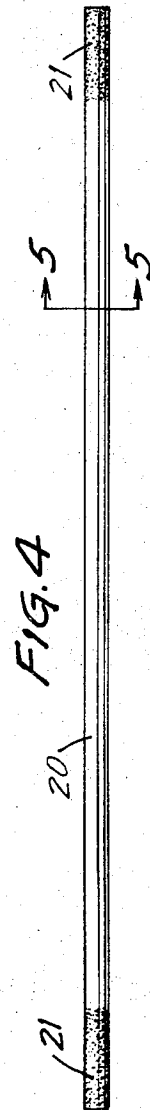
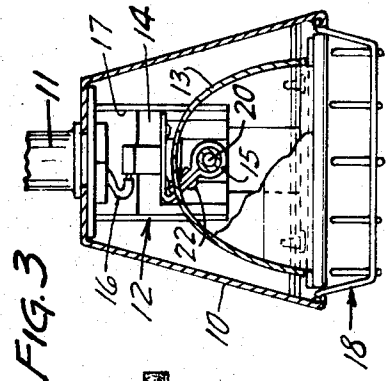
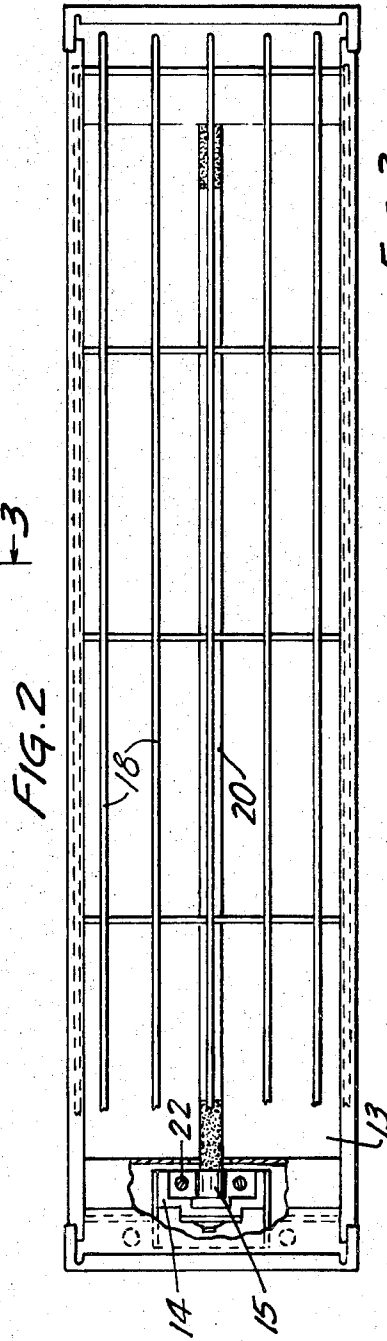
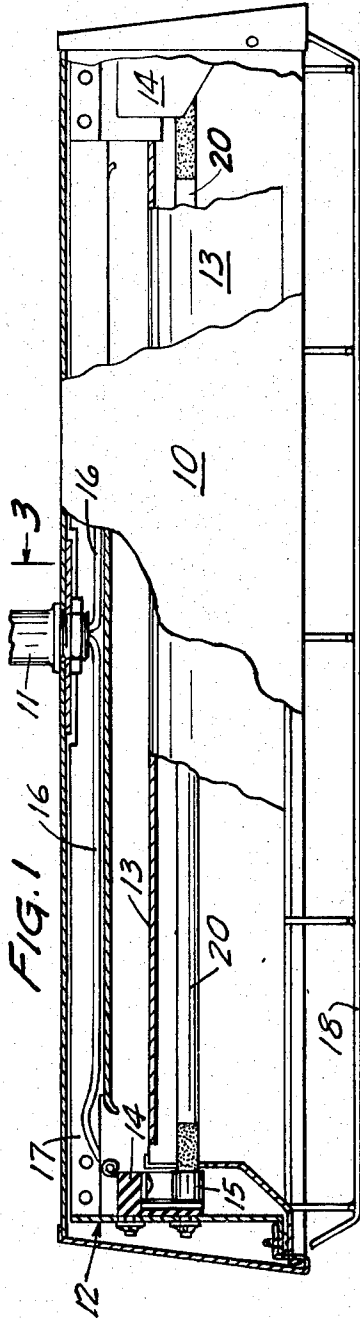
Dec. 28, 1971

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3,630,970

RESISTOR

Filed June 24, 1968



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3,630,970

RESISTOR

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8 Claims

ABSTRACT OF THE DISCLOSURE

Semiconductors useful as electrical resistance heating elements and composed principally of zinc oxide have a resistivity value not higher than ten ohm-cm. at 25° C. and not higher than one ohm-cm. at 925° C., the ratio being between about one and about ten.

This invention relates to electrical resistors, and more specifically to resistors composed principally of zinc oxide. In one important aspect the invention relates to ceramic zinc oxide resistance heating elements and to space heaters incorporating the same; and the invention will for convenience be described primarily in terms of such elements.

The novel electrical resistance heating elements of this invention are characterized as having a resistivity value at normal room temperature (25° C.) of less than about ten ohm-cm. Preferred structures have a room temperature resistivity value not higher than about one ohm-cm. and many are well below that value. The resistivity value at the preferred operating temperature of about 925° C. (1700° F) is in all cases less than one ohm-cm., and the ratio of the resistivity value at 25° C. to that at 925° C. is between about one and about ten. The resistivity value is defined as the resistance in ohms between opposite faces of a 1 x 1 x 1 cm. cube of the material.

Another important characteristic of the resistance heating elements of the invention is their ability to retain substantially constant resistivity value under prolonged operation at high temperature. Furthermore these elements may be made to show a high degree of resistance to mechanical and thermal shock.

These several properties make possible the production of ceramic semiconductor electrical resistance heating elements which are capable of being rapidly brought to full operating temperature and of then being stably maintained at that temperature during prolonged periods of operation at constant voltage, and which are sufficiently rugged to withstand all ordinary handling, vibration, and thermal shock.

Resistors and resistance heating elements comprised principally of zinc oxide have previously been described. In U.S. Pat. No. 2,892,988, elements containing at least 60% of zinc oxide are given a positive temperature coefficient of resistance by the inclusion of nickel oxide or titanium dioxide, whereas oxides of such metals as zirconium, beryllium, iron, aluminum and copper contribute to a negative coefficient. Although fired at 900 to 1400° C. during manufacture, the elements are used only at much lower temperatures, for example at 300–500° C.

Titanium, nickel, magnesium and zirconium oxides are combined with at least 70% of zinc oxide as described in U.S. Pat. No. 2,933,586 to produce resistance heating elements having a positive temperature coefficient of resistance within the suggested operating range of 200 to 500° C. Oxides of titanium and nickel are suggested for the same purpose in U.S. Pat. No. 3,037,942 which provides additional details as to the behavior of these compositions at the lower and higher ends of the temperature range, where a negative temperature coefficient of resistivity is experienced.

It has now been found possible to overcome these and other limitations of prior art resistance heating elements,

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and to produce resistor structures which heat up rapidly and which may be operated at much higher temperatures, e.g. of the order of 925° C., by incorporating with high purity zinc oxide certain metal oxide modifiers in specific small proportions and in a manner all as will be hereinafter described and defined.

The practice of the invention has been found particularly useful in the production of resistance heating elements for domestic space heaters or radiant heaters operating from conventional household electric power supply outlets. One form of such a device is illustrated in the accompanying drawing, wherein:

FIG. 1 is a side elevation, partly broken away to show interior details, of an overhead heater unit,

FIG. 2 is a similar bottom plan view of the unit of FIG. 1,

FIG. 3 is a sectional elevation approximately along line 3—3 of FIG. 1,

FIG. 4 is a plan view of a resistance heating element as used in the unit of FIGS. 1–3, and

FIG. 5 is a sectional view taken along the line 5—5 of FIG. 4.

The heater unit of FIGS. 1–3 comprises an elongate box-like open-faced casing 10 supported from a section of conduit 11. Within the casing is mounted a frame 12 carrying a rounded elongate trough-like reflector 13 and a pair of high-temperature-resistant insulative support members 14 each having a clamp-like contact element 15, the latter being connected to electric power wires 16 entering through the conduit 11 and passing along the open channel provided by the upper U-beam element 17 of the frame 12. An open protective wire grid 18 covers the open face of the casing.

The resistance heating element 20 is suspended centrally of the reflector 13 and is connected to the electrical circuit by the metal clamps 15. The element 20 is in the form of an elongate thin-walled tube as shown in FIGS. 4 and 5, and is provided at each end with a noble metal conductive coating 21. Effective contact is assured by wrapping the contact areas with one or two turns of a resilient metal screen or the like and by tightening the clamp 15 by means of the screw 22.

In a specific example the heating element 20 is 18 inches in length, $\frac{3}{8}$ inch in outside diameter, and has a wall thickness of $\frac{1}{16}$ inch. Silver metal is used as the conductive coating 21, the silver extending $1\frac{1}{2}$ inches along each end of the tube, leaving an active length of 15 inches between contacts. The unit is designed to operate at 110–115 volts AC and at that voltage reaches full temperature within about $1\frac{1}{2}$ –2 minutes and then remains at a surface temperature very close to 925° C. The temperature is conveniently measured by means of a thermocouple inserted within the hollow interior of the tube.

Despite published resistivity values to the contrary, extremely pure zinc oxide has been found capable of yielding heating elements of the form shown in FIGS. 4 and 5 having resistivity values less than ten ohm-cm. As an example, pure zinc oxide containing less than ten parts per million of alkali metal oxides, formed into rods of $\frac{1}{4}$ inch diameter and sintered at 1300–1400° C., has shown resistivity values of 0.4 to 0.7 ohm-cm. Rods or tubes made with pure zinc oxide are found to be fragile and to break or disintegrate when roughly handled or when subjected to vibration, and for this and other reasons have not been found acceptable as resistance heating elements for space heaters as hereinbefore described.

It has now been found possible to toughen and strengthen zinc oxide resistance heating elements while maintaining or improving their low electrical resistivity properties. At the same time it has been found that processing control is greatly simplified, so that duplicate elements of substantially identical properties may be made.

In addition, elements of greatly improved electrical and thermal stability are provided. These and other advantageous properties and results are achieved, in accordance with the principles of this invention, by incorporating with the pure zinc oxide minor quantities of zirconia and/or silica, preferably together with trace amounts of oxides of aluminum, indium, gallium, iron, or mixtures thereof, as will be further described and illustrated.

The incorporation of zirconia in particular, and of silica to a lesser extent, is found to toughen the resulting article to an extent sufficient to prevent breakage under all ordinary handling, and elements of such composition may be packaged, shipped, installed, and subjected to moderately severe vibration without damage. In addition these components contribute greatly increased thermal shock resistance, to the extent that tubes of the material heated to bright red heat may be safely sprinkled with droplets of water without cracking. At least about one or two percent of zirconia is ordinarily required to provide a satisfactory degree of ruggedness. Above about 8% of SiO_2 or neutralizer for trace amounts of alkali metal oxides increases tremendously, apparently due to an inversion of phase, and at the same time the physical structure is weakened; so that the amounts of these two components are to be held below the approximate percentages indicated and within the range wherein the zinc oxide remains as the continuous phase in the ceramic product.

Either silica or zirconia will provide the advantages just noted. An additional advantage is contributed by silica, either alone or in conjunction with zirconia; and for this purpose very small amounts of silica are useful. It is found that silica has the ability to act as a scavenger or neutralizer for trace amounts of alkali metal oxides introduced as impurities in the zinc oxide or in other ways. The alkali metal oxides even in extremely small amounts are found to cause very substantial and usually harmful increase in resistivity values. Since trace amounts of sodium salts in particular are frequently present, or are added as unavoidable impurities during compounding, the inclusion of small proportions of silica is ordinarily desirable in order to maintain the required low resistivity value without unduly increasing the processing costs.

The addition of trace amounts, as before indicated, of oxides of aluminum, iron, indium and gallium is effective in decreasing the resistivity of the zinc oxide heating elements, and to that extent these materials operate in a direction opposed to that of the silica, zirconia and alkali metal oxides. The amounts of these additives must be extremely small, i.e. not above about .03 percent, in order to maintain stability of resistivity during operation of the elements at high temperature. Trace amounts of the order of only a few parts per million of these materials are ordinarily fully adequate in obtaining the required low resistivity values. Small amounts of iron oxide decrease the resistivity of the zinc oxide sinter at high temperatures but increase the low temperature values; the inclusion of traces of silica in such composition reduces the low temperature resistivity.

The well-mixed finely powdered oxides or oxide-forming components may be compacted in dry form under high pressure and then fired at high temperature. The preparation of shaped resistance heating elements such as the tubular element of FIGS. 4 and 5 is preferably accomplished by first pre-mixing the oxides or the like in aqueous suspension; drying to a uniform powder; blending the powder with sufficient pure water, and with small amounts of wetting agents, lubricants, binders and other temporary additives as desired, to form a paste of proper plasticity characteristics; and then extruding or otherwise forming the mass into the appropriate shape under high pressure, drying the green article, and firing at sintering temperature. The resulting resistance element is then desirably further stabilized by prolonged heating at a temperature somewhat below the sintering temperature but above the proposed temperature of operation, and for a time sufficient to provide a stable resistivity value characteristic.

Although the composition may be formed directly from the oxides, it is frequently more convenient to use other and more readily available or more easily stored or mixed compounds as the source of the metal oxides. For such purposes, decomposable salts such as the nitrates or the carbonates may be employed; but compounds containing halogen ion in particular are to be avoided as having an inhibiting effect on the sintering and as preventing attainment of maximum density in the sintered product.

As an illustration of the difficulties involved in maintaining freedom from alkali metal oxides in these compositions, it has been observed that commercial methyl cellulose, commonly employed as a temporary binder for such ceramic materials, may contain as much as 1000 to 2000 parts per million of sodium chloride. The presence of this material acts both to increase the resistivity and to inhibit sintering and densification, and is to be avoided. However in small amounts the sodium ion may be effectively scavenged by the silica content of the composition, as previously noted; and the limited amount of chlorine present in such compositions is not ordinarily sufficient to be harmful. Prolonged extraction with hot distilled water has been found useful in reducing the sodium chloride content of methyl cellulose to insignificant levels of less than ten parts per million.

Somewhat analogously, the mixing or grinding or other processing of the components or mixtures may result in the incorporation of unmeasured small but significant amounts of iron, aluminum or other metallic components which affect the properties of the completed resistor. Such materials must therefore be avoided by proper selection of processing equipment and conditions, or the composition must where possible be properly formulated to compensate for their addition.

Although active impurities in general and alkali metal oxides in particular are to be avoided in the compositions and resistance elements of the invention, it is nonetheless found possible to incorporate small amounts of inert metal oxides, e.g. cobalt and nickel oxides, without significant effect on mechanical or electrical properties and with specific advantages. As an example, from .005 to .5 percent of cobalt oxide, or somewhat larger proportions of nickel oxide, provide permanent coloration of the piece and are useful in color coding or for decorative effects.

The application of noble metal coatings to serve as contact areas is well known in the industry and need not be detailed here. Coatings of silver are satisfactory in most instances, but gold coatings may be employed where higher temperature operations, up to about 1050° C., are indicated, and platinum and palladium may be used for still higher temperatures.

The following examples, in which all proportions are given in parts by weight unless otherwise indicated, will serve further to illustrate the practice of the invention which however is not to be limited thereby.

EXAMPLE 1

The inherent instability of zinc oxide resistors containing more than the indicated proportions of modifiers is indicated by the results obtained using pure USP zinc oxide blended with 0.75 weight percent of aluminum oxide. The mixture is formed into a resistance heating element under pressure and is fired for one hour at 1385° C. The sintered element is then further heated for 19 hours at 1025° C. After applying metallic terminals, the element is connected to a source of electric power through a suitable voltage control device. With the voltage initially at 64 volts, the temperature of the piece rises rapidly to 925° C. During a period of ten days it is found necessary to increase the voltage gradually to 90 volts in order to maintain the 925° C. temperature. The voltage is then held at 90 volts for a further 20 days. After remaining at 925° C. to the fourteenth day, the piece gradually cools, reaching 800° C. after a total of 30 days. At that point the voltage is again increased in an effort to

return the temperature to the 925° C. level. At 111 volts the temperature reaches the desired level; but within twelve hours thereafter the temperature increases to 1075° C. and approaches thermal run-away conditions.

In another example the element is fired for one hour at 1305° C. and held for 40 hours at 1100° C. prior to test. A temperature of 925° C. is first obtained at 56 volts. Over a period of ten days it is necessary to raise the voltage progressively to a maximum of 92 volts in

Sample 1 is again fragile and easily broken, whereas samples 2-6 are resistant to both mechanical and thermal shock. The resistivity values at 925° C. are in each instance somewhat lower than those at room temperature.

EXAMPLE 4

The effect of small amounts of other modifiers is shown in this example, wherein is reported the resistivity values obtained at room temperature and at 925° C.

Sample	ZnO	ZrO ₂	SiO ₂	Al ₂ O ₃	In ₂ O ₃	Ga ₂ O ₃	Fe ₂ O ₃	R ₂₅	R ₉₂₅
1-----	98	2	.03	.003	-----	-----	-----	.04	.04
2-----	98	-----	.03	.0019	-----	-----	-----	.25	.11
3-----	98	-----	.004	-----	-----	-----	-----	.23	.09
4-----	98	-----	-----	-----	.0055	-----	-----	.27	.13
5-----	100	-----	-----	-----	-----	.0075	-----	.4	.1
6-----	98	2	.015	-----	-----	-----	.0075	1.8	.09

order to maintain the initial temperature; at which point thermal run-away occurs.

Such resistors are not amenable to continuous operation at high temperature under fixed voltage, since the temperature either slowly decreases or rapidly increases to a point at which failure of the unit occurs.

EXAMPLE 2

The following compositions are prepared and formed into test elements by the preferred process, using USP grade zinc oxide powder which by analysis is shown to contain no more than three parts of aluminum oxide, five parts of silica, one part of ferric oxide, and less than three parts of alkali metal oxides, per million parts of the powder. The dried compressed bars are heated in air for one to two hours at 1400° C. and are measured for resistivity. Resistivity (R) is reported in ohm-cm. at the subscript temperature.

Sample	ZnO	SiO ₂	Na ₂ CO ₃	R _{25° c.}	R _{925° c.}
1-----	100	.01	-----	.04	.04
2-----	96.5	3.5	-----	.07	.09
3-----	94.5	5.5	-----	.05	.06
4-----	92.5	7.5	-----	.09	.10
5-----	100	-----	.0115	.15	-----
6-----	100	-----	.0346	.700	-----
7-----	100	.15	.0346	.04	-----
8-----	100	2.0	.0346	.04	-----

Under the same conditions, the room temperature resistivity of an element prepared from the USP zinc oxide without modifiers is 0.45 ohm-cm. at room temperature and the sample is less rugged and more easily broken than are those samples containing two or more parts of silica.

When the proportion of silica is progressively increased much beyond that of sample No. 4 the resistivity value rapidly increases to a level at which the product is no longer practical as an electrical resistance heating element. A similar result is experienced when the concentration of soda is increased in the absence of silica, as indicated by the resistivity values reported in samples 5 and 6.

EXAMPLE 3

This example illustrates the resistivity values obtainable with pure zinc oxide in conjunction with zirconium oxide modifier. The zirconium oxide contains less than 0.02 weight percent of aluminum and iron oxides as impurities, which amount is insufficient to produce any significant effect on the resistivity of the article in compositions containing less than about ten weight percent of ZrO₂. The samples are prepared as in Example 2 including sintering for one hour at 1400° C.

Sample	ZnO	ZrO ₂	R ₂₅
1-----	100	0	0.60
2-----	99	1	.09
3-----	97	3	.08
4-----	95	5	.07
5-----	90	10	.08
6-----	70	30	2.0

Samples 1-4 and 6 are prepared by wet mixing, drying, remoistening with water and glycerine, compressing, drying, and sintering at 1400° C. The remoistening is omitted in the preparation of sample 5, the dry powder being pressed into a preform suitable for sintering by pressures of 5,000 to 10,000 p.s.i. The use of soluble salts of the trivalent metals, e.g. gallium nitrate in sample 5, permits thorough blending of the components and provides a homogeneous article. Samples 2-6 are stabilized by further heating for 48 hours at 1025° C.

Samples 1 and 6, containing two percent of zirconia, are strong and rugged, being highly resistant to both mechanical and thermal shock and forming very acceptable electrical resistance heating elements. Samples 2-5 are less rugged, and samples 3-5 are relatively fragile, but in small sizes may be used as resistors and for other applications where they are not subjected to shock. The physical properties of these samples may be improved by the incorporation of zirconia as in samples 1 and 6.

EXAMPLE 5

A composition containing 98 parts of zinc oxide, two parts of zirconium oxide, .03 part of silica and .003 part of alumina, as described also under sample 1 of Example 4, is processed by wet mixing, spray drying, remoistening with water containing glycerine and purified methyl cellulose, compacting by extrusion, drying, and firing, to produce a tubular electrical resistance heating element which is coated at both ends with silver paste to provide contact areas and is then tested for resistivity.

The initial firing is for three hours at 1400° C., after which treatment the tube shows a resistivity of .04 ohm-cm. over the entire range of 25 to 925° C. The tube is then heated an additional 60 hours at 1050° C. Thereafter the resistivity at 25° C. is .3 ohm-cm. and at 925° C. is .1 ohm-cm.; and this resistivity is maintained during long-continued use of the tube as an electrical resistance heating element at temperatures in the neighborhood of 925° C.

Heating at just below sintering temperature and above subsequent operating temperature for a time usually of the order of 30 to 60 hours is effective in bringing the resistivity value to a constant maximum in each of the compositions of the present invention.

A tubular heating element prepared as above described and having an outside diameter of 3/8 inch, a wall thickness of 1/16 inch, and a length between electrodes of 15 inches, is particularly suitable for use in the space heater described in connection with the appended drawings. The tube has a resistance of about 9.6 ohms, draws 1500 watts at 120 volts, and operates at a temperature of approximately 925° C. Tubes of other specific dimensions may easily be designed for operation at other voltages or temperatures where desired.

EXAMPLE 6

Whereas the oxides of aluminum, gallium and indium may serve as sole modifiers of pure zinc oxide in the prep-

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7 aration of low resistivity elements, iron oxide is effective for such purposes primarily in conjunction with silica, as is shown in the following comparison which illustrates also the incorporation of zirconia to provide additional physical ruggedness. The samples are sintered one hour at 1400° C. and stabilized by heating for several days at 925° C.

Sample	ZnO	ZrO ₂	SiO ₂	Fe ₂ O ₃	R ₂₅	R ₉₂₅
1-----	98	2	.015	.0150	4.0	.05
2-----	98	2	.015	.0075	1.8	.09
3-----	98	2	.015	.0025	.21	.10
4-----	100	-----	.015	.0025	.39	.14
5-----	100	-----	-----	.0025	39.0	.21
6-----	100	-----	-----	.0050	40.0	.13

What is claimed is as follows:

1. A ceramic semiconductor resistance element consisting essentially of zinc oxide together with modifiers making up about .002 to about 30 percent of said element and including about one to thirty percent zirconia, about .005 to about one percent silica, and 0-.03 percent of oxide of at least one of the trivalent metals aluminum, gallium, indium and iron, said element being further characterized as having a resistivity value at 25° C. of less than about ten ohm-cm., a resistivity value at 925° C. of less than about one ohm-cm., and the ratio of resistivity value at 25° C. to that at 925° C. being between about one and about ten.
2. The resistance element of claim 1 wherein the resistivity value at 25° C. is less than about one ohm-cm.
3. The resistance element of claim 1 wherein is included about one to about five percent of zirconia.
4. The resistance element of claim 1 wherein is included about .002 to about .03 percent of said trivalent metal oxide.

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5. The resistance element of claim 1 wherein is included about one to about five percent of zirconia, about .005 to about one percent of silica, and about .002 to about .03 percent of said trivalent metal oxide.
6. The resistance element of claim 5 wherein the modifiers are about two percent of zirconia, about .03 percent of silica, and about .003 percent of said trivalent metal oxide.
7. The resistance element of claim 6 wherein the trivalent metal oxide is aluminum oxide.
8. The resistance element of claim 1 wherein is included at least about one percent of zirconia, at least about .005 percent of silica, and at least about .001 percent of alumina, said element being in the form of an elongate tube characterized by resistance to mechanical and thermal shock and by having a substantially constant resistivity value during prolonged heating at 925° C.

References Cited

UNITED STATES PATENTS

2,887,632	5/1959	Dalton	252—512
3,089,856	5/1963	Cyr et al.	252—518
3,264,229	8/1966	Klein	252—518
2,892,988	6/1959	Schusterius	252—520
2,933,586	4/1960	Schusterius	252—520
3,509,073	4/1970	Bowman	117—201
3,515,686	6/1970	Bowman	252—518

OTHER REFERENCES

Chem. Abstracts, vol. 61, 2585b, Valleer et al., 1964.

DOUGLAS J. DRUMMOND, Primary Examiner

U.S. Cl. X.R.

106—296; 23—147

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,630,970 Dated December 28, 1971

Inventor(s) Karl E Nelson

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col 3, line 21,

"or neutralizer for trace amounts of alkali metal oxides"
should be

"or about 30% of ZrO_2 the resistivity of the material"

Signed and sealed this 8th day of August 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents