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2,358,211

METHOD OF FORMING RESISTORS AND THE LIKE

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FIG. 1

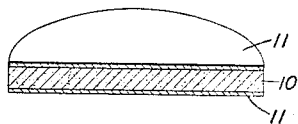


FIG. 2

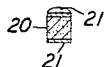


FIG. 3

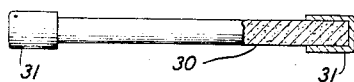


FIG. 4

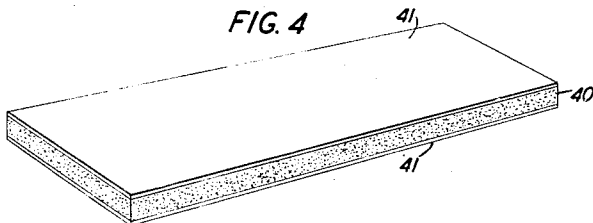
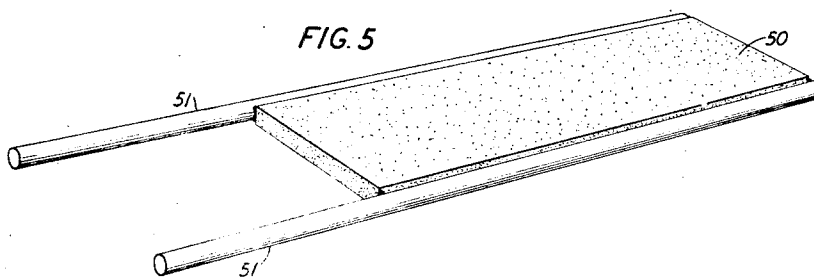


FIG. 5



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METHOD OF FORMING RESISTORS AND
THE LIKE

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10 Claims. (Cl. 201—76)

This invention relates to methods of making formed bodies such as resistors, insulators, and the like from finely divided materials. More particularly, the invention involves the use of a temporary binder for holding the fine particles of material together during the preliminary stages of manufacture. The temporary binders of this invention and the method of using them are particularly applicable to materials comprising those metal-oxygen compounds which are useful in the making of resistors with negative temperature coefficients of resistivity.

In order that features of the invention may be set forth in sufficient detail for a proper understanding thereof, they will be related to the manufacture of resistor discs which are pressed from powdered resistance material and then heat treated. This method, however, basically applies to other ways of forming bodies, such as extruding, pressing, molding and rolling, and, as indicated above, is not limited to resistors or resistance materials.

A temporary binder for use in making resistors and particularly resistors, the resistance characteristics of which are relatively critical, should have certain characteristics which will be herein set forth.

The temporary binder, when mixed with a material to be formed into a body, should impart to the mixture sufficient cohesion to assure reasonable handleability of the formed bodies prior to heat treatment.

The temporary binder should not cause the mixture to adhere to the die, mold, roll, or other forming apparatus.

The temporary binder should render the mixture sufficiently plastic so that it will flow readily into all corners, to completely fill dies or molds; or to allow it to be rolled or extruded properly.

The basic material plus the temporary binder should be of such consistency that it may be machine fed in uniform quantities to dies and the like.

The temporary binder should be of such nature that only a relatively small amount is needed to impart the desired characteristics to the mixture, e. g., less than about 10 per cent.

The temporary binder should leave the formed body during drying or firing without deforming the body or causing it to adhere to adjacent bodies.

The temporary binder should leave no residue in the body. This characteristic is particularly necessary for resistor bodies of the metal-

oxide type since the residue would change the resistance characteristic. For example, many organic binders decompose and leave a residue of carbon which, in turn, will reduce the oxygen content of the conducting oxides when the latter are sintered at an elevated temperature.

Having in mind the above requirements it is an object of this invention to form, from finely divided materials, bodies such as resistors, insulators and the like by a method that employs a temporary binder having the characteristics above set forth.

A feature of this invention is a temporary binder comprising a polymeric ester of methacrylic acid.

Another feature of this invention resides in the controlled heating of the formed bodies to remove the temporary binder prior to sintering, without damage to the bodies.

Other and further objects and features of this invention will be understood more fully and clearly from the following description of illustrative embodiments thereof taken in connection with the appended drawing in which:

Figs. 1 to 5, inclusive, show several forms of resistor devices, the resistance elements of which may be made by means of the process of this invention. Fig. 1 is a disc resistor, Fig. 2 a pellet or short cylinder, and Fig. 3 a rod or stick resistor. Figs. 4 and 5 represent resistors in which the resistance element is a thin sheet of resistance material, the thickness having been exaggerated in the interest of clarity of illustration.

Devices such as those shown in Figs. 1 and 2 may be made by pressing the resistance material in dies. Where the required dimensions of the Fig. 2 type of device are so small that difficulty is encountered in die pressing, they may be made by punching out pellets from larger sheets or discs of suitable thickness or by extruding long strips of proper diameter and then cutting them up into cylinders of appropriate length. The rod or stick device of Fig. 3 may be made by extruding or molding, or by other suitable methods. The thin sheets used in the devices of Figs. 4 and 5 may be made by die pressing or by rolling.

This method has been found particularly suitable for making thermistors, i. e., resistors in which the resistance changes greatly with changes in temperature. Some suitable thermistor materials to which the method of this invention may be applied are one or more of the metal oxides, e. g., those of manganese, nickel, cobalt and copper. The particular method of making the

disc resistor illustrated in Fig. 1 will serve to point out the details of the method of this invention.

The resistance material should be finely divided, that is, in the form of a powder. If, for example, several of the above-mentioned oxides are to be used they should be intimately mixed before further processing.

The prepared resistance material is mixed into a thin paste or slurry with a polymeric ester of methacrylic acid, a plasticizer and a volatile solvent. Some of the suitable methacrylic acid esters are isobutyl methacrylate, normal butyl methacrylate and methyl methacrylate. The phthalates have been found to be suitable as plasticizers. One of these which has been successfully used is dimethyl phthalate. Other suitable plasticizers are butyl phthalyl butyl glycolate, dibutyl sebacate, dibutyl adipate, triethylene glycol di-2-ethyl butyrate, and any of a large number of waxes and softening agents. Any of a considerable number of solvents may be used. A solvent which will not burn or cause an explosive mixture is preferable. Also, the solvent which is most volatile and least toxic is in general the most desirable. The danger from toxic solvents may be substantially eliminated by use of suitable ventilating means. Some solvents presenting a fire hazard but which may be used with suitable precautions are acetone, ethyl acetate, benzene, xylene and a hydrocarbon product known as Solvesso #2. Two solvents presenting no fire hazard are acetylene tetrachloride and a mixture of ethylene dichloride about 75 per cent and carbon tetrachloride about 25 per cent.

The resistance material, methacrylate, plasticizer and solvent are thoroughly mixed and gently heated, if necessary, to drive off the solvent. After sufficient mixing the material takes the form of small doughy lumps or globules. Materials in this form may be spread out to allow any remaining solvent to evaporate. Then the material is reduced to granules by suitable methods, such as pressing through a screen of proper mesh. The granule size may range between 40 and 300 mesh.

The granular material is fed to a die and pressed at about 13,000 pounds per square inch. This may be done in automatic machinery, such as a tablet machine, since the granules will flow freely from a hopper and may be accurately leveled with a shoe or like means. After pressing, the disc will come cleanly from the die because the binder does not cause sticking. The formed discs are tough enough so that they may be handled as much as necessary for completing the processing without danger of breakage, if reasonable care is used.

Next, the binder is removed by gentle heating of the discs. This may be done by spreading them out on a suitable plate, e. g., one of aluminum oxide, and applying radiant heat from heat lamps or like devices thereto. For example, with discs in the order of one inch diameter and one-tenth inch thickness, and a 250-watt heat lamp spaced about eight inches from the disc, a 45-minute radiation for each face of the disc is satisfactory. Then the discs may be put in an oven and further heated to remove the rest of the binder, the temperature being gradually raised until the discs are a dull red. The source of heat is then removed and the discs allowed to cool. During this stage of the process the maximum temperature should be under 600 C. During this heating, the methacrylate polymer breaks down

to the monomer which immediately volatilizes and passes off. Hence the binder passes through no intermediate stage where the binder is all liquid, and thus the danger of the units sticking together is removed. The volatilized organic material should be continuously removed from the vicinity of the discs so that no chemical reduction of the oxides is induced to take place because of the reducing character of the organic vapors. Since many of these vapors are toxic, a suitable means for protecting the operator should be provided.

After complete removal of the temporary binder, the discs may be stacked on a plate of suitable material, e. g., zirconium silicate, with a suitable powder between discs to prevent their sticking together during firing. A powder which has been found satisfactory is 120-mesh aluminum oxide. The loaded plate is placed in a furnace, the temperature of which is initially below 600° C. The temperature is then raised to a proper sintering temperature for the material being processed, e. g., within the range 600° to 1450° C. for thermistors made from one or more of the oxides of manganese, nickel, cobalt and copper. For example, where the resistor material consists of the mixed oxides of manganese and nickel or of manganese, nickel and cobalt, the following treatment may be given: The furnace temperature is raised from below 600° to 1200±25° C. in four hours, maintained at this point for twelve hours and then allowed to cool down to about 600° C. in four hours. The discs are then removed from the furnace and allowed to cool to room temperature.

Resistors in other than disc form may be made by suitable modifications of the foregoing technique. As previously indicated, the short cylinders or pellets of Fig. 2 may be made by extruding long pieces and cutting them up or by making relatively large sheets and punching out the pellets. The rods or sticks of Fig. 3 may be made by extruding or molding. Either pressing or rolling is suitable for making thin sheets of resistance material, such as are used in the resistance of Figs. 4 and 5. The constituents of the temporary binder and the amount of binder used in the mixture may be varied to suit the particular method of forming to be employed.

In order to adapt the various bodies made in accordance with this process for use as resistors or resistance elements, terminal or contact means may be provided. Some forms which these may take are described in connection with the illustrated shapes.

The disc 10, short cylinder or pellet 20, or sheet 40 of Figs. 1, 2 and 4, respectively, may be provided on opposite faces with adherent metallic coatings 11, 21 and 41, respectively. These may be applied by spraying, vapor deposition, electroplating and by other suitable methods. The stick resistor 30 of Fig. 3 may be furnished with metal caps 31 secured by friction or by a suitable cement. The resistance element of Fig. 5 comprising the sheet 50 of resistance material may be provided with rod-like or wire terminals 51. These may be secured to the edge of the sheet by any suitable method, e. g., coating the edges with a metal and then soldering.

In addition to the processing advantages resulting from the use of the plastic binder of this invention, a considerable improvement in the quality of resistors is also obtained. An outstanding feature of improvement is the increased stability and uniformity of resistance, as compared with

resistors made without the use of temporary binders. The following table illustrates these quality improvements:

Aging time in days	Per cent change of resistance			
	Resistors with no binder		Resistors made with temporary binder	
	Average	Maximum	Average	Maximum
10	1.3	2.4	0.60	0.70
20	1.8	3.0	0.65	0.75
50	2.7	4.7	0.75	0.85
100	3.3	5.8	0.83	0.93

The values tabulated above were obtained from resistance readings on a plurality of resistance discs in each of the two categories. As indicated by the above table, the stability of the resistors made with plastic binders is relatively very high. The per cent change in resistance even after one-hundred days is less than 1 per cent whereas the average change in resistors made with no plastic binder is over 3 per cent for the same period. Furthermore, the maximum change varies very little from the average which is clearly not the case with the resistors in which no binder was used. These improvements appear to be due to the fact that the binder makes the material sufficiently plastic so that it forms into a more nearly homogeneous body with considerably smaller pores and fewer of them than is the case where no binder is used. Because of the small number of relatively small pores, the firing process has a better chance to close them completely and prevent atmospheric oxygen or humidity from entering the resistor body and causing a change in the resistance.

Although this invention has been disclosed by means of various illustrative modifications thereof, it should be understood that the invention is not limited thereby but by the scope of the appended claims only.

What is claimed is:

1. The method of making a resistor that comprises mixing finely divided resistance material with a polymeric ester of methacrylic acid, a plasticizer and a volatile solvent, drying the mixture to remove the solvent, reducing the mixture to granules, forming the granules into a body and heat treating the body at gradually increasing temperature up to but not higher than the lowest sintering temperature for the resistance material employed, to depolymerize the methacrylate and completely vaporize and drive off the depolymerized methacrylate and the plasticizer, and then further heat treating the body to sinter it.

2. The method of making a resistor that comprises mixing finely divided metal oxide material with a polymeric ester of methacrylic acid, a plasticizer and a volatile solvent, drying the mixture to remove the solvent, mechanically reducing the mixture to granules, forming the granules into a body and heat treating the body at gradually increasing temperature up to but not higher than about 600° C. to depolymerize the methacrylate and completely vaporize and drive off the depolymerized methacrylate and the plasticizer, and then further heat treating the body between 600° and 1450° C. to sinter it.

3. The method of making a resistor that comprises mixing finely divided oxides of one or more of the metals, manganese, nickel, cobalt, and copper with isobutyl methacrylate, a plasticizer and a volatile solvent, drying the mixture to re-

move the solvent, mechanically reducing the mixture to granules, forming the granules into a body and heat treating the body at gradually increasing temperature up to but not higher than about 600° C. to depolymerize the methacrylate and completely vaporize and drive off the depolymerized methacrylate and the plasticizer, and then further heat treating the body between 600° and 1450° C. to sinter it.

4. The method of making a resistor that comprises mixing finely divided oxides of one or more of the metals, manganese, nickel, cobalt and copper with isobutyl methacrylate, dimethyl phthalate and a volatile solvent, drying the mixture to remove the solvent, mechanically reducing the mixture to granules, pressing the granules into a disc, heating the disc first with radiant heat and then in an oven until said disc assumes a dull red color to depolymerize the methacrylate and completely vaporize and drive off the depolymerized methacrylate and dimethyl phthalate and then further heat treating the body between 600° and 1450° C. to sinter it.

5. The method of making a resistor that comprises mixing finely divided metal oxides with normal butyl methacrylate, a plasticizer and a volatile solvent, allowing the solvent to evaporate, mechanically reducing the mixture to granules, forming the granules into a body and heating the body at gradually increasing temperature up to but not higher than the lowest sintering temperature of the metal oxides to depolymerize the methacrylate and completely vaporize and drive off the depolymerized methacrylate and plasticizer and then further heat treating the body to sinter it.

6. The method of making a resistor that comprises mixing finely divided metal oxide resistance material with methyl methacrylate, a plasticizer and a volatile solvent, allowing the solvent to evaporate, mechanically reducing the mixture to granules, forming the granules into a body and heating the body at gradually increasing temperature up to but not higher than the lowest sintering temperature for the oxides employed to depolymerize the methacrylate and completely vaporize and drive off the depolymerized methacrylate and the plasticizer, and then heat treating the body to sinter it.

7. The method of making a resistor that comprises mixing finely divided metal oxide resistance material with a polymeric ester of methacrylic acid, a plasticizer and a volatile solvent, continuing the mixing until most of the solvent is evaporated, and the mixture is in the form of small, doughy globules, spreading the mixture in a relatively thin layer to allow the remaining solvent to evaporate, reducing the mixture to granules by pressing it through a screen, charging a die with the granules, pressing them into a disc, gradually heating the disc until it assumes a dull red color to depolymerize the methacrylate and vaporize and drive off the depolymerized methacrylate and the plasticizer and then heating at a higher temperature to sinter the resistance material.

8. The method of making a conductive body that comprises mixing finely divided semiconductive material with a polymeric ester of methacrylic acid, a plasticizer and a volatile solvent, allowing the solvent to evaporate, forming the mixed material into granules, forming the granules into a body, gradually heating the body to a temperature below the sintering temperature of the semiconductive material to depolymerize the

methacrylate and completely vaporize and drive off the depolymerized methacrylate and the plasticizer, and then heat treating the body at a temperature sufficient to sinter it.

9. The method of making a conductive body that comprises mixing finely divided, semiconductive, metal oxides with a polymeric ester of methacrylic acid, a plasticizer and a volatile solvent, allowing the solvent to evaporate, reducing the mixture to granules, forming the granules into a body, gradually heating the body to a dull red color to depolymerize the methacrylate and completely vaporize and drive off the depolymerized methacrylate and the plasticizer, and then further heating the body to sinter it. 15

10. In a method of forming finely divided metal oxide semiconductive material into a relatively self-supporting body by holding the material together with a temporary binder prior to sintering in which the binder comprises a polymeric ester of methacrylic acid, a plasticizer and a volatile solvent, the step of removing the binder without damage to the body that comprises first exposing the body to mild radiant heat and then to the heat of an oven until it assumes a dull red color, to depolymerize the methacrylate and drive off the depolymerized methacrylate and the plasticizer.

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