United States Patent [19]

Esper et al.

[11] **3,928,837**

[45] **Dec. 23, 1975**

[54] **CERAMIC OXIDE RESISTOR ELEMENT**

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[73] Assignee: **Robert Bosch G.m.b.H.,** Gerlingen-Schillerhohe, Germany

[22] Filed: **Sept. 6, 1974**

[21] Appl. No.: **503,846**

[30] **Foreign Application Priority Data**

Sept. 27, 1973 Germany 2348589

[52] **U.S. Cl.** .... **338/22 R**; 29/612

[51] **Int. Cl.**^{2} **H01C 7/04**

[58] **Field of Search** .... 338/22 R, 22 SD, 25; 29/612; 252/518, 519

[56] **References Cited**

UNITED STATES PATENTS

2,258,646	10/1941	Grisdale	252/519 X
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2,626,445	1/1953	Albers-Schoenberg	338/22 R
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3,359,632	12/1967	Froemel et al.	338/22 R X
3,477,055	11/1969	Herbst et al.	338/22 R

Primary Examiner—C. L. Albritton
Attorney, Agent, or Firm—Flynn & Frishauf

[57] **ABSTRACT**

A ceramic oxide thermistor having a negative temperature coefficient at elevated temperatures comprising about 30% to 100% Fe_2O_3 and 0% to 70% Al_2O_3. It preferably also contains MnO. The invention also includes a process for manufacturing said thermistor.

10 Claims, 6 Drawing Figures

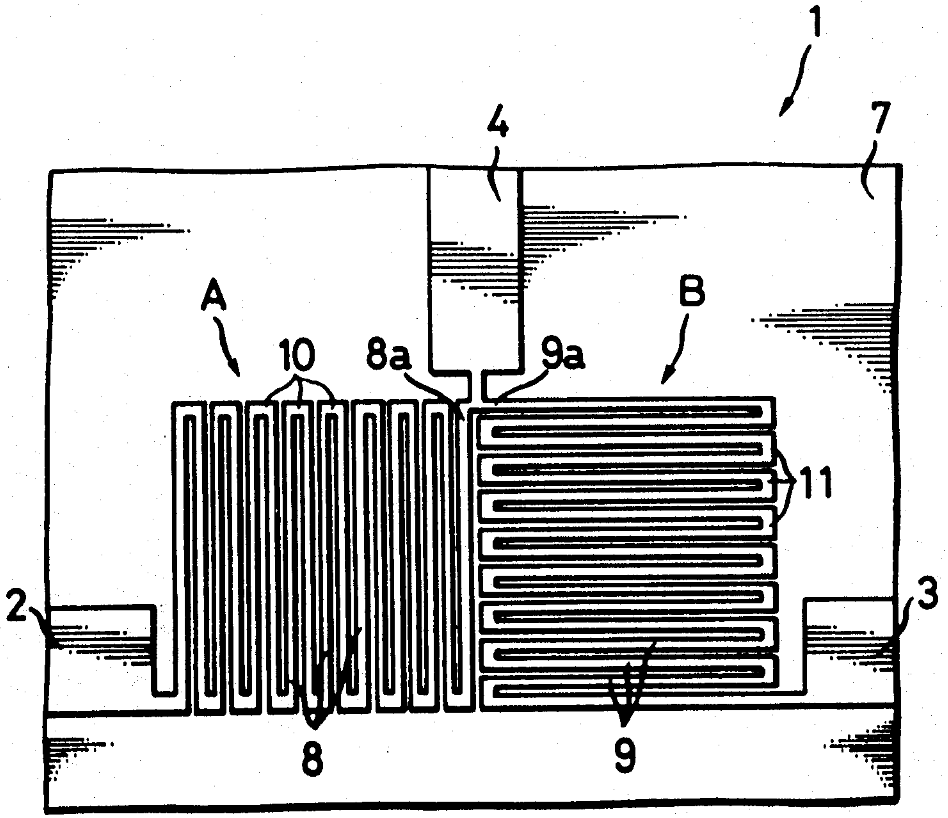


FIG.1

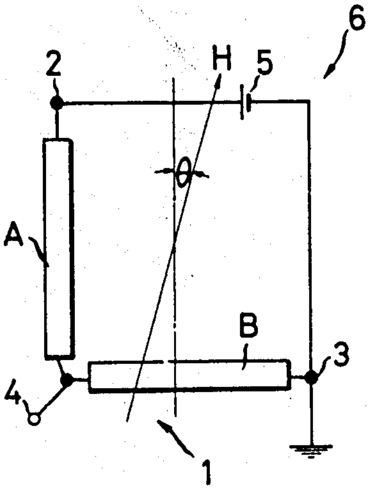


FIG.2

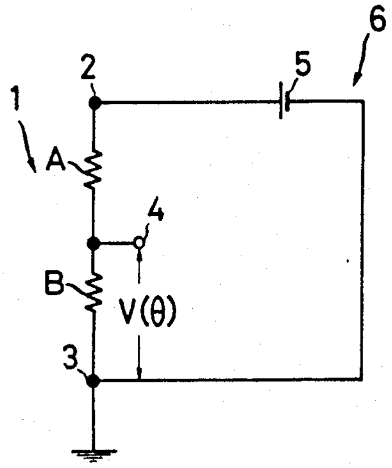


FIG.3

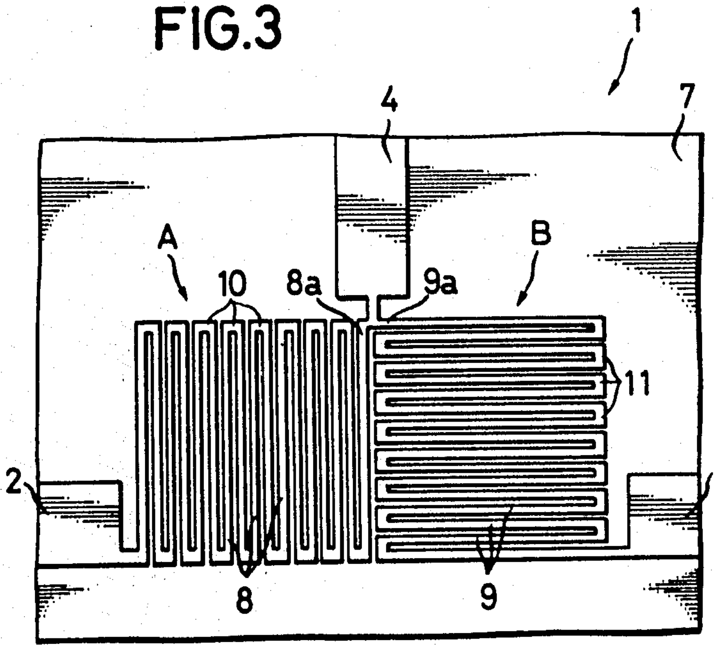


FIG.4

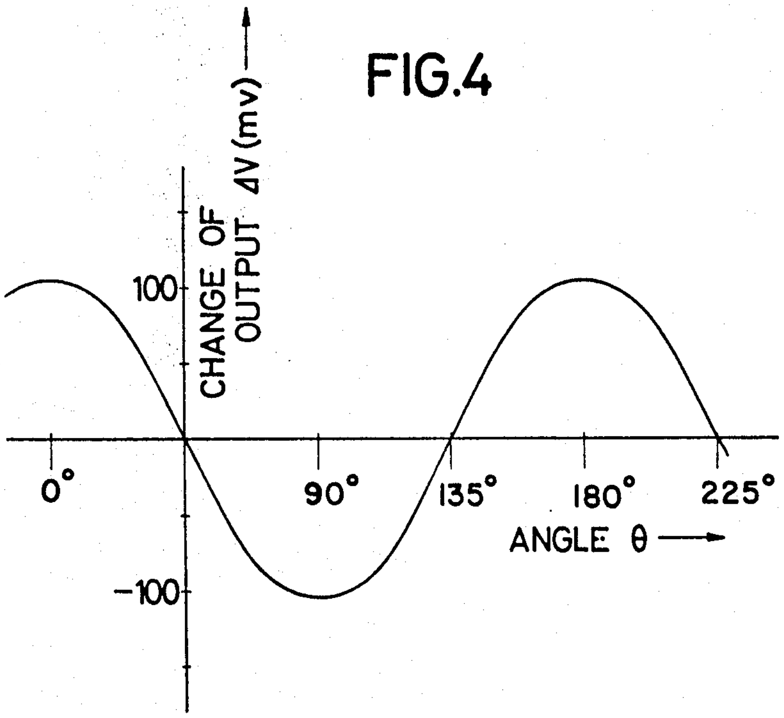

CHANGE OF OUTPUT ΔV (mv)
100
-100
0°
90°
135°
180°
225°
ANGLE θ

FIG.5

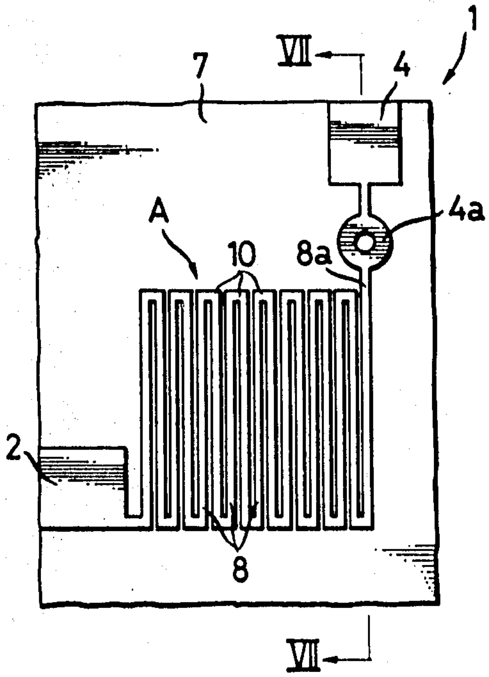

VII
7
4
1
4a
A
10
8a
2
8
VII

FIG.6

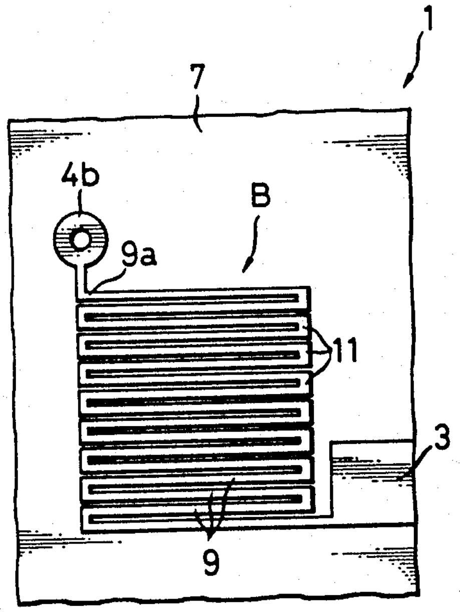


FIG.7

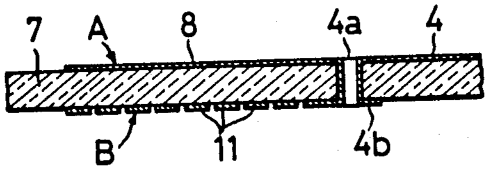
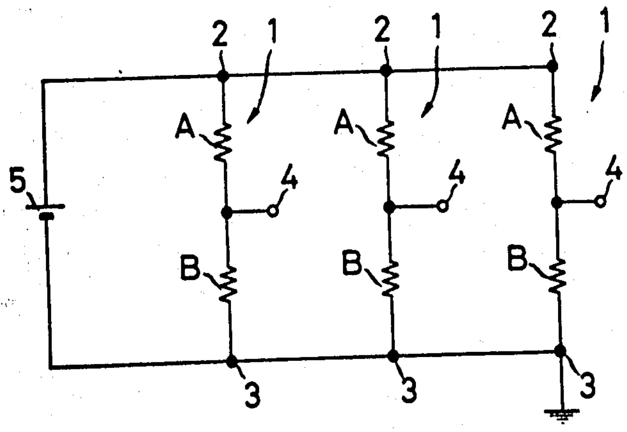


FIG.8



CERAMIC OXIDE RESISTOR ELEMENT

RELATED PATENTS AND APPLICATIONS

U.S. Pat. No. 3,759,232, issued Sept. 18, 1973.

U.S. application Ser. No. 300,047, filed Oct. 24, 1972, Linder et al, now U.S. Pat. No. 3,827,237.

U.S. application, Ser. No. 478,520, filed June 12, 1974, now U.S. Pat. No. 3,890,946, Joseph Wahl, entitled "Method and System to Reduce Noxious Components in the Exhaust Emission from Internal Combustion Engines with Carburetor Supply".

U.S. application Ser. No. 259,157, filed June 2, 1972, Schmidt, et al, now U.S. Pat. No. 3,874,171.

BACKGROUND OF THE INVENTION

The present invention provides ceramic oxide resistors having negative temperature coefficients for use at elevated temperatures, primarily above 400°C. The invention also provides processes for producing such resistors.

Resistance elements which change the resistance characteristics with change in temperature are known as thermistors. Thermistors having negative temperature coefficients and consisting of zirconium dioxide stabilized with yttrium oxide for use at high temperatures are known. Such thermistors do not, however, satisfactorily fulfill the desired requirements for such resistor elements because of the variations in the properties of the resistor element and the variation in the control (regulating) constant B.

The commercially known resistor elements having negative temperature characteristics exhibit irreversible changes in the resistance characteristics at temperatures above 400°C and thus have high aging sensitivity, which is an undesirable characteristic.

There exists a need for a resistance element, particularly for use at temperatures between about 400°C and about 1,100°C which has as steep a characteristic resistance curve as possible concomitant with a control constant B of at least 8,500 K. It is also desired that the characteristic resistance curve, considering its position and steepness, should not change during a long period of service, i.e., its aging sensitivity should be low. It is also desired that the resistance at a specified temperature may be varied, preferably over wide limits, dependent upon the intended use. It is also desired that the variation of the characteristic resistance curves should be small as a result of manufacturing tolerances and additionally that the production yield should be high and the cost economic.

SUBJECT MATTER OF THE INVENTION

The present invention provides a ceramic oxide thermistor having a negative temperature coefficient at elevated temperatures. The said ceramic oxide thermistor (resistance element) comprises Fe_2O_3 and may contain Al_2O_3. The compositions comprise between about 30% and 100% by weight Fe_2O_3 and between 70% to 0% by weight Al_2O_3. The compositions, particularly those for use at temperatures above 600°C, preferably also contain MnO. The thermistors are shaped bodies of the ceramic oxide and contain at least two electrical conductors in electric contact with said shaped body. The two conductors are spaced apart so that when an electric current is passed serially through the conductors and the intervening shaped body, the resistance of said shaped ceramic oxide body may be measured.

The invention also provides a process for manufacturing the ceramic oxide thermistors by finely grinding the oxide materials and heating at temperatures below 1,400°C. The process preferably comprises finely grinding the oxide materials and then heating to form a calcined material which is subsequently finely ground and then again heated at temperatures close to 1,400°C to form the desired shaped thermistor element. This may be followed by a thermal aftertreatment.

The inclusion in the ceramic oxide composition of MnO has the effect of making the characteristic resistance curve steeper. It also decreases the aging sensitivity of the resistor element, particularly at specified MnO contents. The MnO concentration should be in the range defined by the following formula:

$$C_{MnO}=X(C_{Fe_2O_3})^{1.6}$$

wherein X is a constant from about 0.3 to 12 and preferably 0.9 to 4.5. $C_{Mn}O$ is the MnO concentration (in percentage by weight) based upon the total Fe_2O_3 and Al_2O_3 (if any). C_{FeO3} is the Fe_2O_3 concentration in parts by weight also based upon the total Fe_2O_3 and Al_2O_3 (if any).

In the drawings,

FIG. 1 is a graph of the variation of specific resistance with changes in temperature for a number of ceramic oxide thermistors having different MnO contents.

FIG. 2 is a graph of the control constant B for the temperature range of 700°-900°C, and also the temperature coefficient at 850°C, for compositions having varied MnO contents.

FIG. 3 discloses the percentage change in resistance after service for compositions having different MnO contents.

FIGS. 4, 5 and 6 depict different embodiments of the thermistors of the present invention.

The thermistors of the present invention which are resistance elements are useful for measuring temperature since the resistance varies with the temperature. For measurement of temperature it is particularly desirable that the resistance-temperature characteristic curves are as steep as possible, particularly with these negative temperature coefficient thermistors. This is commonly expressed by reference to the constant control B which is defined by the following equation:

$$R_1 = R_2 \cdot e^{B\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

wherein R_1 and R_2 are the resistance values at the temperatures T_1 and T_2 respectively, these temperatures being measured in °K (Kelvin degrees), and e is the basis of the natural logarithm.

The temperature coefficient of the resistor may be calculated from the B-value and the temperature which is being measured in °K (Kelvin) by the following equation:

$$\alpha_T = \left(\frac{-B}{T^2}\right) \cdot 100\ [\%/°K]$$

The resistance for ceramic oxide bodies of the present invention can be varied by the relative content of the Fe_2O_3 and Al_2O_3; and also by the content of the MnO, with the resistance varying in the range of about

10Ω cm to 20 MΩ cm, at a temperature of about 500°C. The MnO content of the ceramic oxide resistor composition also affects the value of the control constant B and the temperature coefficient.

FIGS. **1** and **2** depict the affect of MnO on the characteristic resistant curves and also the control constant B and temperature coefficients of the ceramic oxide resistors. In FIG. **1**, the specific resistance is plotted on a logarithmic scale against the temperature for a ceramic mixture composition containing 50% by weight of Al_2O_3, the specified MnO content from 0% up to 2%, and the balance Fe_2O_3. FIG. **1** discloses that the characteristic curve of the compositions is more level (less steep) for the composition which does not contain MnO than for the other compositions which contain from 0.1% to 2% of MnO. The graph also depicts the affect of the MnO content on the resistance value, i.e., the greater the MnO content, the smaller the specific resistance.

FIG. **2** depicts the control constant B for the temperature range of 700°–900°C for compositions having varied MnO contents. The MnO contents are for the same compositions as in FIG. **1.** FIG. **2** also discloses the temperature coefficient at 850°C for these compositions. FIG. **2** discloses that the values for both the control constant B and for the temperature coefficient (both plotted on the ordinate) are considerably higher for the compositions containing MnO than for the composition which does not contain MnO.

FIG. **3** illustrates the change in resistance of the resistor compositions of FIG. **1** after 100 hours of heat treatment at 1,000°C in air. The ordinate reports the resistance in a percentage which is compared to the resistance of the same composition before the heat treatment. FIG. **3** illustrates that the resistor compositions containing 0.4 and 1% by weight MnO have only a relatively small deviation from the original resistance value after 100 hours. Those compositions having smaller and larger MnO contents have larger variations in the resistance after the heat treatment. It is advantageous that such compositions are subjected to a post-processing heat treatment to stabilize the resistance, as described hereinafter.

FIG. **4** illustrates a cylindrical-shaped ceramic oxide body **410** having metal (preferably gold, silver or platinum) contact layers on each end **411** and **411'**. Wires **412** and **412'** which are electrical conductors are welded or soldered to metal contact **411** and **411'**, respectively.

FIG. **5** illustrates a cylindrical oxide thermistor **510** having electrically conducting platinum or platinum alloy wires **512** and **512'** sintered into opposed ends of the body **510.**

FIG. **6** illustrates a thermistor composition **610** which is a coating on ceramic substrate **613.** The substrate **613** is especially made of high alumina ceramic with an alumina content of at least 99.5% by weight. Strips of electrically conducting material **612** and **612'** are in electrical contact with the ceramic oxide resistor **610.** The ceramic oxide **610** may be applied as a coating composition to the substrate **613** and the conducting strips **612** and **612'** may be applied in the form of conductive inks. The entire article is then subjected to a high temperature heat treatment and the vehicles for the coating composition **610** and the conductive inks **612** and **612'** are volatilized to provide the finished article.

Powdered hematite (Fe_2O_3) may be used as the source of Fe_2O_3; calcined alumina may be used as the source of Al_2O_3; and MnO or other manganese compounds which decompose to the oxide when heated, as the source of MnO. The raw materials are mixed in ceramic mixing apparatus in the desired percentage and then ground in grinding mills following known ceramic procedures. It is preferred in order to obtain a more homogeneous product that the mixed oxide should be ground and then calcined at temperatures of from about 900° to 1,200°C and then again ground to produce a composition having the desired sintering activity. During heating (sintering or calcining) of the compositions, the temperature should not exceed 1,400°C. When heated at higher temperatures than 1,400°C, there is increased production of Fe_3O_4 which results in a large drop in the specific resistance value. Additionally, compositions containing increased amounts of Fe_3O_4 exhibit increased tendency for aging, i.e., the resistance value changes during aging.

The oxide composition which had been mixed and ground and then calcined at from 900° to 1,200°C as aforesaid was then again ground. This ground material is then treated so as to be susceptible to pressing and preparation of a green mass by addition of organic binding and pressing auxiliary agents to the ground ceramic powder, as known in the art. The ground powder admixed with said auxiliary agents is then pressed into cylindrical bodies. The green cylindrical bodies are then coated at their faces with a platinum-containing composition. Alternatively, the pressing bodies may be subjected to an intermediate heating at a temperature of about 800°C and then the end surfaces coated with the platinum compositions. The bodies are then preferably sintered in saggers of high alumina content at sintering temperatures of between about 1,200° to 1,300°C for about 1 to 10 hours in air.

As noted in FIG. **3**, the resistance of some compositions changes with subsequent heating at elevated temperatures for prolonged periods of service. It is particularly advantageous that those ceramic oxide compositions having a MnO content of less than about 0.2% by weight undergo a post-heat treatment of about 1,100°C in air for a period of at least 50 hours to stabilize the values of specific resistance. In addition to the dry pressing described hereinbefore, all known ceramic processing methods may be used to produce the ceramic oxide compositions and articles of the present invention. Thus, extrusion forming, slip casting, printing of a paste through a screen on ceramic substrates, and other suitable processing methods used in ceramic technology may be utilized.

Gold contact layers may be used instead of the exemplified platinum contact layers for surface temperatures up to a maximum of 800°C. Silver contact layers may be used for maximum surface temperatures of about 500°C. Such gold and silver contact layers must be applied to the ceramic oxide resistors (also commonly referred to herein as "thermistors") after the said bodies have been formed and sintered at elevated temperatures. The gold or silver compositions are applied in spaced apart configuration on the ceramic oxide shaped body and then again heated to burn in and form the metallic contact layer which adheres to the ceramic body. This latter processing may also be utilized to form contact layers on the shaped ceramic oxide body. Electrical contacts (wires) are then connected to the contact layers, usually by soldering, welding or pressing. It is also possible to have a simplified construction in which platinum wires may be sintered into the shaped resistor bodies. This has been a more expensive manufacturing procedure than the aforesaid procedure involving application of contact layers and then having the electrical conducting wires attached to the contact layers.

The present invention is further illustrated in the following Examples. All percentages and parts in this application are by weight. The manufacturing procedure described hereinbefore was utilized in the Examples.

EXAMPLE 1

Raw materials:

50% Al_2O_3 (alumina A16 from Firma Alcoa-Deutschland)

49.6% Fe_2O_3 (No. 1352 WF from Farbenfabriken Bayer)

0.4% MnO (No. 13234 from Firma Riedel de Haen)

The raw materials were ground for 2 hours in a vibrating mill having steel milling balls. The ratio of balls to oxide was 1:7 parts by weight. The oxide was then calcined for 2 hours at 1100°C in air and then ground for 4 hours under the same conditions as the first grinding. The ground material was then granualted on a screen with 0.75% of polyvinylalcohol as a binding agent. The granulated material was then pressed into cylindrical shape at a pressure of 2,000 kp/cm^2. A platinum-forming composition No. 1308 from Firma Demetron was coated on oppossed ends of the pressed green mass which was then sintered at 1,250°C in air for 1 hour. The sintering heating rate and cooling rate was approximately 300°C per hour. Platinum wires were then pressed to the platinum contacting layers as depicted in FIG. 4 and the following electrical characteristics determined:

specific resistance: at 600°C 4,500Ω cm } (FIG. 1)
at 850°C 240Ω cm }

control constant B: 700°-900°C 11300 K (FIG. 2)

resistance changes after 100 hours annealing at 1,000°C: + 1%. (FIG. 3)

EXAMPLE 2

This Example demonstrates that the MnO addition to Fe_2O_3 compositions which do not contain Al_2O_3 affects such compositions in the same manner, i.e., the control constant B is raised and aging is essentially eliminated. Such resistors are useful for measuring temperatures between 200°C and 400°C. The grinding and heating procedure of Example 1 was utilized. The raw materials were:

98% Fe_2O_3 (No. 1352 WF from Farbenfabriken Bayer)

2.0% MnO (No. 13234 from Firma Riedel de Haen).

The resistors were tested as in Example 1 and the following determined:

specific resistance: at 250°C 60,000Ω cm
at 350°C 3,800Ω cm

control constant B: 200°-300°C 8,600 K

resistance change after 100 hours annealing at 1,000°C: 0%.

The ceramic oxide resistors of the present invention are particularly useful for measuring temperature because of their thermistor characteristics. They have particular utility in the new systems for eliminating (or substantially minimizing) toxic materials from exhaust gases, particularly, those utilizing catalysts and reactors which have optimum operating characteristics at elevated temperatures. They must, however, be protected against overheating. The ceramic oxide resistors of the present invention have proven especially suitable for use in control and regulation of temperatures in the range of 350°C to 1,100°C in such systems because of the applicable reproducible characteristics as indicated by their characteristic curves. They have good service lives because they only have a minor aging effect and as a practical matter the service characteristics do not change, resulting in excellent reproducibility and high accuracy of measurement.

The following table demonstrates the effect of the Al_2O_3 content on the specific resistance of Fe_2O_3/Al_2O_3 thermistors, the Al_2O_3 content extending from 0 to 56 % by weight:

Fe_2O_3 raw material	Composition % by weight Fe_2O_3	Al_2O_3	MnO	Sintering temperature (°C)	Specific resistance (Ωcm) at the temperature indicated
Bayer No. 1352 wf	60	40	0	1250	350°C : 51000 400°C : 9500
	100	0	0	1250	350°C : 6200 400°C : 1500
Bayer No. 1663	44	56	0	1250	600°C : 21000
	60	40	0	1250	600°C : 2900
	65	35	0	1250	600°C : 2000
	75	25	0	1250	600°C : 1400

We claim:

1. A ceramic oxide resistance element having a negative temperature coefficient at temperatures above about 200°C comprising

a shaped body comprising Fe_2O_3 about 50% by weight of Al_2O_3 and MnO in weight percent based on the total Fe_2O_3 and Al_2O_3 within the range of

$$X(C_{Fe_2O_3})^{1.6}$$

wherein X is from 0.3 to 12, and wherein $C_{Fe\ O}$ is the concentration of Fe_2O_3 in parts by weight based on the total Fe_2O_3 and Al_2O_3; and

at least two electrical conductors in electrical contact with said shaped body, said two conductors being spaced apart so that when an electrical current is passed serially through said two conductors and through said shaped body, the resistance of said shaped body may be measured.

2. The resistance element of claim 1 wherein said electrical conductors are platinum conductors.

3. The resistance element of claim 1 wherein said electrical conductors are gold conductors.

4. The resistance element of claim 1 wherein said electrical conductors are silver conductors.

5. The resistance element of claim 1 wherein X is from 0.9 to 4.5.

6. The resistance element of claim 1 wherein said shaped body comprises about 50% Al_2O_3, between 0.1 and 2% MnO, and the balance Fe_2O_3.

7. The resistance element of claim 6 wherein said shaped body contains about 0.1% MnO and about 49.9% Fe_2O_3.

8. The resistance element of claim 6 wherein said shaped body contains about 0.2% MnO and about 49.8% Fe_2O_3.

9. The resistance element of claim 6 wherein said shaped body contains about 0.4% MnO and about 49.6% Fe_2O_3.

10. The resistance element of claim 6 wherein said shaped body contains about 2% MnO and about 48% Fe_2O_3.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,928,837 Dated December 23, 1975

Inventor(s) Friedrich J. ESPER; Karl-Hermann FRIESE;
Rudolf POLLNER

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

Column 6, line 56, the term "$C_{Fe\ O}$" should read:

--$C_{Fe_2O_3}$--.

The correct drawings for the patent are attached hereto.

Signed and Sealed this

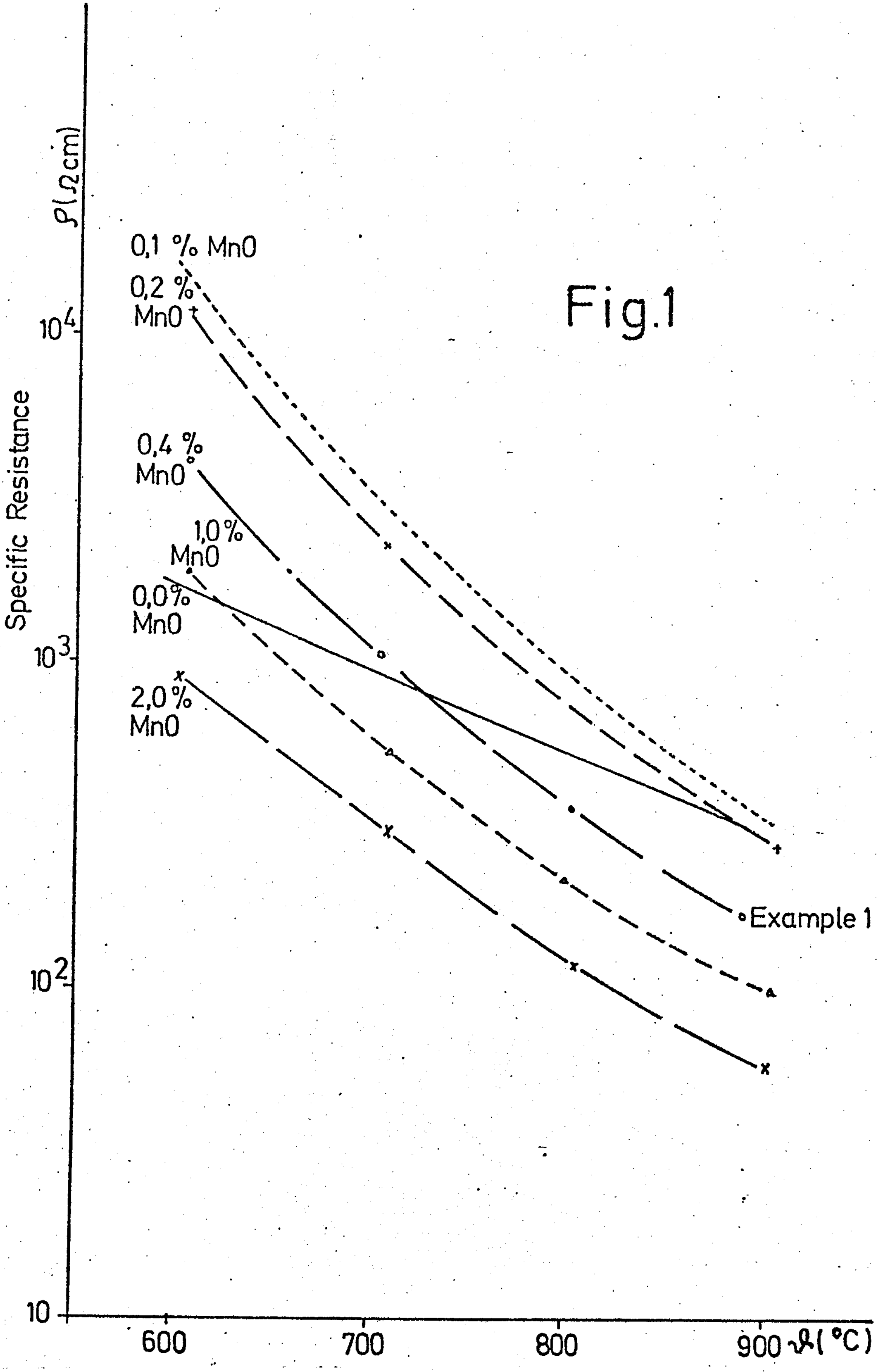
twentieth Day of *April 1976*

[SEAL]

Attest:

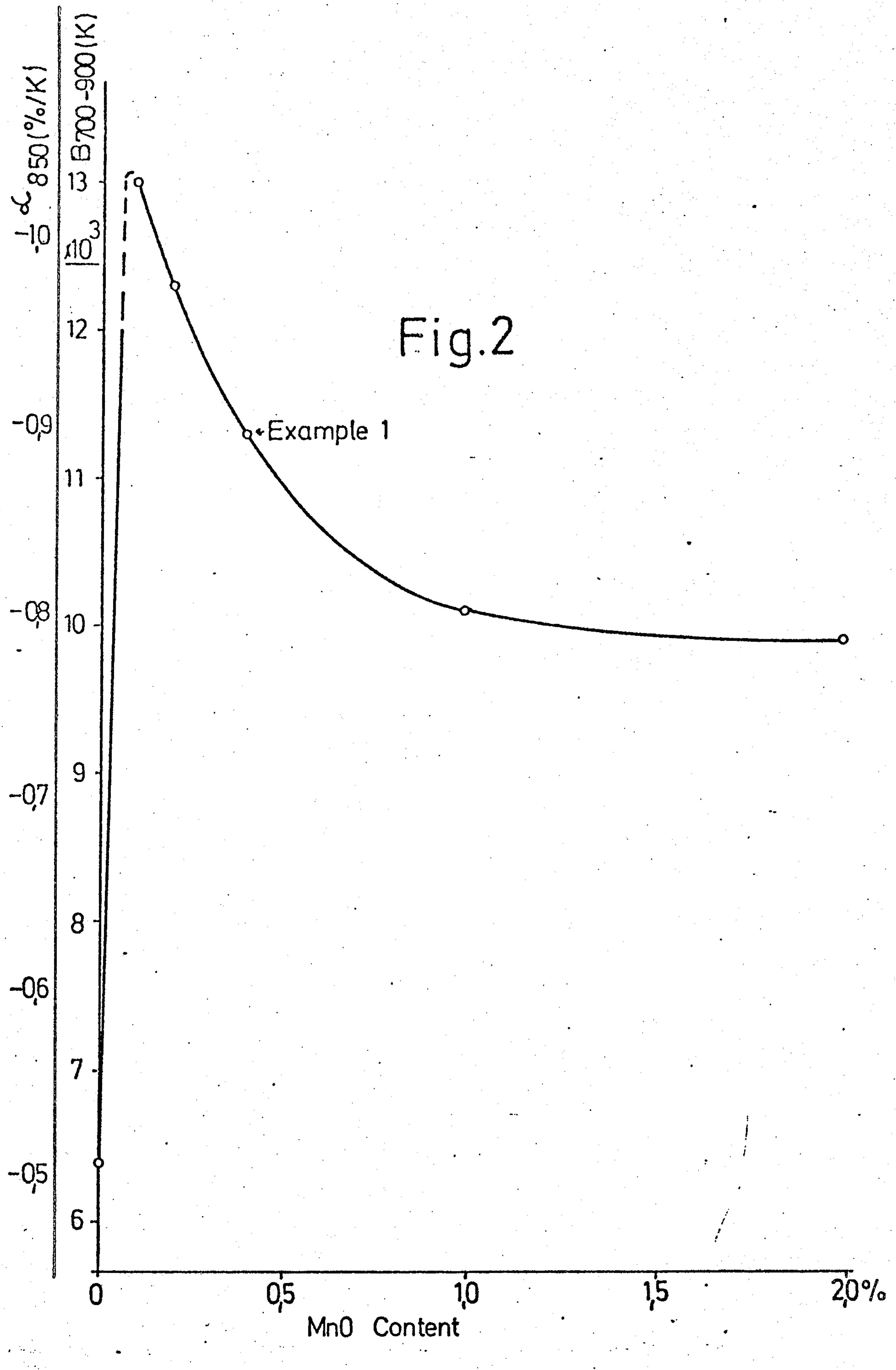
RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks



ρ (Ωcm)
Specific Resistance
10^4
10^3
10^2
10
600
700
800
900
ϑ (°C)
0,1 % MnO
0,2 % MnO
0,4 % MnO
1,0 % MnO
0,0% MnO
2,0 % MnO
Example 1

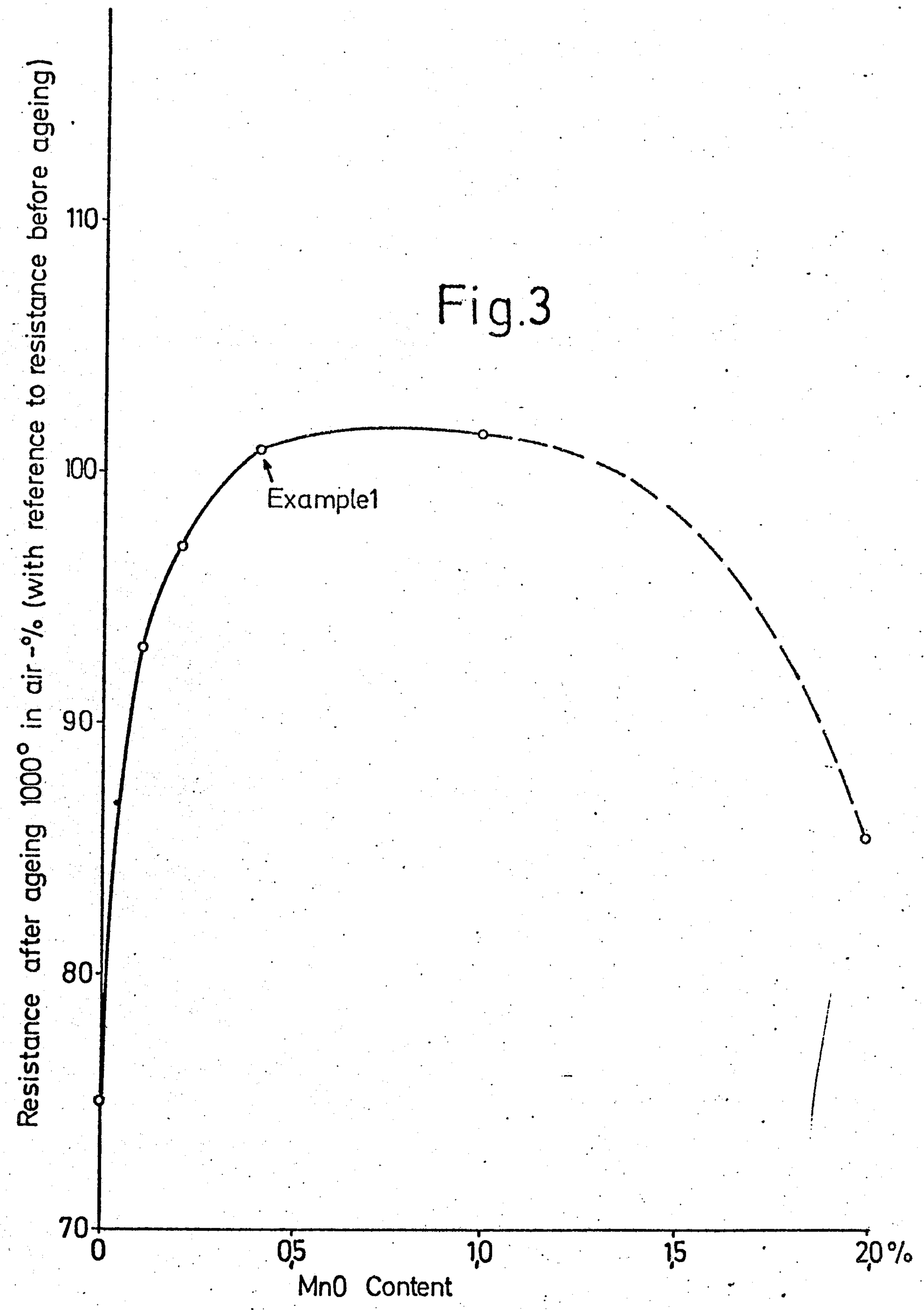
Fig.1



$-\alpha_{850}$ (%/K)
$B_{700-900}$ (K)
x10³
13
12
11
10
9
8
7
6
-1,0
-0,9
-0,8
-0,7
-0,6
-0,5
Example 1
0
0,5
1,0
1,5
2,0%
MnO Content

Fig.2

Fig.3


Resistance after ageing 1000° in air -% (with reference to resistance before ageing)
110
100
90
80
70
Example1
0
0,5
1,0
1,5
2,0 %
MnO Content

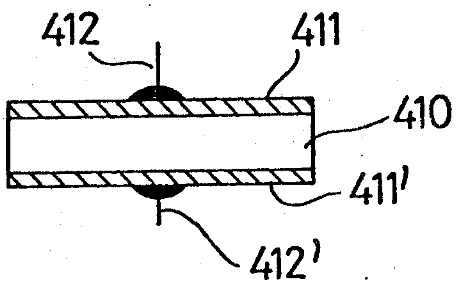


Fig.4

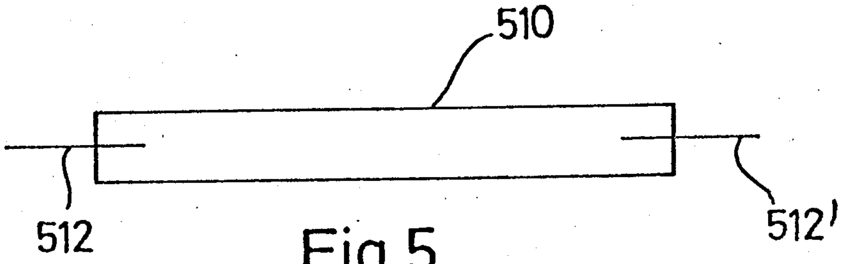


Fig.5

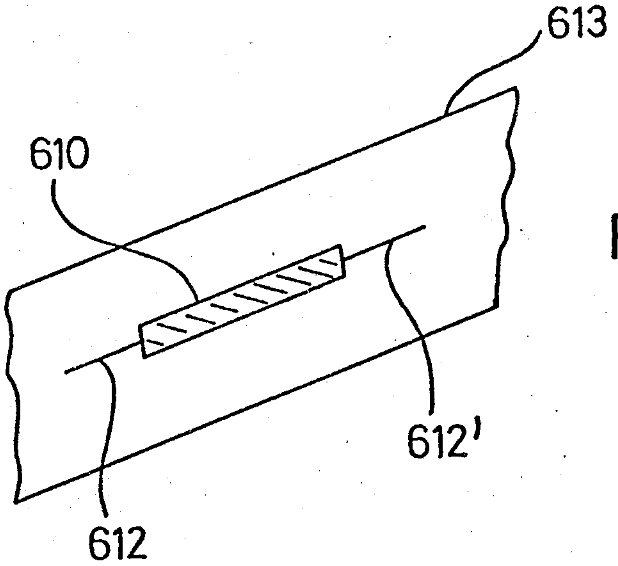


Fig.6