

May 14, 1968

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3,382,574

METHOD OF MAKING AN ELECTRICAL RESISTOR

Filed Nov. 10, 1964

2 Sheets-Sheet 1

FIG. 1

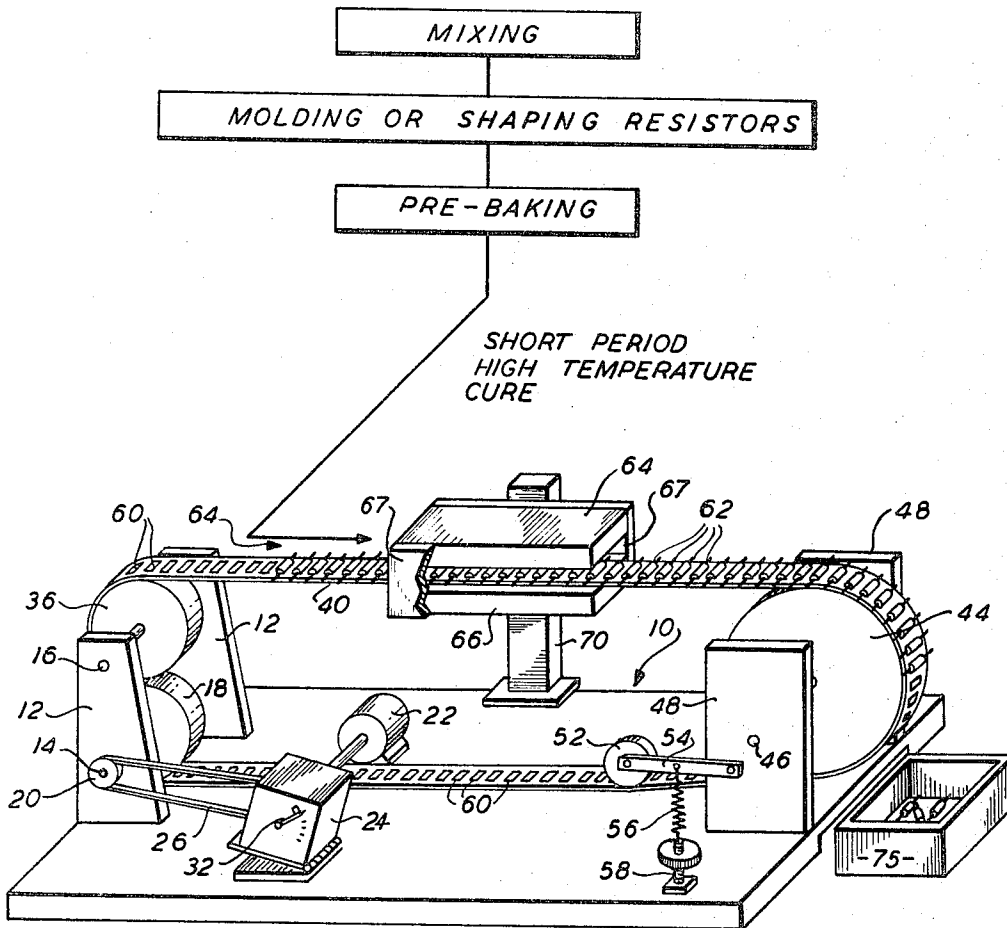


FIG. 2

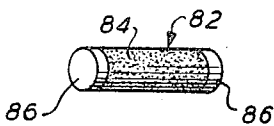


FIG. 3

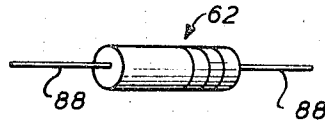
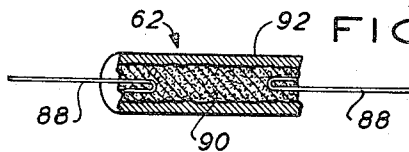


FIG. 4



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2 Sheets-Sheet 2

FIG. 5

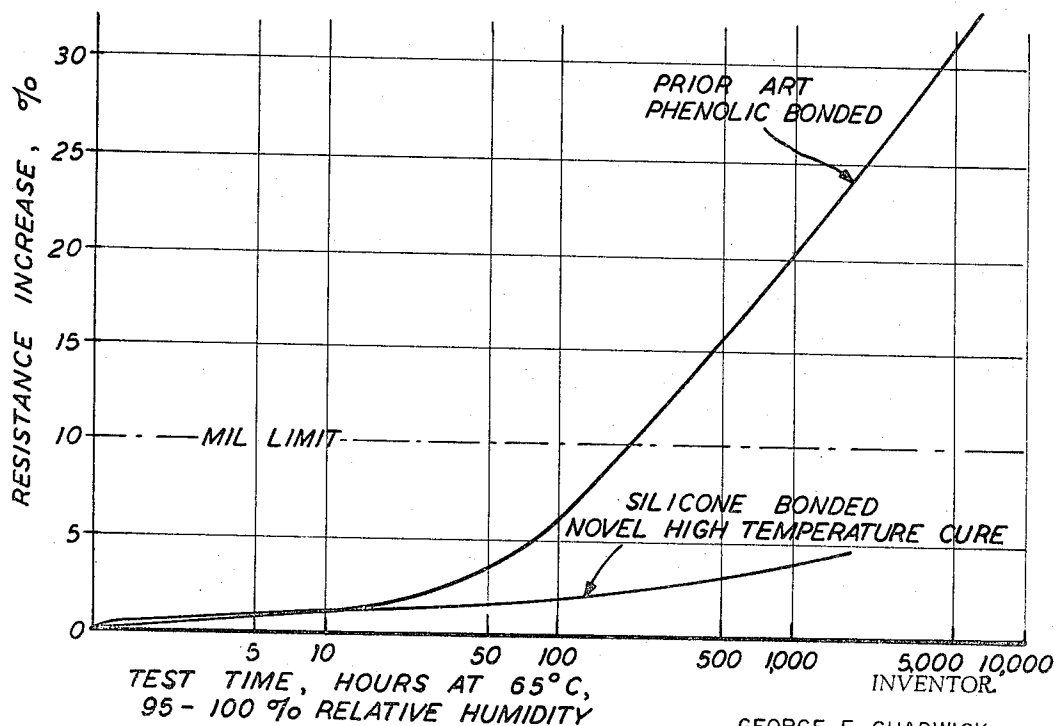
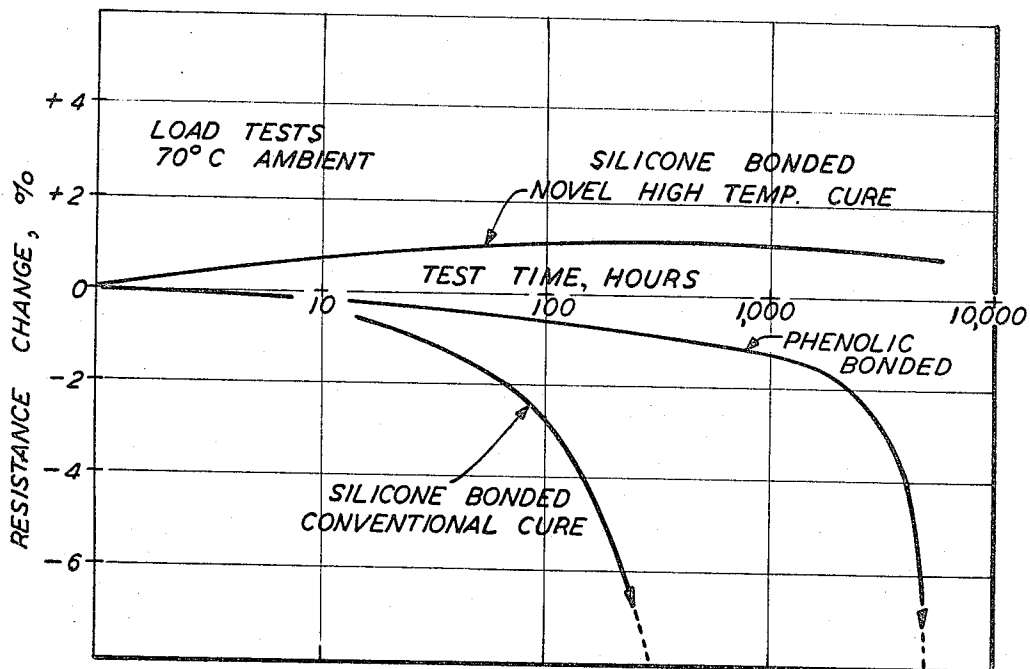


FIG. 6

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3,382,574

METHOD OF MAKING AN ELECTRICAL RESISTOR

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11 Claims. (Cl. 29—610)

ABSTRACT OF THE DISCLOSURE

An electrical resistor in which a mixture of conductive and nonconductive particles are bonded into a unitary structure by a silicone resin binder cured at a temperature of from 400 to 525° C. for a period of from 3 to 15 minutes.

This invention relates to the manufacture of electrical resistors of the type used in such electrical apparatus as radio and television receivers and electrical control equipment. More particularly, the invention relates to the type of electrical resistors known in the trade as "composition resistors." The invention is useful also in making related resistors of other configurations such as those printed on ceramic or composition substrates.

It is an object of this invention to produce a resistor of superior properties by using therein a silicone (polyorgano-siloxane) binder and a special curing cycle. By means of a high temperature short cure, optimum stability of the silicone system is achieved.

It is another object of the invention to provide a method for making a resistor having improved electrical properties, primarily greater heat stability, moisture resistance and longer useful life. The improved results may be obtained by the use of a silicone resin which has the ability to cure, at least partially, by condensation, but which can be further cured under special treatment to produce an exceptionally stable resistor component. Although any reactive silicone can be utilized, the preferred embodiment of the invention uses a condensable type rather than an unsaturated type.

Resistors made according to this invention may be of any convenient shape, such as rods, cubes, etc., and any desired termination such as pressed metallic ends or molded in wire leads.

It is not necessary to advance (polymerize) the resin binder during the mixing operations in order to achieve the superior resistor characteristics of this invention, but to achieve better handling properties during manufacture, the binder may be advanced without loss of the improved stability of the completed resistor.

According to this invention the resistor is first molded or shaped by either a hot molding process or a cold molding process and then given a fast heat cure. If desired, a prebaking or precuring can be carried out concurrently with or immediately after the molding or shaping to impart additional strength to the resistor during further handling and prior to a fast and high-temperature heat cure. As compared with conventional curing, the short-term, high-temperature cure of this invention produces exceptional properties in the resistor.

This invention utilizes two procedures for curing the silicone resins to produce optimum stability and electrical properties. These procedures, which are substantially equivalents, are high-temperature thermal cure and infrared irradiation.

Another object of the invention is to provide improved apparatus for curing resistors in accordance with the method of this invention.

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Other objects, features and advantages of the invention will appear or be pointed out as the description proceeds.

In the drawing, forming a part hereof, in which like reference characters indicate corresponding parts in all the views:

FIGURE 1 is a flow diagram combined with a diagrammatic illustration of apparatus for making resistors with the short-period, high-temperature cure of this invention;

FIGURE 2 is an isometric view of a leadless resistor made in accordance with this invention;

FIGURE 3 is an isometric view of another resistor, having leads at both ends, and made in accordance with this invention;

FIGURE 4 is a sectional view taken through the longitudinal axis of the resistor shown in FIGURE 3;

FIGURE 5 is a graph comparing resistance change of prior art resistors with that of resistors made in accordance with the present invention when subjected to electrical load for extended periods; and

FIGURE 6 is a graph comparing resistance change of prior art resistors with that of resistors made in accordance with the present invention when subjected to moisture for extended periods.

The mixture used for making resistors, in accordance with this invention, includes a silicone resin binder and a filler, which may be considered the "basic mix." To this basic mix is added a quantity of electrically-conductive material, the amount of which depends upon the desired resistance of the resistor.

Neglecting such solvents as may be used to facilitate the mixing, the basic mix includes the following ranges of proportions (all percentages stated herein being by weight):

	Percent
Silicone resin (solids) _____	15-50
Filler, such as pulverized silica, mica, wollastonite, asbestos fibers, chopped fiber glass, or a mixture of these and other materials _____	50-85

To this basic mix is preferably added from 1/10 to 10% of calcined carbon black or graphite as the electrically-conductive material. Carbon or graphite in amounts greater than 10% may be added to the mix to decrease the resistance of the resulting resistor if desired. The carbon or graphite can be included in the original mixing of the ingredients of the basic mix to produce what may be considered as homogeneous mix; or the carbon or graphite can be added later to the already-mixed basic mix to produce what may be considered a heterogeneous mixture. Better results are obtained by using carbon black calcined at 1,000° C. or even higher temperatures.

As a typical example of the invention, a pulverized silica sand (silica flour which would pass a 325-mesh screen), with sufficient toluene to prepare a wet paste, was mixed with the silicone resin in a sigma mixer, the mixer being preheated to about 90° C.

After allowing thorough intermixing a liquid catalyst was added. Exhaust was applied immediately to remove solvent vapors as rapidly as possible. Mixing was continued until all solvent was removed, as evidenced by the dry granular appearance of the mix and a complete lack of toluene odor.

After mixing with gentle warming (60-70° C.), to decrease viscosity and to improve mixing, the resin filler mixture began to form dry, crumbly balls.

The granules were dumped out onto a clean paper or into pans for cooling. After cooling, the coarse mix was ground, using a corn mill or hammer mill. The mix was then screened (through 40-mesh) and was used both for

the shell and for the core of heterogeneous type resistors. For use as core, the 40-mesh granules were placed in a clean, dry ball mill and the desired carbon black added. The ball mill was then filled to about one-third capacity with clean balls and the mix was tumbled for thirty minutes.

The silicone resin is preferably a heat-condensable resin and excellent results have been obtained with both alkyl, aryl and alkyl silicones in the resistor or with either silicone in the resistor. Among those giving especially good results are the silicones sold by the General Electric Company under the trade designations 81888 and SR211. Other suitable resins include General Electric SR220 and Dow Corning 5061 and 2105A. The preferred percentage of resin is between 18 and 22% of the basic mix when silica flour is the principal filler. All percentages are by weight. 21% has been used with very good results.

It is desirable to include 10% of asbestos fines in the filler, this percentage being taken as a portion of the basic mix; or 10% of glass fibers of mixtures of asbestos fines and glass fibers are especially desirable. $\frac{1}{32}$ " glass fibers have been used with good results. The glass fibers and asbestos result in a materially stronger resistor without harm to the thermal stability and moisture resistance. It was found that by including 10% asbestos fines in place of some of the silica powder, an almost two-fold increase in the "fiber strength" of the mix resulted.

A catalyst and mild pressure have been used to advantage to give the original green-molded resistor somewhat greater strength. The amount of catalyst used has been up to 1% of the mix, but the catalyst is not essential.

The General Electric Company supplies a proprietary quaternary ammonium compound to promote silicone polymerization. A number of other catalysts were also used for this invention but did not produce any better results than the General Electric catalyst. Neither the catalyst type nor its concentration was found to affect the final resistor properties obtained. The catalyst was found to improve the precured strength, however, which permitted more severe final cures. Examples of other catalysts which were used include: hexamethylenetetramine; hexamethylenetetramine ethiodide; boron trifluoride; dicyandiamine; cobalt and manganese driers; and arsenic pentoxide.

Resistors were prepared from this mix by compression molding in regular production presses in multicavity dies. The resistors were cured for five minutes at 425° C. No impregnation was necessary to produce the desired resistor properties. The cure can be accomplished by baking in an oven, by infrared radiation, by microwave, or other means for supplying the energy required.

Another example of the invention was prepared with a mix in the following percentages:

	Percent
Solids silicone resin	22
Asbestos fines	7.8
Silica flour	70.2

To this mix was added 0.3% of catalyst. The catalyst used was a quaternary amine supplied by the General Electric Company under the designation 81784.

The silicone in this mix can be varied between 10 and 25% with good results but better results are obtained within a range of 18-24%; and with proportionate reduction in the asbestos and silica but higher initial strength for handling is obtained if there is little or no reduction in the asbestos.

After all solvent was removed, as indicated by the dry appearance and lack of odor, the granular mix was ground to the desired size (40, 60 mesh). Grinding was done successfully on different lots using a corn mill, a hammer mill and a Stokes Tornado mill. All three mills were satisfactory, though size distribution differed somewhat with the grinder used. Carbon black was added by the usual ball mill technique (30 minutes).

The molding pressure is preferably of the order of

20,000 pounds per square inch. The application of substantial pressure increased the density of the resistor and adds correspondingly to its strength. Much better results are obtained if an internal lubricant is included in the mixture to facilitate ejection from the mold. Zinc stearate and Carnauba wax are suitable as lubricants.

This invention can be used to make leadless-type resistors having metal ends, and it can be used for making conventional style resistors with wire leads embedded in the conductive core and with a jacket of electrically-insulating material converging the core.

Experience shows that the molded (green) resistors may lack sufficient strength to be supported by their leads during a high-temperature cure. It was found, however, that the use of a short, lower-temperature precure, advanced the silicones sufficiently to sustain further handling and more severe heat treatment, as previously explained. When a precure is used, 15 to 30 minutes at about 150 to 185° C. was found to yield improved strength without having any apparent effect on the electrical properties. Optional low temperature precure is not to be confused with the short high temperature final cure essential to the present invention.

Two standard tests used in evaluating these resistors and resistors of the prior art were the "load test" and the "170° C. oven stability" test. In the standard load test an appropriate electrical load (2 watts and not over 500 volts for a 2 watt resistor for example) is applied at 70° C. for 1,000 hours. The load is applied in cycles—90 minutes load and 30 minutes no load. The stability of the resistor is judged by comparing the resistance before and after the test. The military specification on this test requires an average change in resistance not exceeding 6% and a maximum deviation for any one piece not to exceed plus or minus 10%. The oven stability test subjects the components of known resistance value to an ambient temperature of 170° C. (at no load) for an arbitrary period of 500 or 1,000 hours, after which the resistance values of the test pieces are again determined.

Attempts to achieve satisfactory thermal and load stability in resistors given a final cure at low temperatures for extended times were singularly unsuccessful. This conclusion was based on both the load and 170° C. oven stability tests. Very high positive temperature coefficients were noted, together with rapidly decreasing resistance on load.

With the high-temperature, short-period cure of this invention, resistance temperature coefficients became less positive as the cure is continued and finally become somewhat parabolic and slightly negative. The 170° C. oven stability improves as more drastic cure is used, up to a temperature of about 500° C. The 170° C. oven stability and load-life results correlate very closely.

The short-period, high-temperature heat cure may be for a period of about 3 to 15 minutes. The preferred time is between about 5 and 6 minutes. The temperature should be about between 400° to 525° C. and preferably between about 425° to 475° C. This time does not seem to be affected by whether or not the resistor was subjected to a prebaking or low-temperature cure for increasing the strength of the green-mold resistor prior to further handling.

As previously stated resistors made according to the present invention are characterized by their superior stability and useful life under conditions of varying temperature, moisture and load. This superiority over the prior art carbon composition resistors has been demonstrated by comparing resistors made according to the present invention with such prior art resistors in standard tests. FIGURE 5 illustrates the change in resistance with time under standard load conditions for (1) resistors made in accordance with the present invention, (2) silicone bonded resistors with the conventional low temperature cure, and (3) conventional phenolic bonded resistors. It is quite apparent from reference to FIGURE 5 that the novel resistor of the present invention completely out-

classes prior art silicone bonded resistors after less than 500 hours under load and is similarly superior to the conventional phenolic bonded resistors after less than 5,000 hours.

As seen from the above, this invention produces resistors of outstanding load-life stability. However, it has been found that even better results are obtained when the resistor is cured in a nitrogen atmosphere as opposed to being cured in air. For example, with tunnel curing in nitrogen, after a 9,000-hour test, resistors cured for about five minutes at 525° C. are scarcely changed in resistance, the change averaging about plus 1.5%.

Load and oven stability tests show somewhat different results with different silicone resins, but variations are within satisfactory limits of thermal stability. Experience with this invention indicates that the short, high-temperature cure is applicable to all silicone resins.

Another important characteristic of an electrical resistor is its ability to operate in a humid atmosphere without suffering a material change in resistance value. Resistors made according to the present invention exhibit outstanding properties in this respect. This can best be appreciated by reference to FIGURE 6 of the drawings which shows typical resistor behavior during extended moisture exposure for commercial phenolic bonded resistors and for silicone bonded resistors made according to the present invention. While both types fall well within the 10% resistance increase tolerance of the military specification after 75 hours of accelerated testing at 65° C., 95-100% relative humidity, the resistors of the present invention exhibit much less change. However, after 1,000 hours or more the novel resistors are obviously vastly superior. Experience indicates that moisture changes of 3% or less can be expected in accordance with the present invention.

Illustrative characteristics of silicone-bonded resistors made in accordance with this invention are set forth in Table I.

TABLE I

	Average	Maximum
Resistance-temperature characteristic:		
-55° C., percent.....	+3.1	+3.8
+105.....	2.7	4.0
Voltage coefficient.....	0.007	0.009
Low temperature operation.....	±1.0	+4.9
Temperature cycling.....	-1.6	-2.9
Moisture resistance (MIL).....	+3.5	+6.2
Accelerated moisture resistance.....	±0.4	+1.1
.....		-0.3
Accelerated humidity.....	+1.3	+2.6
Short-time overload.....	-1.8	-1.9
Terminal strength.....	±4.6	+13.3
Soldering.....	+3.4	+17.6

Hours						
	50	150	225	550	750	1,000
Load life.....	-0.2	-1.2	-1.7	-2.2	-----	3.0
	0.2	3.8	-4.0	-4.6	-----	5.1
Oven stability at 150° C.	-3.8	-6.5	-7.5	-8.9	-9.4	-10.3
	4.3	7.3	-8.4	-10.2	-10.6	-11.7

Resistors can be cured by subjection to infrared radiation. Intense infrared radiation rapidly heats the silicone resistors, probably because of their strong infrared absorption around 9 microns. Further, the solder-coated lead wires reflect most of the radiation and thus are less severely degraded than during equivalent thermal cure. A continuous-belt conveyor assembly was used to provide for simultaneous radiation on both sides of the resistors. The degree of heating of the resistor material with infrared heating is substantially the same as with ordinary thermal heating.

With both thermal and infrared cured resistors, a 10 or 25% of General Electric 81888 resin used with General Electric XR-211 resin produced somewhat more stable resistors than using either alone.

The drawing illustrates the steps of mixing the ingredients; molding or shaping the resistor; and prebaking, if such a step is to be used for increasing the strength of the green-molded resistor for further handling. The attachment of terminals is not illustrated since it is conventional, well understood in the art, and its inclusion in this application is not necessary for a complete understanding of the invention.

The resistors are then subjected to a short-time, high-temperature cure. This short, high-temperature cure is at elevated temperatures which were previously considered undesirable. In accordance with the teaching of this invention, however, the short-period, high-temperature cure produces exceptionally good results which are better than those obtained with conventional curing.

The curing apparatus shown in the drawing includes a base 10 with blocks 12 in which there are bearings for shafts 14 and 16. There is a wheel 18 on the shaft 14 between the blocks 12, and a pulley 20 on the shaft 14 beyond the blocks 12.

Power is transmitted to the shaft 14 from a motor 22 which drives a speed reducer 24 having a belt 26 that drives the pulley 20. The speed reducer 24 has an adjustment 32 for changing the speed of rotation of the pulley 20.

The pulley 20 and wheel 18 are secured to the shaft 14 so that rotation imparted to the pulley 20 causes rotation of the wheel 18 in the same direction.

There is a wheel 36 on the shaft 16; and a conveyor belt 40 passes around the wheels 18 and 36 to reverse its direction of run.

At the other end of the base 10, the conveyor belt 40 passes around a wheel 44 supported by a shaft 46 in bearings in blocks 48 extending upwardly from the base 10. Some tension is imparted to the conveyor belt 40, to hold it in firm contact with the wheels 18, 36, and 44, by an idler roller 52 carried by an arm 54. This arm 54 may be loaded by a spring 56, the tension of which is adjustable by a lead screw 58.

The conveyor belt 40 is preferably made of an endless metal strip having openings 60 at evenly-spaced locations along its length. These openings 60 are of a size to receive resistors 62 and the drawing shows resistors 62 located in the openings 60 beyond a region 64 which may be considered the loading station for the conveyor. These resistors 62 can be placed in the openings 60, which constitute holders for the resistors either manually or by automatic feeding means.

There is a heater 64 located above the top run of the conveyor belt 40 for a portion of the length of the belt; and there is a corresponding heater 66 located below the same portion of the belt. These heaters 64 and 66 are carried on a support 70 which maintains them in parallel relation to one another and to the path of travel of the conveyor belt 40 between the heaters 64 and 66.

The speed reducer 24 is adjusted, in proportion to the length of run of the conveyor belt 40, between the heaters 64 and 66 so as to maintain each resistor 62 between the heaters for the length of time required for the high-temperature cure.

The heaters 64 and 66 are preferably infrared radiant heaters and the space between them is not substantially greater than the height of the resistors 62. This results in a rapid and intense heating of the resistors 62 with the lower portions of the resistors exposed to radiant heat from the lower heater 66 as a result of the openings 60 in the conveyor. There are walls 67 enclosing both sides of the space between the heaters 64 and 66 so as to provide a tunnel in which a special atmosphere can be maintained, such as a nitrogen atmosphere.

The wheel 44 is located some distance beyond the heaters 64 and 66 so that there will be a substantial cooling of the resistors before the conveyor belt 40 reaches the wheel 44. As the belt 40 curves around the circumference of the wheel 44, the resistors 62 are pushed out of

the openings 60 by the surface of the wheel 44; and the displaced resistors drop into a tote box 75.

FIGURE 2 shows a leadless-type resistor 82 having an electrically-conductive core 84 and metal ends 86 which are preferably made of metal powder.

FIGURE 3 shows one of the resistors 62 with wire leads 88 extending from both ends of a conductive core 90 (FIGURE 4). Each of the resistor leads 88 preferably has its end portion, which extends into the core 90, coated with a lead dope consisting of approximately 37.5% silicone resin and 62.5% graphite mixed with enough toluene to give proper flow. The resistors 62 preferably have an outside jacket 92 of electrically-insulating material.

The preferred embodiment of the invention has been illustrated and described, but changes and modifications can be made and some features can be used in different combinations without departing from the invention as defined in the claims.

I claim:

1. The method of making an electrical resistor which comprises mixing together a heat-condensable silicone resin binder with a filler and a quantity of powdered electrical conductor material, shaping the mixture to the desired contour and cross section and curing the resin by subjecting it to a temperature between about 400 to 525° C. for a period of about 3 to 15 minutes.

2. The method described in claim 1 characterized by the curing being performed in a nitrogen atmosphere.

3. The method described in claim 1 characterized by the curing being performed by subjecting the mixture to a temperature between about 450 to 500° C. for a period of about 5 to 6 minutes.

4. The method described in claim 1 characterized by the resistor being molded at substantially room temperature and then being subjected to a low-temperature precure immediately after the molding and before further handling, the low-temperature precure being for a period of about 15 to 30 minutes at a temperature of about 150 to 185° C. to improve the physical strength of the resistor, and thereafter heating the resistor to a temperature between about 400 and 525° C. for a period of about 3 to 15 minutes to cure the resin.

5. The method described in claim 1 characterized by the resistor being shaped by molding in a space under high pressure of about 20,000 pounds per square inch, and being then ejected from the space in which it was molded.

6. The method described in claim 5 characterized by

mixing an internal lubricant with the resistor composition before inserting it in the space in which the mixture is molded under pressure.

7. In the manufacture of an electric resistor element from a mixture of from 15 to 50% solids of a silicone resin binder, from 50 to 85% filler, and up to 10% of electrically-conductive material, the improvement which comprises molding the mixture at relatively low temperature and after molding to the desired shape, subjecting the mixture at a temperature of about 400 to 525° C. for long enough to cure the resin binder.

8. The method described in claim 7 characterized by the mixture being made with a silicone from the group consisting of condensable alkyl aryl silicones and alkyl silicones.

9. The method described in claim 8 characterized by the silicone being in an amount between about 18 to 22% and the filler including about 10% asbestos fines, and strengthening the resistor prior to curing by including in the mix a catalyst for the silicone.

10. The method described in claim 9 characterized by the resistor being molded in a space under pressure of about 20,000 pounds per square inch, ejecting the resistor from the space, and reducing the force for ejection by including in the mixture about 1% of an internal lubricant.

11. In the manufacture of cold-molded, short-cure composition resistors having a silicone resin binder, the process comprising: admixing pulverized silica, silicone resin and finely-divided carbon; cold-molding the mix to form a dense, green, composition body; and heating the body at a temperature in excess of 400° C. and for approximately 3 to 15 minutes duration to cause condensation of the resin of said body to form a permanent, dense mechanically strong, conductive composition resistor.

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