Aug. 5, 1941. W. LEHFELDT ET AL 2,251,745

METHOD FOR MANUFACTURING SEMICONDUCTING RESISTORS

Filed Dec. 23, 1938

FIG. 1.

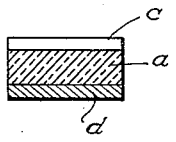


FIG. 2.

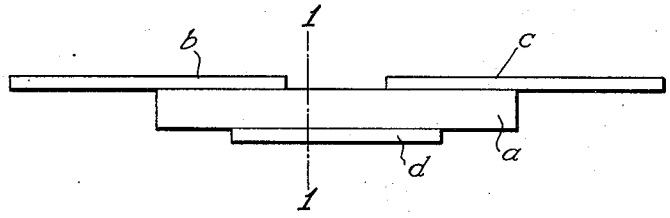
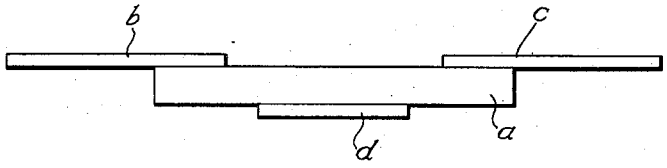


FIG. 3.



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Patented Aug. 5, 1941 2,251,745

UNITED STATES PATENT OFFICE

2,251,745

METHOD FOR MANUFACTURING SEMICONDUCTING RESISTORS

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Application December 23, 1938, Serial No. 247,382

In Germany December 18, 1937

8 Claims. (Cl. 201—76)

The present invention relates to a method of manufacturing semi-conducting resistors.

It has been difficult to manufacture semi-conducting resistors from metal compounds or metal oxides so as to obtain a predetermined resistance. An object of the invention is to eliminate or substantially reduce this difficulty.

Known methods of manufacturing semi-conducting resistors, particularly resistors of thermo-negative material whose resistance depends upon their oxygen content, consist in influencing the specific resistance of the semi-conductor, for instance, by a heat treatment in air or by removing the oxygen to a considerable extent, for instance under high vacuum. These methods require a strict adherence to exacting manufacturing conditions. Furthermore, when employing such resistors, the percentage of oxygen may easily vary, particularly at elevated temperatures and depending on the purity of the starting material. An object of the invention, more particularly, is to remove these drawbacks.

Different electric resistors manufactured from the same starting material under similar manufacturing conditions have, as a rule, different resistance values and always depart somewhat from the desired value. To attain values as accurate as possible, i. e. to reduce the unavoidable tolerance to a minimum, various methods have been proposed substantially in adjusting the finished resistor under the control of a measuring device or in subjecting it, preferably during the last stage of manufacture, to a resistance control effected with the aid of a measuring device. The adjustment even in the last stage of manufacture is often effected by removing active resistance material, for instance, by manufacturing wire resistors with plus tolerance and by then unwinding an amount of wire, under the control of a measuring device, necessary to attain the calculated value. In the case of resistors formed of layers, i. e., resistors which consist of a thin layer applied to a support, parts of the resistance layer are removed, for instance, by punching them out together with parts of the support or by scraping or grinding in order to reduce the cross-section or to increase the conductance. In the case of resistors consisting of a mixture of conducting and semi-conducting particles it is also possible to vary the resistance by removing resistance material; however, this method is not convenient, since in this manner the dimensions of the resistor are altered. For this reason they are subjected to a subsequent heat treatment or a subsequent pressure is applied in some cases during the manufacturing of resistors composed of the above-mentioned mixture in order to vary the resistance. These methods are time absorbing and expensive and permit only to maintain mean resistance values.

The method according to the invention consists in adding to the raw material before pressing the same a small percentage of alkali or alkaline earth compounds, for instance, of sodium or potassium preferably in the form of hydroxides or carbonates and in heat treating, for instance, sintering the pressed means.

Depending upon a lower or higher percentage of these admixtures it is possible to reduce on the one hand the specific resistance to a value varying from $\frac{1}{10}$ to $\frac{1}{10,000}$ and to attain in accordance with the purity of the starting material a tolerance variation of the resistors of at most 1:2 instead of 1:4000 as has hitherto often been the case, as well as to improve also the constancy for a considerably greater length of time. The method may also be employed for the known oxygen responsive semi-conductors in which the conductivity increases with increasing oxygen content. The method evidently has the effect that the excess oxygen ions determining the resistance are replaced by alkaline metal ions, and the high constancy and the possibility of reproducing accurate resistance values are due to the fact that the alkaline ion has not the same tendency to diffuse out of the body as the oxygen. It is therefore no longer necessary to effect the sintering in air or oxygen at super-atmospheric pressure, although the use of a super-atmospheric oxygen pressure of 100 at. permits applying temperatures approximately 100 degrees centigrade higher than when sintering in air, so that an increase of the electric constancy may be obtained. The most favorable effect as to the obtaining of a predetermined resistance value is produced by adding to the resistance material alkali or alkaline earth admixtures in an amount of about 0.05 to 10%

When applying the method to resistors made of copper oxide a quantity of 0.1% to 1% sodium or potassium is added in the form of hydroxide or carbonate. In this case specific resistances varying from 1 to 1000 ohm. cm. depending upon the amount of admixture are obtained even when sintering without an increased oxygen pressure, provided the starting materials without admixture have a specific resistance of at least 10^4 ohm. cm.

With pressings of copper oxide containing admixtures according to the invention a sintering

temperature of more than 700 degrees centigrade has proved particularly suitable.

After the resistors of semi-conductive material have been prepared and sintered as described in the foregoing and thus exhibit the desired specific resistance, they may be further calibrated to the desired resistance value. To this end, according to the invention, the geometrical dimensions of highly conductive, preferably metallic layers provided on the surface of the resistors are reduced, for instance by grinding. It is known that portions of the surface of a resistor which are provided with a layer of material more conductive than the resistance material, are more or less short-circuited depending upon the ratio of the resistance values of both materials. This is utilized according to the invention in a convenient manner. The resistor itself is produced with a resistance value above the calculated value, and its final value is reduced to a value below the calculated value by applying a highly conductive mass to a portion of the resistor. The resistor is then connected to a measuring device and the material of the layer of higher conductivity is removed by scraping, grinding or the like until the correspondingly increasing resistance value indicated by the measuring device attains the calculated value. Consequently, the cross-section or the other dimensions of the resistor are not altered at all but the resistance value is reduced by the effect of the mass of higher conductivity in contact with a portion of the resistor.

In a particularly advantageous form of the invention the terminal contacts required for the current supply are used at the same time as adjusting layers, for which purpose the contacting portions of these terminals are made larger than is necessary and when reduced in contacting area, bring about an adjustment of the resistance value.

The adjusting layers may be produced, for instance, by applying dissolved colloidal silver and by reducing the solution under the action of heat. Silver layers may also be produced by applying silver oxide and by reducing it simultaneously with a firing or sintering treatment. These layers may also be welded to rigid metal contacts during their course of production.

The method according to the invention is particularly suitable for manufacturing negative resistors which consist of a mixture of semiconductors, especially of metal oxides, for which purpose copper oxide, titanium oxide, uranium oxide and the like are suitable.

The form in which a resistor according to the invention may be constructed, is shown in the accompanying drawing, in which—

Fig. 1 represents a transverse section through the resistor in Fig. 2 on line 1—1.

Fig. 2 represents a side view of the resistor before completing the resistance calibration, and

Fig. 3 represents a side view of the completely calibrated resistor.

In the drawing, the body denoted by *a* is formed of a semi-conductive resistor proper and consists of a metal oxide as specified above, for instance copper oxide, and an admixture as above specified, for instance 0.1 to 1% of hydroxide or carbonate of sodium or potassium. Reference characters *b* and *c* denote metallic terminals for passing the operating current through the resistor body, and *d* is a metal layer deposited on the body *a* for calibrating purposes. Terminals *b* and *c* and layer *d* consist, for instance, of silver.

If the resistor bodies are made in the form of a bar *a* as shown in Figs. 1–3, and the metal terminal contacts *b* and *c* for the current supply are arranged in the same plane, the advantage is obtained, first, that the connecting ends are exactly opposite to one another. Secondly, by providing an additional metal layer on the opposite side of the resistor body, for instance, in the case of rectangular bars, the layer *d* as shown in Figs. 1–3 of the drawing, the greater portion of the current lines are caused to run through the body itself and not along the surface. In this manner a uniform distribution of current is effected, so that no local heating and therefore no punctures due to heat can occur. Furthermore, the resistor may be completely finished in the form shown in Fig. 2, since the adjustment is effected after the thermal aging so that no further contact points are created which must be subjected to a further ageing, which might cause further changes in resistance. Then the adjustment to the calculated value of the resistance is effected by reducing the contacting areas of the metal layers *b*, *c* and *d* so that the resistor eventually assumes the form shown in Fig. 3.

What is claimed is:

1. The method of producing semi-conductive precision resistors from metal oxygen compounds whose conductivity depends on their oxygen content, which comprises admixing to a substance consisting substantially all of said compound an amount of 0.05% to 10% of substance selected from the group consisting of alkali and alkaline earth compounds, and shaping and sintering the mixture.

2. The method of producing semi-conductive precision resistors of negative temperature coefficient, from metal oxides whose conductivity depends on their oxygen content, which comprises admixing to said oxide an amount of 0.05% to 10% of substance selected from the group consisting of the hydroxides and carbonates of the alkali and alkaline earth metals, and shaping and sintering the mixture.

3. The method of producing semi-conductive resistors of negative temperature coefficient from copper oxide, which comprises admixing to copper oxide a compound of a metal from the group consisting of sodium and potassium, and shaping and sintering the mixture.

4. The method of producing semi-conductive precision resistors from metal oxygen compounds whose conductivity depends on their oxygen content, which comprises admixing to a substance consisting of substantially all of said compound an amount of 0.05% to 10% of substance selected from the group consisting of alkali and alkaline earth compounds, shaping the mixture and heating it to a temperature above 700° C.

5. The method of producing semi-conductive resistors of negative temperature coefficient from copper oxide, which comprises admixing to copper oxide a compound of a metal from the group consisting of sodium and potassium, shaping the mixture and heating it to a temperature above 700° C.

6. The method of producing semi-conductive precision resistors of negative temperature coefficient, from metal oxides whose conductivity depends on their oxygen content which comprises admixing to a metal oxide of high purity so as to have a specific resistance of at least 10^4 ohm. cm. an amount of 0.05% to 10% of an alkaline compound, and shaping and sintering the mixture.

7. The method of producing semi-conductive precision resistors from metal oxygen compounds whose conductivity depends on their oxygen content, which comprises admixing to a substance consisting substantially all of said compound an amount of 0.05% to 10% of substance selected from the group consisting of alkali and alkaline earth compounds, shaping and sintering the mixture so as to obtain a body with a resistance slightly above the desired rating, providing said body with a coating of a conductivity greater than that of said sintered mixture so as to obtain a total resistance slightly below the desired rating, and removing part of said coating to obtain the rated resistance value.

8. The method of producing semi-conductive precision resistors from metal oxygen compounds whose conductivity depends on their oxygen content, which comprises admixing to a substance consisting substantially all of said compound an amount of 0.05% to 10% of substance selected from the group consisting of alkali and alkaline earth compounds, shaping and sintering the mixture to a body of a resistance higher than the intended rating, providing said body with a coating of a conductivity greater than that of said sintered mixture, thermically aging the resistor after the application of the coating so as to obtain a total resistance slightly below the desired rating, and removing part of said coating to obtain the rated resistance value.

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