USE OF AN UNADVANCED SILICONE RESIN BINDER IN RESISTOR MANUFACTURE

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Related U.S. Application Data
Continuation of Ser. No. 690,897, Dec. 15, 1967, abandoned, which is a continuation-in-part of Ser. No. 410,091, Nov. 10, 1964, Pat. No. 3,382,574.

Int. Cl. H01c 7/00
Field of Search 264/104, 105, 236, 347; 252/511, 512

References Cited

UNITED STATES PATENTS
2,526,059 10/1950 Zabel et al..........................252/511
2,907,971 10/1959 Krellner...........................264/104
3,056,750 10/1962 Pass..............................252/512
3,382,574 5/1968 Chadwick.........................264/104
3,358,064 12/1967 Belko, Jr..........................264/236

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Assistant Examiner—John H. Miller
Attorney—Hefan J. Klawber, H. Hume Matthews and Edmund H. Bopp

ABSTRACT
A carbon composition resistor and method for manufacture thereof is disclosed, the resistor being characterized as having a body comprising a conductive particulate component, a nonconductive particulate component, and a silicone resin binder for said components, said binder being advanced and cross-linked entirely in situ in the body.

1 Claim, 1 Drawing Figure
LOAD TESTS
70°C AMBIENT

SILICONE BONDED CURE
IN ACCORDANCE WITH INVENTION
100 1000 10,000

SILICONE BONDED
CONVENTIONAL CURE

RESISTANCE CHANGE, %
USE OF AN UNADVANCED SILICONE RESIN BINDER IN RESISTOR MANUFACTURE

BACKGROUND OF THE INVENTION

This application is a continuation of my copending application Ser. No. 690,897, now abandoned, which application is a continuation-in-part of my prior application Ser. No. 410,091, now U.S. Pat. No. 3,382,574.

This invention relates generally to composition electrical resistors of the type including a particulate conductive material such as, for example, carbon black, dispersed in a suitable binder matrix. The invention relates more specifically to a resistor of the aforementioned type in which the binder for the resistor body constitutes a polymerized silicone resin.

In U.S. Pat. No. 2,526,059 to H. H. Zabel, et al. there is described a method for formation of a resistor body of the general type with which the present invention is concerned. According to the teaching of this patent, the resistor body is formed by combining an advanced organo-silicone polymer binder with a conductive particulate component (and, as desired, inert fillers), and thereafter subjecting the combined composition to hot molding at relatively high temperatures. The same patent also teaches that cold molding may be utilized to form the resistor body in those instances where the binder has already been subjected to substantial advancement of the cold molding process.

In my prior U.S. Pat. No. 3,382,574 previously allowed to, I have disclosed my discovery that silicone resin-bound resistors of improved heat and load stability may be produced by a special curing cycle according to which the silicone resin binder of the molded product is subjected to a short duration high temperature cure of from about 400° to 525°C for a period of from 3 to 15 minutes. Now in accordance with the present invention, I have found that a much broader range of temperatures may be employed in curing a silicone resin-bound resistor in those instances where initial cold molding of the unadvanced resin-bound resistor body is effected; and I have moreover found that excellent products thereby result at surprisingly low cure temperatures.

In accordance with the foregoing, it may be regarded as an object of the present invention to provide a method for producing a resistor having improved electrical properties, primarily greater heat stability, better moisture resistance, and longer useful life. It is also an object of the invention to produce by the aforesaid method a resistor body which displays the qualities set forth.

SUMMARY OF INVENTION

Now in accordance with the present invention, I have found that resistors displaying unusually excellent properties of heat stability, moisture resistance, and life expectancy, may be prepared by cold-molding a composition including a dispersed conductive phase, an unadvanced silicone binder, and as appropriate, inert fillers, and only thereafter subjecting the cold-molded resistor body to the heat curing which effects polymerization of the binder. Because much linear polymerization and essentially all cross-linking occurring in the binder takes place in situ, which is to say in the fully formed resistor body, unusually fine uniformity results through the cured body of the resistor, in contrast to the usual practice of producing a molded body first, then subjecting it to heat curing, which results in a less uniform, often excessively hard cured body.

To this basic mix is preferably added from one-tenth to 10 percent of calcined carbon black or graphite as the electrically-conductive material. Carbon or graphite in amounts greater than 10 percent 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 blending of ingredients of the basic mix to produce what may be considered a 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.

In constructing the typical leadless or lead-type resistors such as are shown in FIGS. 2 to 4 of my prior U.S. Pat. No. 3,382,574, it will of course be usual practice to provide an insulating shell for the conductive mix referred to. The "basic mix" alluded to may be utilized for this shell, that is to say that a composition resembling the resistor core—but minus the conductive component—may form the insulating sleeve for the core. A typical formulation for such a shell might thus include 20.0 percent silicone resin, 78.4 percent 5-
3 micron silica sand, 0.8 percent black iron oxide, and 0.8 percent red iron oxide, the latter two ingredients being added merely to provide desired pigmentation. It is often desirable to include 10 percent of asbestos fines in the filler, this percentage being taken as a portion of the basic mix; similarly, 10 percent of glass fibers or of mixtures of asbestos fines and glass fibers yield especially good results. The glass fibers and asbestos result in a materially stronger resistor without harm to the thermal stability and moisture resistance. It was thus found that by including 10 percent asbestos fines in place of some of the silica powder, an almost two-fold increase in the "fiber strength" of the mix resulted.

The silicone resin utilized in the invention is preferably a heat-condensable resin, and excellent results have been obtained by incorporating both alkyl aryl and alkyl silicones simultaneously into the resistor, or by utilizing either resin alone. Among those resins giving especially good results are the silicones sold by the General Electric Company under trade designations 81808, SR-50, SR-211, and SR-350. Other suitable resins include the General Electric products SR-220 and the Dow Corning products 5061, 5581, and 2105A. The preferred compositional range for the resins utilized in the invention is between 18 and 22 percent by weight of the basic mix, when silica flour is the principal filler.

The essence of the present inventive process resides in utilizing such techniques that essentially no advancement of the silicone resin binders occurs prior to such time as the completely molded resistor is subjected to the heat curing which effects gross polymerization and cross-linking of the binder. In the analogous parlance of phenolic resin technology, this mode of operation is thus equivalent to maintaining the resins prior to completion of molding below the so-called B stage of polymerization, that is to say below the stage of polymerization at which the resins products are no longer soluble in such organic solvents as acetone. During the initial process steps of mixing and roll-milling, the absence of such silicone advancement is assured by merely eliminating the use of temperatures which could effect advancement, a proscription which is generally contrary to teachings of the prior art. The following examples are illustrative of the mixing and milling techniques:

EXAMPLE I

In this example, which is illustrative of "dry processing" via a sigma blade mixer plus a roll mill, a core mix similar to that described in connection with Example I was utilized. Initially, the jacket of the sigma blade mixer (Day) was heated to 82°C. Acetone and the silicone resin were then added, and blended 15 minutes to dissolve the resin. The other components were then added and mixed 30 minutes, with the lid on, after which the lid was removed, acetone exhausted, and the mix run to dryness. About 30 to 45 minutes was required to desolvette the mix. The resulting dry, powdery composition was then roll-milled in the manner that has been described in connection with Example I.

Following the mixing and milling steps set forth in the preceding examples, the resulting compositions are prepared for cold molding by hammer-milling and screening the mixtures:

EXAMPLE III

A cooled sheet prepared in accordance with Examples I or II (50 mils thick) was broken into smaller pieces and hammer-milled to give a free flowing powder, which was then screened to a 40 to +325 mesh particle size for molding.

It should be carefully observed that thus far in the practice of the present invention only temperatures have been utilized which are below those at which advancement of the silicone binder occurs. That the binder does not in fact advance to B staging has been conclusively demonstrated, by experiments of the following type:

EXAMPLE IV

A core mix was formulated containing approximately 25 percent silicone resin, 6 percent calcined carbon black, and 69 percent silica filler. A suitable solvent was added, the mix was "wet processed" in a sigma blade mixer, and desolveted to dryness at 82°C. The mix was divided into two parts and further processed on a warm roll mill. Part A was roll milled 5 minutes to a final sheet temperature of 82°C. Part B was roll milled 10 minutes to a final sheet temperature of 88°C. Both parts were hammer-milled and screened to a 40 to +325 mesh particle size. Aliquots of each were then extracted with acetone at room temperature by tumbling four hours in sealed containers. Filtration to retain the fillers and desolvetion of the filtrate to recrystallize the dissolved resin gave the following results:

<table>
<thead>
<tr>
<th>Part</th>
<th>Wt. % of filler recovered on filter</th>
<th>Wt. % of resin recovered in filtrate</th>
<th>M.P. range of recovered resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>96</td>
<td>98</td>
<td>63-67°C</td>
</tr>
<tr>
<td>B</td>
<td>100</td>
<td>96</td>
<td>63-67°C</td>
</tr>
</tbody>
</table>
The composition resulting from the screening and hammermilling operation is thereafter, in accordance with the invention, subjected to a cold molding process in apparatus well-known and conventional in the art. Typically, the resistor shell is thus pre-formed at 1.0 to 1.5 T.S.I. (tons per square inch) for 30 seconds. Thereafter, the core mix is added, leads are inserted, and the entire resistor is molded at 8–10 T.S.I. for 30 seconds. Throughout such molding process the maximum die temperature utilized is about 35°C, so as previously indicated, no advancement of the binder occurs. Preferably, the leads referred to will be provided at their end portions with a lead dope coating consisting of approximately 37.5 percent silicone resin and 62.5 percent graphite mixed with enough toluene to give proper flow. Subsequent to cold molding, the formed resistors are ejected, and are ready for curing.

Heat curing of the cold molded resistors can be accomplished by baking in an oven, by infrared radiation, by microwave irradiation, or via other means for supplying the energy required. Reference may be had in this connection to my copending application Ser. No. 410,091 application wherein a form of apparatus suitable for this purpose is depicted. Regardless of the particular mechanism used to provide curing energy, however, the important point to note is that essentially all advancement and cross-linking of the silicone binder takes place during this cure cycle, which is to say with the binder in situ in the completely formed resistor body. The result of such action is to yield a resistor which displays outstanding properties of electrical stability.

Table I is illustrative of the results achieved where a large group of 2-watt resistors were prepared in accordance with the cold molding method used in this invention and then subjected to appropriate heat curing cycles. The resins used in the various test are listed in the first column, all the SR notations representing product designations of the supplier, General Electric Company. In all instances, as is seen from the second column, cold mold temperatures are utilized prior to curing.

As may be observed from the next column of Table I, (that depicting the cure treatment) the present invention, in general, utilizes a considerably lower range of temperatures than has previously been considered desirable in this technology, for curing of silicone binders. Temperatures are thus seen from this Table I.
fore and after the test. Data of the type collected in this column is also graphically plotted for a typical resistor prepared in accordance with the invention, in the figure appended to this specification. As may be readily seen from the graph, the improvement in stability, as compared to a conventional silicone-bound resistor—that is to say a resistor prepared with hot molding and/or substantial advancement of the binder prior to molding—is most impressive.

while the present invention has been particularly described in terms of specific embodiments thereof, it will be evident that in view of the present disclosure numerous modifications and variations of the invention may now be readily devised by those skilled in the art without yet departing from the teaching herein. Accordingly, the invention is to be broadly construed, and limited only by the scope and spirit of the claims appended hereto.

I claim:

1. The method of making an electrical resistor body which comprises
   a. mixing 15–50 percent by weight unadvanced heat-condensable silicone resin binder with 85–50 percent by weight of particulate non-conductive filler selected from the group consisting of silica, mica, wollastonite, asbestos, glass and mixtures thereof, and 0.10 to 10 percent by weight of the total of binder and filler of electrically conductive material selected from carbon black and graphite, said mixing being carried out at a temperature at which the silicone resin in the mix remains unadvanced,
   b. pulverizing the mixture while maintaining the temperature below that at which advancement of the resin takes place,
   c. forming a shaped body by pressing the pulverized mixture in a die while maintaining the temperature below that at which advancement of the resin takes place,
   d. removing the shaped body from the die, and
   e. subjecting the shaped body to a temperature of 200°C–400°C for from 20 minutes to 2 hours to cure the silicone resin.

* * * * *
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,689,618 Dated September 5, 1972

Inventor(s) George F. Chadwick

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:
The Abstract in the printed patent is incorrect. It should have been replaced with a "Continuation Abstract" sent to the Patent Office on August 5, 1970, which reads as follows:

"Electrical resistor bodies are made by mixing together an unadvanced heat-condensable silicone resin binder with a filler and a quantity of particulate electrically-conductive material, the mixing being effected with moderate heating of the mixture but without causing any significant curing of the resin, followed by cooling and pulverizing, cold molding the mixture to the desired shape, and curing the resin at a temperature of 200°C to 400°C for 20 minutes to 2 hours."

Column 1, line 68, "through" should be --throughout--
Column 5, line 65, "test" should be --tests--
Table I, 6th line from the bottom:
"SR-350 do 23 min. at 200°C..." should read
--SR-350 do 23 min. at 300°C...--

Also, on this patent the name of Attorney "Hefan J. Klawber" should be --Stefan J. Klauber--
The name of Attorney "H. Hume Matthews" should be --H. Hume Mathews--
The name of Attorney "Edmund H. Bopp" should be --Edmund W. Bopp--

The Assignee on this patent should be AIRCO, INC., in accordance with the assignment filed in the Patent Office December 8, 1971.

Signed and sealed this 13th day of March 1973.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR. ROBERT GOTTSCALK
Attesting Officer Commissioner of Patents