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2,795,680

PRINTED RESISTORS AND INKS

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No Drawing. Application May 16, 1952,
Serial No. 288,305

4 Claims. (Cl. 201—63)

This invention relates to improved electrical devices such as resistors and specifically refers to improved resistors of the printed type.

There are numerous forms and types of electrical resistors such as wire wound, carbon composition, carbon film, metal film, etc. One type which has come into some use is the so-called printed resistor which is produced by laying down through a silk or steel screen a suspension of carbon black or graphite in a solution of resinous binder, followed by the removal of solvent and curing of the resin. The base materials used for such resistors include Bakelite, ceramic and glass.

While such printed resistors are essentially an inexpensive type and theoretically capable of close manufacturing control, it is found in practical operation that the resistors offer numerous problems discouraging their use.

One typical and common problem is the stability of the printed resistor per se or resistor in a complex printed circuit. The usual processing steps which follow laying down of the resistor are curing of the resin, screening a protective resin coat over the resistor, curing this coat, soldering of lead wires to the usually silvered contact areas, degreasing the resin from the soldered joints, applying an outer protective coat resin, curing this latter resin and finally vacuum wax impregnating the protective resin coat. The various heating operations involved here, as well as the degreasing solvent and protective coat solvent, affect the resistance value and characteristics of the printed resistor remarkably. Usually the resistance value is greatly increased by the various processing operations; unfortunately, however, this increase is non-uniform, making it difficult, if not impossible, to maintain the appropriate resistance value tolerances. In some instances, actual control of the resistance value of the screened resistor is in itself difficult, due to viscosity problems, suspension uniformity problems and variations in the extent of resin polymerization during and following this screening operation. In such cases, it is common for the operator to adjust the resistance value by scraping off some of the resistance layer after resin curing.

Another disadvantage of present printed resistors resides in the negative temperature coefficient of resistance which is obtained. As a result, overloading of the resistor to even a minor degree will result in a drop in resistance value causing a further overload and higher temperature, etc., until the resistor burns out. A positive temperature coefficient of resistance would overcome this serious disadvantage.

It is an object of the present invention to overcome the foregoing and related disadvantages. A further object is to produce new and useful printed resistors. A still further object is to produce printed resistors having exceptional process and operational stability. Additional objects will become apparent from the following description and claims.

These objects are obtained in accordance with the present invention wherein there is produced a printed resistor

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comprising an insulating base with terminal points upon which and against which, respectively, is deposited an adherent resistance layer consisting of a resinous binder selected from the class containing cross-linked epoxy resins and finely divided particles of conducting material.

In a more restricted sense, the invention is concerned with a printed resistor comprising a ceramic base, upon which is deposited an adherent layer of resistance material consisting of from about 50% to about 95% of a cross-linked epoxy resin, from about 50% to about 5% of finely divided conducting particles and from about 25% to about 0% of finely divided non-conducting particles, terminal contact areas being provided at the ends of said layer.

The invention is also concerned with the preparation of resistor ink, consisting of a solution of a predominant amount of an epoxy type resin dissolved in a high boiling solvent, a significant amount of conducting particles suspended in said solution and minor amounts of a cross-linking agent, active only at temperatures exceeding 75° C.

In accordance with one of the preferred embodiments of the invention, the cross-linking agent is in the form of finely divided particles suspended in said solution.

It has been found possible to produce printed resistors with excellent electrical characteristics by a simple and efficient manufacturing process utilizing specific types of resins which are capable of reacting to substantially insoluble and thermo-setting states under selected thermal processing conditions.

In the prior art, resins which have been suggested for use in printed resistors and resistor inks include the phenol-formaldehyde resins, the urea-formaldehyde resins, the melamine-formaldehyde resins, the linseed soya and castor oil type resins, the silicone resins and other resins which can be dissolved in a solvent and subsequently processed thermally to give tough and durable coatings. It has been found that inks made from the resins described above normally possess poor process stability and when fabricated in printed resistor form have a negative temperature coefficient of resistance. Further certain of these resins are what is termed noisy; that is, superfluous noise will result in an electrical circuit employing such resistors in stages where signals are being handled.

Therefore, the present invention employs as the basic resin binder, a resin from the class containing epoxy resins. These can be formed by condensation of epichlorohydrin with di-hydroxy compounds of aromatic and aliphatic nature. One common and suitable resin is obtained by condensation of epichlorohydrin with bisphenol to give resins varying from a liquid monomer up through a relatively high polymer in which 10 or more bisphenol groups are condensed into a linear chain. However, numerous other types of compounds may be condensed with epichlorohydrin to form basic resins to be used in accordance with the present invention. Included among such reactants are the following compounds: Bis-p-hydroxy biphenyl, p-di-hydroxy benzene, ethylene glycol and higher glycols, bis-p-hydroxy di-benzyl, as well as substituted, particularly chlorinated, derivatives thereof. These resins will vary from viscous liquids to solids with very high melting points.

These epoxy resins are perhaps better known as ethoxylene resins and are characterized in the uncured form by substantially reactive oxide groups at the end of the aliphatic-aromatic chains. Various specific examples of known types of these resins are listed in Letters Patent Nos. 2,324,483 and 2,444,333. Other descriptions of this class of resins may be found in contemporary literature, as for example, "British Plastics" for November, 1948, at pp. 521, 527 and "Electrical Manufacturing" for July, 1949, at pp. 78 through 81 inclusive, 164 and 166.

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Where a solvent is desired, the resins can be dissolved in butyl carbitol and other ether alcohols; in methyl ethyl ketone and other ketones; in Cellosolve acetate and other esters, etc. Preferred among these solvents are those with a boiling point above about 175° C. at atmospheric pressure in those cases where the ink is to be used in a screening operation. For painting or spraying it is possible to use lower boiling solvents. The type of cross-linking which is employed in accordance with the present invention is preferably an amine type and where possible a polyfunctional amine as represented by the formula $R(NH_2)_x$ where the integer x is from 2 to 5 is employed; a preferred amine cross linking agent is hexamethylene diamine. Piperidine is also a useful cross-linking agent but is used only in those limited cases where short pot life at room temperature can be tolerated. Much preferred, however, are those cross-linking agents for the final curing and cross-linking of the resin which are completely unreactive at temperatures less than 75° C. and where possible are solids which do not dissolve in the resin mix until the temperature of at least 100° C. is reached. Thus they may be present as finely divided particles suspended in the resistor ink. A preferred cross-linking agent in this category is dicyandiamide, sometimes known as param.

It is also possible to employ organic alcohols and acids to effect the modification through the reaction of the available hydrogen from these compounds. Typical alcohols are butane-diol and decamethylene glycol while suitable acids include terephthalic acid and sebacic acid.

In cases where the epoxy end group reacts to give a cross-linked resin simply by catalytic effect of the agent notably piperidine, small amounts of agent give good results. To improve the stability for processing as well as to modify the preferred resin it is preferred to treat the resin with a material e. g. di-isocyanate, which will react with the hydroxy group resulting from cross-linking and result in a final product possessing reduced solubility and/or humidity sensitivity.

It is also possible to modify the epoxy resin, prior to incorporation thereof, into the resistor ink formulation. One type of modification involves an esterification in which the hydroxy groups between the end chains of the epoxy resin molecule are reacted with a suitable acidic material. The reaction may be accomplished by heating at fairly high temperatures, for example 500° F. Among the fatty acids which may be used with good results are stearic acid, linoleic acid, and also oleic acid.

In addition it is to be understood that inks made from the epoxy resins may be printed with or without chemical reaction with such resins as the oxidizing alkyd types, the non-oxidizing alkyds, the styrene alkyds and the long alkyds; the phenolic resins, the urea resins, the sulfone resins, etc.

One of the preferred ink compositions of the invention comprises an epoxy resin admixed with a butylated urea formaldehyde resin which may subsequently be reacted by thermal treatment with or without a catalyst. The stability of such prints at room temperature is very good.

The following examples of preparation of resistor inks in accordance with the present invention will illustrate various combinations which give outstanding results.

The general method of preparation of resistor links is hereafter set forth:

1. The epoxy resin is dissolved with heating in a high boiling solvent as butyl Carbitol, butyl Carbitol acetate, butyl Cellosolve or others previously listed, e. g. 85-90° C. with butyl Carbitol acetate.

2. If the cross-linking agent is of the resinous type such as butylated urea formaldehyde or of the type which is inert until heated to accelerated temperatures, it is added to the epoxy resin-solvent mixture, which has been cooled to room temperature.

3. A quantity of a conducting material such as carbon black and/or graphite, silver flake, copper flake, nickel

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flake, iron carbonyl, ferrites, and other conducting and semi-conducting compounds is added to the combined resin-solvent mixture in order to obtain the desired resistance value.

4. In the case of resistance values above 1×10^4 ohms per square, a quantity of an inert filler such as talc, silica, alumina or zirconia may be added.

5. The various ingredients are then mixed by hand and/or mechanical stirring until the dry materials are thoroughly wet. The addition of small quantities of a non-ionic wetting agent, e. g. Sharples non-ionic #2543, may be used.

6. A quantity of a low boiling solvent such as acetone or methyl ethyl ketone is added to obtain the desired viscosity of the ink, and the entire mixture is placed in a porcelain ball mill jar with an appropriate quantity of porcelain, flint or steel balls.

7. The ink is then milled for a period of time of from 1 to 10 days, with the temperature preferably maintained at $25^\circ C. \pm 5^\circ$ where a cross linking agent inert until heated to elevated temperature is used.

8. In some cases sufficient mixing may be accomplished by mechanical stirring or the use of a conventional paint mill either with or without the addition of the low boiling solvent of step 6.

9. The ink is then removed from the ball mill jar and separated from the balls by any practical means.

10. The ink is then vacuum distilled at a low temperature to remove the low boiling solvent, and if necessary quantities of the high boiling solvent are added to obtain the desired viscosity.

11. The ink is then considered ready for use.

12. By blending various quantities of inks containing different amounts of conducting materials, inks possessing resistance value between the resistance values of the blending inks may be made.

13. If the cross-linking agent is other than the resinous or inert types, it is added to the ink immediately before the screening operation.

Some typical formulations with various characteristics of the resulting inks follow:

Example I

To an ink of the following composition sufficient solvent, butyl carbitol acetate, was added

	Percent
Epoxy-butylated urea formaldehyde resin solids	79
Lamp black (Wirt's calcined)	21

to achieve the desired viscosity of about 35,000 centipoises. The weight ratio of epoxy resin solids to butylated urea formaldehyde resin solids was 4 to 1. The screened resistance units were cured for ninety minutes at 250° C.

Experimentally determined characteristics of this ink are:

Per JAN Specs. R-11:	
Resistance ¹ value	7.41×10^3 ohms/sq.
Voltage coefficient ¹	0.0192%/volt.
Temperature characteristic ¹	
at 65° C.	+2.76%.
at 105° C.	+2.2%.
Noise ¹	Less than 1 micro volt/volt.

After screening to end of process:

Process change ²	0%.
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¹ = per JAN Specification R-11.

² = resistance value changes between initial screened and cured resistor and final processed element.

Example II

To an ink of the following composition sufficient solvent, butyl carbitol acetate, was added

	Percent
Epoxy-butylated urea formaldehyde resin solids	80
Lamp black (Wirt's calcined)	8.56
Inert filler (talc)	11.44

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to achieve the desired viscosity of about 35,000 centipoises. The weight ratio of epoxy resin solids to butylated urea formaldehyde resin solids was 4 to 1. Curing was at 250° C. for ninety minutes.

Experimentally determined characteristics of this ink are:

Resistance value ¹ -----	5.2×10 ⁵ ohms/sq.
Voltage coefficient ¹ -----	+0.0036%/volt.
Temperature characteristic ¹ :	
at 65° C-----	+2.53%.
at 105° C-----	+10.75%.
Noise ¹ -----	1.85 micro volts/volt.
Process change ² -----	+12.2%

¹ = per JAN Specification R-11.

² = resistance value changes between initial screened and cured resistor and final processed element.

Example III

The ink was of the following composition:

	Percent
Epoxy-butylated urea formaldehyde resin solids-----	38.85
High boiling solvent (butyl carbitol acetate)-----	27.2
Low boiling solvent (methyl ethyl ketone)-----	19.15
Lamp black (Wirt's calcined)-----	5.03
Inert filler (talc)-----	4.90
Non-ionic wetting agent (Sharples non-ionic #2543)-----	0.10
Low temperature cross-linking agent (diethylene triamine)-----	4.77

The low boiling solvent was removed by low temperature distillation, vacuum distillation at 40-45° C. at 10⁻⁴ cm. mercury pressure, and the low temperature cross-linking agent was not added until immediately before screening. Curing was at 150° C. for ninety minutes.

Experimentally determined characteristics are:

Resistance value ¹ -----	3.59×10 ⁴ .
Voltage coefficient ¹ -----	+0.0521%/volt.
Temperature characteristics ¹ at	
110° C-----	+5.66%.
Noise ¹ -----	0.194 micro volt/volt.

¹ = per JAN Specification R-11.

The next three examples were catalyzed just prior to screening the resistor ink upon a non-conducting ceramic base by admixture of the catalyst. Curing was at 250° C. for ninety minutes.

Example IV

Ink composition:

	Percent
Epoxy-butylated urea formaldehyde resin solids-----	78.4
Lamp black (Wirt's calcined)-----	19.6
Diethylene triamine-----	2.0

Electrical characteristics:

Process change-----	+12.5%.
Noise-----	Less than 1 micro volt/volt.
Voltage coefficient-----	.029%/volt.

Example V

Ink composition:

	Percent
Epoxy-butylated urea formaldehyde resin solids-----	78.4
Lamp black (Wirt's calcined)-----	19.6
Piperidine-----	2.0

Electrical characteristics:

Process change-----	+15.7%.
Noise-----	Less than 1 micro volt/volt.
Voltage coefficient-----	.021%/volt.

Example VI

Ink composition:

	Percent
Epoxy-butylated urea formaldehyde resin solids-----	78.4
Lamp black (Wirt's calcined)-----	19.6
Dicyandiamide-----	2.0

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Electrical characteristics:

Process change-----	14.3%.
Noise-----	1.88 micro volts/volt.
Voltage coefficient-----	.018%/volt.

A resistor ink of the present invention was compared in aging characteristics with a prior art type ink using phenol-formaldehyde resin as the binder. A is the epoxy-butylated urea formaldehyde resin type while B is the ink using phenol-formaldehyde.

The compositions are:

	A ¹	B ²
15 Epoxy-butylated urea formaldehyde-----	75.5	75.5
Phenol-formaldehyde-----		14.0
Lamp Black (Wirt's calcined)-----	14.0	14.0
Inert filler (whiting)-----	10.5	10.5

The aging tests were started immediately after the final processing step, wax impregnation, by maintaining them within the temperature range of 25±5.0° C.

Results:

Days of Aging	Percent Change In Resistance	
	A ¹	B ²
1-----	0.66	2.10
2-----	1.11	2.85
3-----	1.33	
4-----		4.44
5-----	1.33	4.47
6-----	1.51	5.20
7-----	1.51	5.45
8-----	1.51	
9-----	1.51	
20-----	1.51	6.53
30-----	1.51	7.71
40-----	1.51	11.50
50-----	1.33	15.85

A¹—cured for 90 minutes at 250° C.

B²—cured for 120 minutes at 157° C.

According to one of the limited embodiments of this invention the epoxy resin is modified by treatment with organic isocyanate, preferably a polyfunctional isocyanate. Through such treatment with the latter an extremely tough, cross-linked resin can be obtained, possessing unique thermal stability and other desirable properties; suitable compounds are: hexamethylene diisocyanate and tolylene di-isocyanate-2,4.

The above discussion has been directed towards the use of a relatively solid non-porous base for deposition of the resistor. It has been found that a particularly useful though special form of printed resistor can be obtained by coating a semi-porous and flexible inorganic base with the resistor inks of this invention and by attachment of this flexible base to a fixed base in any desired position and in any desired configuration. Base materials which have been found particularly suitable for this form of the present invention are paper made with fine glass fiber, asbestos fiber paper and glass cloth. The latter has been found particularly satisfactory when thicknesses in the order of 2 to 5 mils are employed. The ink is applied to one side of the flexible cloth and allowed to dry to remove the low boiling solvent, leaving a tacky resinous surface. The cloth thus treated can be then applied to a base or stored by rolling up with polyethylene or polytetrafluoroethylene films. After application of the tacky surface of the coated flexible base against the fixed base and the final removal of the solvent if any be present the curing of the resin is conducted. The exposed and uncoated surface of the flexible base may be treated with resin, preferably the same resin as that employed as the binder in the resistor ink, to protect the resistor from atmospheric conditions.

It is also possible to employ semi-porous or non-porous flexible organic bases such as regenerated cellulose, poly-

amides, polyesters, polymers obtained by condensing terephthalic acid with ethylene glycol, and polyacrylonitrile. These may be rolled up or laminated to other layers after application and processing of the resistance layer and its terminals.

Generally speaking, the printed resistors and printed circuits employing such resistors, should be provided with a protective insulating housing; generally this takes the form of what is known as a cover coat. For optimum results it has been found that the cover coat should consist of a resin of the type described herein as an ink binder resin. In such instances, of course, a non-conducting filler would be employed. The particular particle size and concentration of the filler may be selected so as to modify the thermal expansion characteristics of the cover coat and to permit impregnation of the cover coat with a wax or other hydrocarbon moisture barrier after removal of the solvent and curing of the resin.

In accordance with another limited embodiment of the present invention the resistor ink binder has no cross-linking agent in the ink formulation. After laying down of the resistor and removal of the solvent, if any be present, the screened or printed resistor is dipped in a solution of the cross-linking agent or preferably treated with its vapors (for this purpose ammonia or organic amine is particularly suitable) in order to accelerate the curing of the resin. In this way, it is possible to produce resistor inks with indefinite shelf life yet which possess rapid curing characteristics when subsequently processed by the simple and inexpensive procedure of treatment with the cross-linking agent. Preferably this treatment is conducted in the oven used for curing the resin; hence no additional equipment is required. In accordance with another embodiment of the present invention the resistor ink composition includes a protective wax or resin which will bleed out of the resin during the curing operation and protect the surface of the latter from the effects of humidity and other adverse conditions. This is accomplished through the reduced solubility of the resin following cure of the said resin to a higher molecular state.

As many apparently widely different embodiments of this invention may be made without departing from the

spirit and scope hereof, it is to be understood that the invention is not limited to the specific embodiments hereof except as defined in the appended claims.

What is claimed is:

1. A printed resistor comprising a ceramic base, an adherent layer of resistance material consisting of from about 50% to about 95% of cross-linked epoxy resin, from about 50% to about 5% of finely divided conducting particles and from about 25% to about 0% of finely divided non-conducting particles deposited upon said base, and terminal contact areas provided at spaced portions of said layer.

2. A printed resistor comprising an insulating base and adherent layer of resistance material consisting of about 50% to about 95% by weight cross-linked epoxy resin, from about 50% to about 5% of finely divided conducting particles and from about 25% to about 0% of finely divided non-conducting particles deposited upon said base and terminal conducting areas provided at spaced portions of said layer.

3. The printed resistor of claim 2 in which the conducting particles are carbon.

4. The printed resistor of claim 2 in which the conducting particles are silver.

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