

PATENT SPECIFICATION

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(54) IMPROVEMENTS IN VARISTORS

(71) We, GENERAL ELECTRIC COMPANY, a corporation organized and existing under the Laws of the State of New York, United States of America, of 1 River Road, Schenectady 12305, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to varistors.

The current flowing between two spaced points is generally directly proportional to the potential difference between those points. For most known substances, current conduction therethrough is equal to the applied potential difference divided by a constant, which has been defined by Ohm's law to be its resistance. There are, however, a few substances which exhibit non-linear resistance. Some devices, such as metal oxide varistors, utilize these substances and require resort to the following equation (1) to quantitatively relate current and voltage:

$$I = \left(\frac{V}{C} \right)^\alpha$$

where V is the voltage applied to the device, I is the current flowing through the device, C is a constant and α is an exponent greater than 1. Inasmuch as the value of α determines the degree of non-linearity and exhibited by the device, it is generally desired that α be relatively high. α is calculated according to the following equation (2):

$$\alpha = \frac{\log_{10} (I_2/I_1)}{\log_{10} (V_2/V_1)} \quad (2)$$

where V_1 and V_2 are the device voltages at given currents I_1 and I_2 , respectively.

At very low voltages and very high voltages metal oxide varistors deviate from the characteristics expressed by equation (1) and

approach linear resistance characteristics. However, for a very broad useful voltage range the response of metal oxide varistors is as expressed by equation (1).

The values of C and α can be varied over wide ranges by changing the varistor formulation and the manufacturing process. Another useful varistor characteristic is the varistor voltage which can be defined as the voltage across the device when a given current is flowing through it. It is common to measure varistor voltage at a current of one milli-ampere and subsequent reference to varistor voltage shall be for voltage so measured. The foregoing is, of course, well known in the prior art.

Metal oxide varistors are usually manufactured as follows. A plurality of additives is mixed with a powdered metal oxide, commonly zinc oxide. Typically four to twelve additives are employed, yet together they comprise only a small portion of the end product, for example less than one mole percent. The types and amounts of additives employed vary with the properties sought in the varistor. Copious literature describes metal oxide varistors utilizing various additive combinations. For example, see U.S. Patent Number 3,663,458. A portion of the metal oxide and additive mixture is then pressed into a body of a desired shape and size. The body is then sintered for an appropriate time at a suitable temperature as is well known in the prior art. Sintering causes the necessary reactions among the additives and the metal oxide and fuses the mixture into a coherent pellet. A passivating coating is, sometimes applied to the sintered body. If a coating is applied, the body with the coating is generally reheated. Next, metallic contacts are applied to the body. The contacts can, for example, be applied by techniques such as application of a silver paste or by metallic flame spraying.

A problem encountered in metal oxide varistors manufactured by the prior art methods has been contact failure. Occasionally a contact will develop a crack or tear near

the lead attachment or will peel from the varistor body entirely. Either of these events can, of course, lead to device failure. It is believed that both of the above failure mechanisms are caused by inadequate contact adhesion. Thus, contact adhesion has become a matter of concern to varistor manufacturers.

According to the present invention, a varistor is provided comprising a body portion defining at least two major surface areas, said body portion having a coating thereon, said coating comprising means providing an irregular surface on the coating, and wherein said varistor further comprises metallic contacts overlying said coating on at least a portion of said two major surface areas.

The present invention will be further described, by way of example only, with reference to the accompanying drawings wherein:—

Figure 1 is a sectional view of a preferred metal oxide varistor; and

Figure 2 is a detailed sectional view of a portion of the varistor depicted in Figure 1.

This invention may be characterized by a metal oxide varistor comprising a body portion that is composed essentially of a metal oxide and a small percentage of a plurality of preselected additives. The metal oxide and the additives are mixed and a portion of the mixture is pressed into a body of a desired shape and size. The pressed body is then sintered to form the varistor body in a manner well known in the prior art. Next a coating is applied to the body and it is reheated as described below. Finally, metal contacts are applied and wire leads are attached to the contacts. The device is then ready to be encapsulated.

Preferably the irregular surface of the coating is provided by particulate matter included in the coating and the step of heating the coating will then be carried out, as described below, at a temperature that does not melt the particulate matter.

In as much as metal contacts, when applied by such conventional methods as the application and heating of silver paste or the utilization of a metallic flame spray, closely conform to the contour of the substrate surface, in this case the varistor pellet surface, it will be appreciated that a substantial increase in contact adhesion will be realized by the utilization of a coating having an irregular (or rough) surface.

It is, of course, realized that other methods of providing an irregular surface can be employed. For example, a coating that shrinks as cured can be employed. The shrinking coating will develop cracks that create irregular surface.

In as much as coatings are often applied to varistor bodies when manufactured by conventional methods, it will be appreciated that little extra cost will be incurred in the manu-

facture of the subject varistor if a conventional coating currently in use is modified to provide an irregular surface thereon.

Another preferred feature of the coating is that it is free of silver and other monovalent ions that tend to diffuse rapidly into the varistor pellet during the step of heating the coating. It is advantageous to prevent such ion diffusion in as much as it causes high leakage current and other effects on the varistor properties that are difficult to predict. Furthermore, the coating can be made free of silicon as disclosed below. It has been found that the inclusion of silicon in a varistor pellet coating increases the varistor voltage of the treated device. Thus, when fabricating low voltage varistors, it is preferable that the coating be free of silicon.

Still another preferred feature of the coating used in this invention is that it is a passivating coating and substantially improves the stability of the devices as discussed below. In order to provide a coating compatible with the varistor body portion, the preselected additives form a major portion of the coating. Thus, compatibility of the coating and the varistor is assured.

The preselected additives can be pre-reacted to form a reaction product which is ground and then mixed with the metal oxide prior to pellet pressing and sintering. It has been found that such a technique provides a varistor with very desirable electrical properties, high stability and of a very uniform composition. A full discussion of the method for fabricating a varistor by prereacting the additives is in our co-pending Application No. 41270/74 (now Serial No. 1,481,453) which describes and claims a method for making a varistor body comprising a primary component and a plurality of additives, which method comprises the steps of mixing together and reacting said plurality of additives, said reacted additives forming a reaction product, mixing said reaction product with said primary component to form a final mixture, and forming said body by pressing and sintering said final mixture. Moreover, the coating can comprise the reaction product of at least some of said additives to provide a passivating coating as described and claimed in co-pending Application No. 42154/74 (Serial No. 1,483,811). Also, a carrier can be included, as is disclosed below, to enhance the adhesion of the reaction product to the varistor body portion surface. In order to further assure compatibility, where the prepared particulate matter is included in the coating to provide the irregular surface this can be grains of the said reaction product.

Consequently, it will be appreciated that there can be provided a coating for metal oxide varistors that functions as a passivating coating to improve the stability of the device. The coating is fully compatible with the varis-

tor body portion, and, in as much as the coating is free of monovalent ions, does not adversely alter the electrical properties of the varistor. Furthermore, the coating can be free of silicon if a low voltage device is being manufactured. Finally, the coating being one with an irregular surface in accordance with the invention enhances the adhesion of the contacts to the varistor body portion.

Referring next to Figure 1 there is shown a metal oxide varistor that includes a sintered body portion 11 composed essentially of a metal oxide and a plurality of preselected additives. The body 11 can be manufactured by methods well known in the prior art or by an improved technique to be discussed below. Surrounding the body portion is a passivating coating 12 and, overlying the coating on two major surface areas of the body, are two metallic contacts 13 and 14. Two wire leads 15 and 16 are coupled to the contacts 13 and 14, respectively, by conductive couplers such as solder 17 and 18.

Referring now to Figure 2 there is shown a portion of the varistor 10 shown in Figure 1. Specifically, a corner of the body portion 11 is shown in Figure 2. In the enlarged Figure 2, the passivating coating 12 is more clearly visible. It is seen to consist of a coating material with particulate matter embedded therein. It will be appreciated that some of the grains 19 of the particulate matter project beyond the surface of the coating 12 while other grains, such as the grains 20, are completely encapsulated by the coating. It will be appreciated that the surface of the coating 12 is rendered irregular or roughened as compared to what it would be were the particles as represented by the grains 19 and 20 absent. It has been found that contacts applied by the conventional methods such as by application of silver paste or by metallic flame spraying do closely conform to surface irregularities. Thus, it will be appreciated that the contact 13 will adhere more tenaciously to the irregular surface than to a smooth surface. The inclusion of the particulate matter as described below has been found to increase the surface irregularity by at least one order of magnitude. Consequently, a substantial enhancement of contact adhesion is obtained.

In order to provide good passivating qualities and to be fully compatible with the pellet 11, the coating 12 preferably comprises at least some of the preselected additives. For example, it has been found that an effective passivating coating can be provided utilizing the "reaction product" used in the method of our co-pending Application No. 41270/74. (Serial No. 1,481,453). Briefly, the reaction product described therein is formed by thoroughly mixing the preselected additives in the absence of the metal oxide and then prereacting the additives. For example, the additives can be heated and cooled and thus

fused into a solid body. This body is then ground to form the reaction product. The metal oxide is mixed with the reaction product and pressed and sintered in the conventional manner.

As specifically described in this co-pending application, a varistor with excellent electrical characteristics can be fabricated from 98 mole percent zinc oxide, 0.5 mole percent bismuth oxide, 0.5 mole percent cobalt oxide, 0.5 mole percent manganese oxide, and 0.5 mole percent titanium oxide. In accordance with the method of said co-pending application, the oxides of bismuth, cobalt, manganese and titanium are thoroughly mixed in equal molar amounts, then heated and cooled to form a crystalline solid body. The crystalline solid body is ground to form the reaction product. Zinc oxide and the reaction product are thoroughly mixed and a portion of the mixture is pressed and sintered to form the varistor body 11.

For the specific formulation of a varistor described above, effective passivating coatings can be produced as described in our co-pending Application No. 42154/74 (Serial No. 1,483,811) and in accordance with the invention claimed therein from any of the following base materials:

1. 16 gms. Reaction Product 95
2. 10.5 gms. Reaction Product + 5.7 gms. Bi_2O_3
3. 14.5 gms. Reaction Product + 2.6 gms. H_3BO_3
4. 10.5 gms. Reaction Product + 5.7 gms. Bi_2O_3 + 1.9 gms. H_3BO_3 100
5. 10.5 gms. Reaction Product + 5.7 gms. Bi_2O_3 + 1.9 gms. H_3BO_3 + 3.6 gms. Sb_2O_3
6. 50 gms. Reaction Product + 30 gms. Bi_2O_3 + 15 gms. H_3BO_3 + 7 gms. SiO_2 105

With respect to the above formulas, it will be appreciated that the sixth formula can be used in medium or high voltage varistors, but it may be desired to avoid the sixth formula, which includes silicon, in the manufacture of low voltage varistors inasmuch as silicon increases the voltage rating of a varistor. Furthermore, it will be appreciated that each of the above formulations is free of silver and other monovalent ions that would tend to diffuse rapidly through the varistor body 11 during the coating heating step to be described subsequently. Such a diffusion of monovalent ions could adversely affect the stability of the varistor 10 and affect the final electrical properties of the device in a manner difficult to predict. Thus, it is beneficial to omit silver and other monovalent ions from the varistor formulation.

The compounds of bismuth, boron, antimony, and silicon, where included, are car-

riers and serve to ultimately enhance the adhesion of the grains 19 and 20 to the body 11.

In order to apply the passivating coating, any of the above formulas is selected and mixed with a vehicle to facilitate handling. A vehicle that has been found effective for the above formulations is composed of 135 grams of n-butyl acetate, 20 grams of ethyl cellulose and 15 grams of butyl carbitol.

Application of the coating is as follows. The coating, which when mixed with the vehicle is fluid, is poured over the sintered bodies 11 or the bodies 11 are dipped in the coating. The vehicle is then dried at a relatively low temperature. The devices are then heated to a temperature in the range of 600 to 1000°C for a preselected time. The temperature and time selected should ensure that the carrier is fused and thus enhances the adhesion of the grains 19 and 20 to the body 11. However, the grains 19 and 20 should not melt so that a body 11 with the coating 12 and the irregular surface depicted in Figure 2 is provided. Following the heating step, the metal contacts 13 and 14 are applied by conventional techniques such as the application of silver paste or flame spraying. As mentioned previously, the contacts 13 and 14 will closely conform to the irregular surface of the body 11 and thus adhere tightly thereto.

It will be appreciated that if it is desired for any reason, the carrier can be utilized with different particulate matter. For example, other suitable particulate matter is grains of aluminum oxide.

In summary it will be appreciated that there has been provided a varistor with a coating which enhances contact adhesion and which in accordance with preferred features as described can be a passivating coating that reduces leakage current, and improves device stability. Tests have shown that contact adhesion can be improved by at least one order of magnitude and leakage current can be reduced by several orders of magnitude. Thus, an extremely desirable varistor and method of manufacture have been disclosed.

Many modifications and variations of the subject invention will be apparent to those skilled in the art. For example, other carriers and vehicles can be used. In addition, it will be appreciated that when the aforementioned first formula is used, only reaction product and vehicle is put on the body. Thus when

using the first formula, the coating is the reaction product only. Furthermore, it will be appreciated that when certain carriers are employed, they are substantially entirely absorbed into the outer portion of the varistor body but do aid in the adhesion of the particulate matter, which is still "embedded" therein, although only partially.

WHAT WE CLAIM IS:—

1. A varistor comprising a body portion defining at least two major surface areas, said body portion having a coating thereon, said coating comprising means providing an irregular surface on the coating, and wherein said varistor further comprises metallic contacts overlying said coating on at least a portion of said two major surface areas.

2. A varistor according to Claim 1 wherein said irregular surface is provided by particulate matter embedded in said coating.

3. A varistor according to either of Claims 1 or 2 wherein said coating is a passivating coating.

4. A varistor according to any one of the preceding claims wherein said coating is free of monovalent ions.

5. A varistor according to any one of the preceding claims wherein said coating is free of silver.

6. A varistor according to any one of the preceding claims wherein said body portion consists essentially of a metal oxide and a reaction product formed by heating together a plurality of preselected additives.

7. A varistor according to claim 2 and claim 6 wherein said particulate matter comprises said reaction product.

8. A varistor according to claim 6 or claim 7 wherein said metal oxide is zinc oxide and said preselected additives comprise the oxides of bismuth, cobalt, titanium and manganese.

9. A varistor according to any one of the preceding claims wherein said coating includes at least one compound of bismuth, boron, silicon or antimony.

10. A varistor according to claim 1 substantially as hereinbefore described with reference to and as illustrated in the accompanying drawings.

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