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ELECTRICAL RESISTOR COMPOSITIONS, ELEMENTS AND METHOD OF MAKING SAME

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ABSTRACT OF THE DISCLOSURE

A resistor composition which is applied to a ceramic substrate by silk screening and subsequently fired. The composition comprises a non-polar linear resin from the group of polystyrene, polyalphamethylstyrene and polyterpene, the resin having an average molecular weight in the range of 500 to 7000. The resin is dissolved in a non-polar hydrocarbon solvent having a boiling range of from 450° F. to 588° F. The solvent has a vapor pressure of less than 0.01 mm. of mercury at room temperature and a vapor pressure of from 10 to 20 mm. of mercury at 212° F.

This invention relates to electrical resistance compositions, vehicles for such compositions, resistance elements, and method of making same. More particularly, this invention relates to non-polar resistor compositions and vehicles therefor which make possible the production of resistor elements within close size and resistive value tolerances, and to methods of forming resistor elements particularly adapted to mass production techniques.

In modern electrical apparatus, particularly computer apparatus and the like, there is an ever increasing use of microelectronic circuit techniques. Typical of such recent technique developments is the microminiaturized circuit module. The circuit module is typically a one half inch square of ceramic, a fraction of an inch in thickness, having functional components mounted thereon which are electrically connected with printed wiring. The functional components are active and passive electric circuit elements capable of performing useful functions or operations. Passive devices, such as resistors, are normally applied to the substrate by printing techniques and subsequently fired to solidify the resistance composition by driving out and burning the vehicle, and fusing the resistor. These techniques, though simple in principle, are in practice fraught with many difficulties. Normally, the resistor compositions are applied to the substrate through a silk screen overlying the substrate, in which all but the resistor areas are covered with a blanking polyvinyl emulsion. A suitable resistor composition or paste is applied over the silk screen which penetrates the screen through the unblanked portions to form the shape of the resistor. The resistor is then fired and may be subsequently trimmed to obtain the desired resistor value. The trimming operation is a relatively exacting one which adds considerable expense to the operation of a production line turning out circuit modules. The trimming operation becomes more exacting as the sizes of the resistors become smaller. While it would be desirable initially to form the resistor on the substrate in a manner adapted to obtain resistance values within the desired tolerances, present

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resistor compositions and techniques employed in the art do not make this possible.

There are a number of reasons why resistor compositions and techniques for applying same known to the prior art make the attainment of the aforementioned objective impossible as a practical matter. The present resistor compositions are, in general, composed of components that are polar in nature. The polar molecules of the known resistor compositions have the effect of deteriorating or weakening the polyvinyl emulsions used on silk screen masks which make their replacement at periodic intervals necessary. Further, the openings in the silk screen masks for forming the resistors vary over a period of time because of the corroding effect. This change of size affects the resistance of the finished resistor placing it outside the tolerances desired and making a trimming operation necessary.

Resistor compositions known to the prior art contain a solvent and other components which evaporate to an appreciable extent at room temperature. Evaporation of such components changes the viscosity of the composition which in turn affects the uniformity of application through the silk screen mask. In general, in production line techniques, the resistor composition is exposed to the atmosphere while the line is in operation. The thicknesses of the resultant resistor elements may therefore vary, which cause correspondency in variations in electrical resistance.

In resistor compositions known to the prior art, the relatively small variations in the mode of firing same frequency have the effect of materially changing the resistor value. For example, when a resistor composition applied to a substrate is fired at a slightly higher temperature, the electrical resistance of the resistor element may be higher or lower than if it were fired at a somewhat lower temperature. The length of time that resistors are fired also has an effect on the electrical resistances of the resistors. As a practical consequence, the resistor elements produced from known resistor compositions, will vary in electrical resistance, since there is normally an inevitable fluctuation of temperature in a firing apparatus.

Often there may also be a variation in the time that the resistor element is warmed up, cooled off, and/or exposed in the firing apparatus or oven. This factor may also necessitate trimming of the resistors.

An object of this invention is to provide new compositions for producing printed electrical components.

Another object of this invention is to provide new resistor compositions which will not deteriorate or corrode silk screen apparatus.

Yet another object of this invention is to provide new resistor compositions which are non-polar in nature.

Another object of this invention is to provide resistor compositions having a long shelf and pot life.

Another object of this invention is to provide new resistor compositions provided with a vehicle having a low vapor pressure at room temperatures.

Still another object of this invention is to provide a new resistor composition which will not appreciably deteriorate or change physical flow characteristics when exposed to the atmosphere at room temperature.

Still another object of this invention is to provide new resistor compositions in which the variation of electrical resistance of resistors produced therefrom due to firing fluctuations will be minimized.

An object of this invention is to provide new resistor compositions in which the variation of the temperature coefficient of resistance of resistors produced therefrom due to firing fluctuations is minimized.

Another object of this invention is to provide resistance compositions having superior flow control characteristics.

Yet another object of this invention is to provide new resistor compositions which make possible the consistent production of resistors by coating or silk screening techniques to values within very close tolerances.

Still another object of this invention is to provide new resistor compositions which can be used to produce printed resistor elements which do not require trimming operations.

Another object of this invention is to provide a new method of producing resistor elements in which resistor compositions are utilized which have a long shelf and pot life and which do not deteriorate the emulsion normally used on silk screen masks.

Another object of this invention is to provide a new method of producing resistor elements which makes possible the consistent producing of resistors within very close tolerances.

These and other objects of the invention will become more apparent in the detailed description and examples which follow.

We have invented new resistor compositions and vehicles for such compositions which overcome many of the problems prevalent to resistor compositions and vehicles therefore known to the prior art. The resistor composition of our invention, which is adapted to be applied to and fired on a suitable substrate, has 50-83% by weight of a finely divided electrically conductive pigment combined with 17-50% by weight of a vehicle. The vehicle has 20-80% by weight of a non-polar hydrocarbon solvent. Also included in the vehicle is 20-80% by weight of a non-polar polymer resin soluble in the solvent and having an average molecular weight in the range of 500-7000. The resin can be a polystyrene resin, a polyterpene resin, a poly alpha methylstyrene resin, or the like, or mixtures thereof.

The new method of making an electrical resistor of our invention includes the steps of forming a resistor composition consisting essentially of 50-83% by weight of an electrically conductive pigment and 17-50% by weight of a non-polar vehicle. The vehicle has 20-80% by weight of a non-polar hydrocarbon solvent, and 20-80% by weight of a non-polar polymer resin soluble in the solvent and having an average molecular weight in the range of 500-7000. The resistor composition is then applied to the substrate by screening techniques. The substrate with the mixture thereon is then heated to a temperature sufficient to fire same.

The new resistor compositions of our invention solve many of the present problems prevalent in the printing of resistors and the like. The new resistor compositions of our invention are non-polar and will not in use weaken or deteriorate the emulsion normally used to blank off portions of silk screens. Consequently, silk screens used in printing resistors and the like on the substrate or other circuit backing will have a much longer useful life. The patterns in the silk screen will remain distinct thereby making possible consistent printing of resistors and the like to within very close tolerances.

The vehicle in the resistor compositions of our invention employs solvents having a low vapor pressure at room temperature, but yet have a relatively high vapor pressure at elevated temperatures. The employment of such solvents in the vehicle produces resistor compositions which are very stable at room temperature. While the composition is being applied, normally in a production line, it is usually exposed to the atmosphere and therefore subject to evaporation of the vehicle. Evaporation of even a small amount of the solvent of the vehicle of a resistance composition will cause a significant change in its viscosity. A

change in viscosity is quite objectionable because it presents a factor which inevitably effects the accurate and consistent reproduction of resistors or like elements. A change in viscosity can cause a variation in the thickness of the layer of resistor composition if the application techniques are not varied to accommodate the change. If the viscosity of a composition can be depended upon to remain the same during use, as in the compositions of the present invention, the most desirable viscosity can be determined and this viscosity maintained. This is an important aspect of the present invention since it makes possible a more accurate printing of resistors to within close tolerances and better control over the flow characteristics than is possible with resistor compositions known to the prior art. In our resistor compositions, the solvent provided in same has a relatively high vapor pressure at elevated temperatures. This insures a rapid and dependable vaporization of the solvent prior to and during the firing of the resistor.

In the new resistor compositions of our invention, we have found that it is possible to control the resistor properties by the type and amount of resin in the vehicle. In specific preferred embodiments of our composition it is possible to minimize the variation of resistance values of printed resistors that normally occur when the firing temperatures and times fluctuate. This characteristic in a resistor composition makes possible the production of resistors within close tolerances.

The new resistor compositions of our invention represent a significant advance in the resistor screening technique. The resistor compositions of our invention, since they have a very low volatility at room temperature, are therefore stable at room temperature and have a long pot life. The new resistor compositions are also non-polar in nature and therefore do not attack the screen emulsion on the silk screens normally used to produce the resistors. Still further, the resistor compositions of our invention minimize the resistance change that normally results from firing fluctuations. The end result is a very improved resistor composition which makes possible production of resistors to within very close tolerances.

The new method of producing resistor elements of our invention solves many of the problems inherent to methods of producing resistors known to the prior art. In the new method a new resistor composition is utilized which is non-polar in nature, therefore not deleterious to silk screen emulsions, and is stable at room temperature. The new method of our invention makes possible the production of resistor elements to within very close tolerances.

The new resistor composition of our invention is a combination of an electrically conductive pigment and a non-polar vehicle. The composition can be applied to a suitable backing element or substrate by conventional printing techniques, normally silk screen printing. More specifically, a silk screen mask having portions where no printing is desired blanked off with a polyvinyl emulsion is placed in overlying relation to the substrate. The composition is then applied over the mask with a suitable applicator, such as a rubber squeegee. The mask is subsequently removed and the resultant printed resistor allowed to dry. The physical dimensions of the resistor are dictated by the desired resistance values of the resistor and are controlled by the resistor paste rheology, screen mesh, emulsion thickness, and screening technique. The resistor, normally mounted on a ceramic substrate, is then fired in a furnace for a suitable time interval at a temperature in the range of 700° C. to 1000° C.

In our new resistor compositions, any suitable electrically conductive pigment can be used. A preferred pigment for use in our composition is one that includes a metal, and/or oxide, glass frit, colloidal silicon dioxide, and dopant ions. The most common of such metals and metal oxides currently in use in resistor compositions are silver, indium, antimony, chromium, palladium, copper, and mixtures thereof. A preferred pigment for use in the

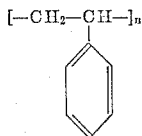
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practice of our invention has 30-50% by weight of a finely divided noble metal or metal oxide, or mixtures thereof, 50-70% by weight of finely divided glass frit, and 0-5% by weight of silicon dioxide. The component materials of the pigment are ground to a very small particle size, preferably in the range of 1-50 microns. In our composition the pigment will constitute 50-83% by weight, more preferably 70-80% by weight of the composition.

The pigment is combined with a non-polar vehicle which has a dielectric constant less than 3. The vehicle is essentially composed of a non-polar solvent and a resin. Preferably, a surface active additive, commonly referred to as a surfactant, is also included as a component in the vehicle of the composition of our invention. In general, the surfactant is used to wet the pigment particles to give good dispersion, reduce settling, and promote screenability. The vehicles will constitute 17-50%, more preferably 20-30% by weight of the weight of our resistor compositions.

The resin component of the vehicle in combination with a solvent gives the resistor composition the desired flow characteristics, that is, it is an agent that exerts a very large degree of control on the viscosity. The composition must be fluid enough to allow the employment of silk screening techniques, but must be sufficiently firm after being printed or transferred to the substrate to maintain the desired physical dimensions. Obviously, a composition that flows excessively will not normally produce printed resistors of consistent sizes and values. Quite frequently a viscosity reading on a viscosimeter will not give an accurate and true indication of flow characteristics of a printing composition. A non-newtonian composition, which is the nature of such a dispersion having a high viscosity reading, as measured on a viscosimeter where the molecules are subjected to a relatively high sheer velocity, may exhibit an excessive amount of slow flow at low shear rates. This indicates that dynamic and static viscosities are not synonymous. Further, it is desirable that the viscosity of the printing composition remain relatively constant over a broad range of temperatures. The resistor compositions of the invention which utilize the novel combination of components in our vehicle exhibit very consistent and desirable flow properties over broad temperature ranges.

The vehicle of our invention contains 20-80%, more preferably 30-50% by weight of a non-polar linear polymer resin. The resin has an average molecular weight in the range of 500-7000, more preferably 800-1500. A preferred resin is linear polystyrene having the molecular configuration



This resin is sold under the trademark Piccolastic by Pennsylvania Industrial Chemical Corporation, 120 State St., Clairton, Pa. The resin is available in a large number of varying compositions differing from each mainly in average molecular weight. A very useful grade of Piccolastic polystyrene resin is D-100 having the following characteristics:

Melting point, ball and ring OC	100
Color, Gardner	3-6
Estimated molecular weight	1500
Specific gravity	1.06
Pounds per gallon	9.3
Acid number, less than	1.0
Saponification number, less than	1.0

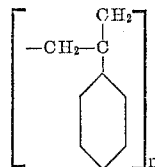
The polystyrene resin is also available in a grade that is very useful in the composition which is indicated by D-150 having the following physical characteristics:

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Melting point, ball and ring OC	150
Estimated molecular weight	5000
Specific gravity	1.06
Pounds per gallon	9.2
Acid number, less than	1.0
Saponification number, less than	1.0

These resins and others are amply described in a technical pamphlet entitled "Piccolastic Versatile Low Molecular Weight Styrene Resins," PPN-102.

Another suitable linear polymer resin for use in the resistor compositions of our invention is poly alpha methylstyrene having the molecular configuration



A typical resin of this type is sold under the trademark Amoco Resin 18 by Amoco Chemical Corporation, 130 E. Randolph Drive, Chicago 1, Ill. The resin is available in varying grades differing mainly from each other in average molecular weight. A preferred grade of Amoco Resin 18 is identified by the number 18-240 having the following properties:

Softening point, ring and ball, degrees F.	240
Acid number	Nil
Saponification number	Nil
Specific gravity, 60/60° F.	1.07
Molecular weight	850

Another grade of Amoco Resin 18 useful in the practice of the invention is identified by the number 18-290 having the following properties:

Softening point, ring and ball, degrees F.	290
Acid number	Nil
Saponification number	Nil
Specific gravity, 60/60° F.	1.07
Molecular weight	1100

The various linear alpha methylstyrene polymers marketed under the trademark AMOCO Resin 18 are described in Bulletin R3a, published February 1963 by Amoco Chemicals Corporation, 130 E. Randolph Drive, Chicago 1, Ill.

Another preferred linear non-polar polymer resin is a polyterpene resin composed essentially of polymers of pinenes, predominately beta pinene (nopinene). A resin of this type is commercially available and sold under the trademark Piccolyte by Pennsylvania Industrial Chemical Corporation, Clairton, Pa. which is a polymer of beta pinene. The polyterpene resin is available in a number of different grades, which grades are described in the technical pamphlet entitled "Piccolyte, the Versatile Resin," copyright 1948 Pennsylvania Industrial Chemical Corporation.

The resins of the aforementioned type are combined with a solvent capable of dissolving them. The molecular weight of the thermoplastic polymer resins can be utilized to control the rheological properties of the resistor pastes. The lower molecular weights can be used to produce resistor compositions having controlled flow characteristics of a lower viscosity. Poly alpha methylstyrene is particularly desirable as a resin because it volatilizes or burns out very rapidly during the firing of the printed resistor and leaves very little or no ash. In general, the resin selected for the vehicle should be completely free of active functional groups, such as carboxyls, nitrate, halogens, sulfur or nitrogen-containing groups, etc. which would render the molecules more polar and thus having a deteriorating effect on the emulsion on silk screen masks, as well as creating corrosive or toxic vapors during the firing process.

The solvent in the vehicle of our compositions is a non-polar organic solvent having a relatively low vapor

pressure at room temperatures, preferably less than 0.01 mm. of mercury, most preferably in the range of 0.001–0.01 mm. of mercury. At elevated temperatures, the vapor pressure should be relatively high to insure rapid vaporization during the drying and firing phase of the resistors. Preferably the vapor pressure should be in range of 10–20 mm. of mercury at 212° F. The solvent will constitute from 20–80%, more preferably 50–70% by weight of the vehicle.

Typical examples of non-polar solvents for use in the vehicle are ethyl naphthalene, phenylcyclohexane, highly aliphatic hydrocarbon mixtures, aromatic naphthenic hydrocarbon mixtures and mixtures thereof. A preferred aromatic naphthenic hydrocarbon mixture for use in the practice of the invention is sold under the trademark AMSCO-SOLV H-CC (E-1). This hydrocarbon solvent is a distillation cut from crude petroleum having the following properties:

	Distillation, Percent	° F.
	IBP	450
	5	470
Specific Gravity at 60° F., .9285.....	10	477
	20	483
Kauri-Butanol No. (cc.), 73.....	30	487
	40	492
Aromatics (percent), 65.....	50	498
	60	505
Boiling point range, 450°–588° F.....	70	514
	80	522
	90	543
	95	558
	*EP	588

*ASTM

Suitable highly aliphatic solvents for use in the practice of the invention are sold under the general designation of ink oils. A preferred ink oil is sold under the trade name of AMSCO ink oil 10–500. This solvent is a paraffinic distillation cut from crude petroleum having the following properties:

	Distillation, Percent	° F.
	IBP	474
	5	484
Specific Gravity at 60° F., .8174.....	10	486
	20	383
Viscosity at 100° F. (SU), 35.4.....	30	400
	40	451
Aniline Point (°C.), 76.4.....	50	493
	60	494
Kauri-Butanol No. (cc.), 28.1.....	70	495
	80	499
Aromatics and Unsaturates (percent), 17.....	90	563
	95	586
	EP	523

Suitable surface activators or surfactants that can be included in the vehicle of our invention to wet the pigment particles to thereby obtain good dispersion, reduce settling and promote screenability are nonionic derivatives of ethylene glycol, alkylaryl sulfonate, fatty acid esters, polyoxyethylene, and the like. A preferred surfactant is nonyl phenoxy polyoxyethylene ethanol.

In the new method for producing a resistance element on a substrate there is formed a resistor composition by mixing an electrical conductive pigment with a non-polar vehicle. The vehicle will include 20–80%, more preferably 50–70%, by weight of a non-polar hydrocarbon solvent having a vapor pressure less than 0.01 mm. of mercury at room temperature, and a vapor pressure of from 10–20% of mercury at 212° F. The solvents suitable for use in the resistor composition have been described previously. Included also in the vehicle is 20–80%, more preferably 30–50%, by weight of a non-polar linear polymer resin of the type that has been discussed previously. The resin will have an average molecular weight in the range of 500–7000, more preferably 800–1500 and be soluble in the solvent. The resistor composition is applied to the substrate by any suitable printing technique,

such as silk screening and the like. The print may be dried at 70–300° C. for 15–45 minutes to drive off the solvent. The resultant printed resistor is then fired at a temperature between 700–1000° C. for a time interval in the range of 2 minutes to 100 minutes. The element is subsequently cooled to room temperature.

The following examples are included merely to aid in the understanding of the invention, and variations may be made by one skilled in the art without departing from the spirit and scope of the invention.

Example 1

An electrically conductive pigment dry-mix was prepared from the following finely divided materials:

	Percent by weight
Palladium oxide	22.3
Silver	17.8
Glass	56.4
SiO ₂	3

The above dry powders were thoroughly mixed by shaking in a closed container in a paint mixing apparatus for one hour.

Three different vehicles were prepared from the following:

#1

	Parts by weight
Aromatic solvent (Amsco H-CC)	57
Polystyrene resin (Piccolastic D-100)	37
Surfactant (nonyl phenoxy polyoxyethylene ethanol) ..	6

#2

Aromatic solvent (Amsco H-CC)	57
Poly alpha methylstyrene (Amoco 18–290)	37
Surfactant (nonyl phenoxy polyoxyethylene ethanol) ..	6

#3

Aromatic solvent (Amsco H-CC)	57
Poly alpha methylstyrene (Amoco 18–240)	37
Surfactant (nonyl phenoxy polyoxyethylene ethanol) ..	6

Three separate resistor paste compositions were prepared using the No. 1, No. 2 and No. 3 vehicles in combination with the aforescribed pigment dry mix. In each instance, the resistor compositions were composed of 80% by weight of the pigment and 20% by weight of each of the respective vehicles. The mixed dry powders and vehicle of each composition were mixed and dispersed on a three roll mill set at a medium tight setting and subjected to ten passes through the rollers. The aforescribed resistance compositions were thoroughly tested and found to have no deleterious effect on the polyvinyl emulsion used to blank out portions of silk screen apparatus, and a very long shelf life, that is the physical properties and characteristics of the respective resins did not change appreciably when exposed to the atmosphere at room temperature. It was also noted the flow characteristics of the compositions were very good and that the compositions could be used to reproduce printed resistor elements within close dimensional and resistive tolerances.

Examples 2–4

Five resistors were produced on individual substrates from each of the resistor paste compositions described in Example 1. The resistors were tested to determine the effects on the resistance values caused by using different firing cycles. In the table in the column heading under firing cycles, the first number indicates the time in minutes that was used to heat the resistors from room temperature to the full heat of the firing furnace. The second or center number in the column headings indicates the time in minutes that the resistors were subjected to the full heat of the firing furnace. The third or last number in each column heading indicates the time in minutes that was used to gradually remove the fired resistors from

the furnace to an environment at room temperature. The temperature within the furnace was $755^{\circ} \pm 5^{\circ}$ C.

occur in production, will have a less effect than when using known resistor compositions.

PERCENT VARIANCE OF RESISTANCE VALUES

Composition	Firing Cycles				
	15.0-13-15.0	17.5-13-17.5	21.0-13-21.0	25.4-13-25.4	29.0-13-29.0
No. 1-----	50.3	74.2	89.3	100.0	108.4
No. 2-----	84.4	85.7	99.4	100.0	105.2
No. 3-----	83.5	86.6	93.3	100.0	104.6

In the above example, the resistances of the respective resistors cured by the firing cycle 25.4-13-25.4 were used as the standards and the remaining resistance values of the resistors of each of the respective group calculated as a percent thereof for comparison. In comparing the relative percent resistance changes in composition No. 1 containing vehicle No. 1, between the first and the fifth firing cycle there was a resistance change of approximately 59% in the resistance values of the respective resistors. In compositions No. 2 and No. 3 the resistance percent values of the resistors were not as greatly affected by the varying firing conditions. This ample demonstrates the stabilizing effect, in regard to variance of firing conditions, that is obtained by using poly alpha methyl resin in the vehicle.

Examples 5-8

A comparison of variances, with firing cycles, of temperature coefficients of resistance of typical resin compositions of the invention, and a commercially available resistor composition was made. The commercial paste was composed of a pigment of the following:

	Percent by weight
Silver -----	13.8-15.3
Palladium -----	10.7-13.2
Lead-borosilicate glass -----	36.8-43.5

The pigment constituted 65 to 68 percent by weight of the composition. The vehicle contained 10 to 15 percent ethyl cellulose in mixed alpha and beta terpeneol solvent. The resistance compositions, number 1 and number 3, prepared in Examples 2 through 4, were compared with a popular commercial resistor competition. The results are as follows:

TEMPERATURE COEFFICIENT OF RESISTANCE
[Over range 25° to 100° C.]

Paste Composition	Firing Cycles			
	15.0-13-15.0	18.5-13-18.5	25.5-13-25.5	29.0-13-29.0
Commercial paste-----	4.5	4.0	3.7	3.6
No. 1-----	-0.2	-0.4	-0.5	-0.8
No. 3-----	-1.2	-1.2	-1.4	-1.4

In the above table the firing cycle numeral arrangement at the top of each column has the same significance as described in Examples 2 through 4. In each instance, three resistors from each sample for each of the firing cycles were produced, fired, temperature coefficient of resistance measured, and the average temperature coefficient of resistance of each set of three resistors entered in the above table.

As the results indicate, the differences in the firing cycles caused considerably less variation in the temperature coefficient of resistances of the resistor compositions Nos. 1 and 3 of the invention than with the commercial resistor composition. In the comparison the total variance of the temperature coefficient of resistance in the commercial resistor composition was 0.9, whereas the variance in composition No. 1 was 0.6 and in composition No. 3 only 0.2.

When using the resistor compositions of the invention, it is therefore possible to maintain the electrical properties, namely electrical resistance and temperature coefficient of resistance, of the fired resistors within close standards, since variations of the firing cycle, which inevitably

While the invention has been particularly shown and described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that the foregoing and other changes in form and details can be made therein without departing from the spirit and scope of the invention.

What is claimed is:

1. A resistor composition adapted to be applied to and fired on a suitable substrate to form an electrical resistor film comprising:

70-80% by weight of a finely divided electrically conductive pigment,

said pigment having 30-50% by weight of a finely divided metal and metal oxide selected from the group consisting of silver, palladium, tin, indium, chromium, and mixtures thereof, 50-70% by weight of finely divided glass frit, 0.5% by weight of silicon dioxide, 20-30% by weight of a vehicle,

said vehicle having from 50-70% by weight of a non-polar organic solvent having a vapor pressure in the range of 0.001-0.01 mm. of mercury at room temperature, and a vapor pressure of 10-20 mm. of mercury at 212° F., said solvent selected from a group consisting of ethyl naphthalene, phenylcyclohexane, an aromatic naphthenic hydrocarbon mixture having boiling point range of 450° F. to 588° F., a highly aliphatic hydrocarbon mixture having a boiling point range of 474° to 523° F., and mixtures thereof, 30-50% by weight of a non-polar polymer resin selected from the group consisting of polystyrene, polyalpha methylstyrene, polyterpene, and mixtures thereof, said resin having an average molecular weight in range of 800-1500, and being soluble in said solvent, and 0-10% by weight of a surfactant, said surfactant selected from the group consisting of polyethylene glycol derivatives, and mixtures thereof.

2. A resistor composition adapted to be applied to and fired on a suitable substrate to form an electrical resistor film comprising:

70-80% by weight of a finely divided electrically conductive pigment,

20-30% by weight of a vehicle, said vehicle having from 50-70% by weight of a non-polar solvent having a vapor pressure less than 0.01 mm. of mercury at room temperature, and a vapor pressure of from 10 to 20 mm. of mercury at 212° F., said solvent selected from a group consisting of ethyl naphthalene, phenylcyclohexane, an aromatic naphthenic hydrocarbon mixture having a boiling point range of from 450° F. to 588° F., a highly aliphatic hydrocarbon mixture having a boiling point range of 474° to 525° F., and mixtures thereof, 40-50% by weight of a non-polar linear polymer resin selected from a group consisting of polystyrene, polyalpha methylstyrene, polyterpene, and mixtures thereof, said resin having an average molecular weight in range of 800-1500, and being soluble in said solvent.

3. A resistor composition adapted to be applied to and fired on a suitable substrate comprising:

50-83% by weight of a finely divided electrically conductive pigment,

17-50% by weight of a vehicle, said vehicle having from 20-80% by weight of a non-polar solvent selected from the group consisting of

ethyl naphthalene, phenylcyclohexane, an aromatic naphthenic hydrocarbon mixture having a boiling point range of 450° F. to 588° F., a highly aliphatic hydrocarbon mixture having a boiling point range of from 474° to 525° F., and mixtures thereof, 20-80% by weight of a non-polar linear polymer resin selected from the group consisting of polystyrene, polyalpha methylstyrene, polyterpene, and mixtures thereof, said resin having an average molecular weight in the range of 500-7000, and being soluble in said solvent.

4. A resistor composition adapted to be applied to and fired on a suitable substrate comprising:

50-83% by weight of a finely divided electrically conductive pigment,

17-50% by weight of a vehicle,

said vehicle having from 20-80% by weight of a non-polar hydrocarbon solvent having a vapor pressure less than 0.01 mm. of mercury at room temperature, and a vapor pressure of from 10-20 mm. of mercury at 212° F., said solvent selected from the group consisting of ethyl naphthalene, phenylcyclohexane, an aromatic naphthenic hydrocarbon mixture having a boiling point range of from 450° to 588° F., an aliphatic hydrocarbon mixture having a boiling point range of from 474° to 523° F., and mixtures thereof, 20-80% by weight of a non-polar polymer resin soluble in said solvent and having an average molecular weight in the range of 500-7000, and selected from the group consisting of polystyrene, polyterpene, poly alpha methylstyrene, and mixtures thereof.

5. A resistor composition adapted to be applied to and fired on a suitable substrate comprising:

50-83% by weight of a finely divided electrically conductive pigment,

17-50% by weight of a vehicle,

said vehicle having from 20-80% by weight of a non-polar hydrocarbon solvent,

20-80% by weight of a non-polar polymer resin soluble in said solvent and having an average molecular weight in the range of 500-7000, and selected from the group consisting of polystyrene, polyterpene, poly alpha methylstyrene, and mixtures thereof.

6. A method for producing a resistor element on a substrate comprising:

forming a resistor composition by mixing an electrically conductive pigment with a nonpolar vehicle, said vehicle constituting 20-30% by weight of the composition and including 50-70% by weight of a non-polar hydrocarbon solvent having a vapor pressure of

less than 0.01 mm. of mercury at room temperature and a vapor pressure of 10-20 mm. of mercury at 212° F., said solvent selected from the group consisting of ethyl naphthalene, phenylcyclohexane, an aromatic naphthenic hydrocarbon mixture having a boiling point range of 450° F. to 588° F., a highly aliphatic mixture having a boiling point range of 474° F. to 523° F., and mixtures thereof, 30-50% by weight of a non-polar linear polymer resin selected from the group consisting of polystyrene, poly alpha methylstyrene, polyterpene, and mixtures thereof, said resin having an average molecular weight in the range of 800-1500 and being soluble in said solvent, applying said composition to said substrate, firing said composition on said substrate at a temperature between 700°-1000° C. to form said resistor element, and cooling said element to room temperature.

7. A method of producing a resistor element on a substrate comprising:

forming a resistor composition by mixing an electrically conductive pigment with a non-polar vehicle, said vehicle including 20-80% by weight of a non-polar hydrocarbon solvent, 20-80% by weight of a non-polar polymer resin soluble in said solvent and having an average molecular weight in the range of 500-7000, and selected from the group consisting of polystyrene, polyterpene, poly alpha methylstyrene, and mixtures thereof,

applying said composition to said substrate, firing composition on said substrate, and cooling said element to room temperature.

8. The resistor composition of claim 4 wherein said non-polar polymer resin comprises polyalphanaphthylstyrene.

9. The resistor composition of claim 5 wherein said non-polar polymer resin comprises polyalphanaphthylstyrene.

10. The method of claim 7 wherein said composition is applied to the substrate through a screen stencil.

11. The method of claim 6 wherein said composition is applied to the substrate by silk screening.

References Cited

UNITED STATES PATENTS

2,950,996 8/1960 Place et al. ----- 252-514 XR

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50 J. D. WELSH, *Assistant Examiner*.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

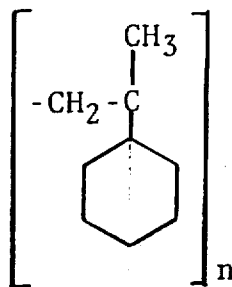
Patent No. 3,390,104

June 25, 1968

Lewis F. Miller et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 31, "fraquency" should read -- frequently --
Column 3, line 12, "compositoins" should read -- compositions --
Column 6, lines 13 to 20, the formula should appear as shown below:



Column 7, first table, third column, line 10 thereof, "522" should read -- 525 --; same column, second table, third column, line 4 thereof, "388" should read -- 488 --. Columns 9 and 10, in the table, sixth column, line 1 thereof, "108.4" should read -- 109.4 --. Column 10, line 63, "40-50%" should read -- 30-50% --. Column 11, line 19, "mecury" should read -- mercury --.

Signed and sealed this 10th day of March 1970.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

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