

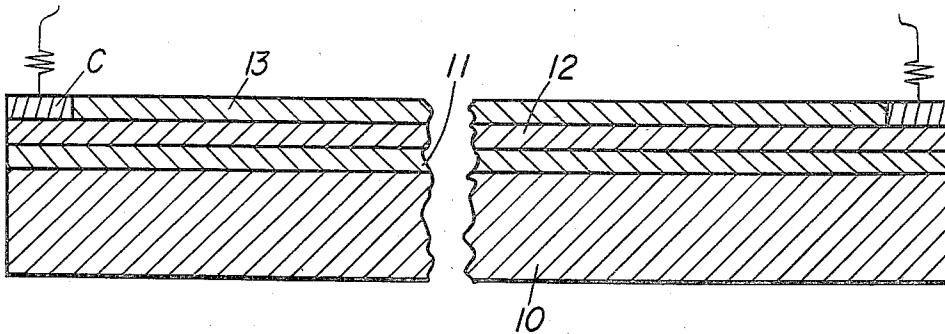
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HEATING ELEMENTS IN FILM FORM

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HEATING ELEMENTS IN FILM FORM

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This invention has to do with improvements in heating elements or heating media, particularly of the film type comprising finely divided particles together having appropriate electrical conductive and resistive properties, held together in a binder having initially a fluid form permitting dispersion of the contained particles, and finally a solid condition fixing the particles in proper contact and orientation. In certain of its aspects, the present invention is an improvement upon the subject matter of a copending application Serial Number 243,733, filed August 25, 1951, by Ralph D. Hall, on "Electrically Conductive Films," now Patent No. 2,679,569, issued May 25, 1954.

The objects and advantages of the invention will be understood to best advantage following a brief consideration of the general characteristics of this type of heating element. The latter comprises as its electrically conductive component finely divided particles of metal predominantly under 40 microns, and preferably under

10 microns, of which silver, aluminum, chromium, copper and nickel, and mixtures thereof, are typical. Extensive experience has indicated silver to be the preferred metal. In addition to their small size, these metal particles are further characterized by their being preferably in flake form, the particular advantage of which is that in the heating film they assume contacting overlapping or shingle-like relation which stabilizes their contact and the conductivity of the film as a whole against such effects as contraction, expansion or other deformation of the film that might otherwise tend to produce interruptions in the inter-particle contact. And as indicated, the capacity of the flakes for orientation in such relation is assured by the initial fluidity of the binder.

The electrically resistive component of the film is supplied by using a non-conductive binder and using also, if desired, in uniform mixture with the metal particles, finely divided particles which are non-conductive or less conductive than the metal particles. Such non-conductive or less conductive particles may include any of various metallic oxides, of which antimony oxide is typical, as well as carbon or graphite. It is preferred to use flake graphite which, like the metal particles gives best results in sizes below 40 microns, and preferably with the particles predominantly below 10 microns. Any of various oxides may be used with the graphite. Antimony oxide is preferred because of its property of rendering the film fire resistant because of the flame snuffing tendency of the antimony oxide.

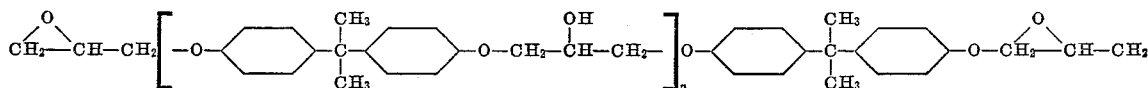
However effective may be the conductive and resistive properties of these particles as such, the efficiency and sustained electrical and thermal qualities of the film composite depends upon the binder and its having in addi-

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tion to non-conductivity a necessary combination of properties that will maintain the physical relation between the particles despite use of the film in wide temperature range atmospheres tending to contract or expand the film, or under conditions such that the film is otherwise subjected to deformation. Heretofore various kinds of binders generally classifiable as resins and elastomers, have been proposed and used in heating or resistance elements with varying degrees of success. Among these binders that harden to essentially non-elastomeric form, the property found to be most lacking and yet most needed, is the capacity of the binder to completely or very closely restore to its initial dimension following deformation of an elongative or contractive nature, and to retain constancy of resistance after repeated wide temperature range cycling.

The present invention has for its primary object to provide in electrically energized heating films of the type described, a resinous binder which more completely approaches the ideal requirements for the binder medium than any materials heretofore used for this purpose. From extensive determinations I have found that the commercially known resins sold by Shell Chemical Corporation under the trade-name "Epon" resins, have properties that give unique superiority as binder and insulative film components in the present type of element. Primarily they are characterized in addition to their adhesive and resistance qualities, by the capacity given the film to restore dimensionally practically completely following temperature changes ranging e. g. from -70° to $+350^{\circ}$ F.

These "Epon" or epoxide resins appear to have the general formula:



The reactive epoxy and hydroxyl groups of these resins will esterify with organic acids under the influence of heat. Esters of varying properties are obtainable by reaction of compounds corresponding to the formula with long chain fatty acids, say within the 8 to 18 carbon range, obtained from such materials as castor, linseed, soy bean and coconut oils.

Departing for the moment from reference to the chemical nature of the resin compositions herein employed, and with reference to the physical form of the films used, the invention while being primarily concerned with the composition of the heating element film, also contemplates the use of a resinous film as an electrical insulative coating to be applied to the surface of the object or material to carry the heating film. By way of example, the latter may be used for the surface heating of various metallic or non-metallic airplane parts, e. g. instruments, purge tanks and the like, as well as for such other purposes as the making of heat radiating panels and the like. Prior to application of the heating element film, I may coat the carrier surface, as by spray application, with a resinous composition to form what may be designated as a base insulative layer.

Broadly considered, the base layer, when used, may have any of various insulative compositions, as in the class of resins such as the alkyd resins. In some instances it may be found desirable to apply the heating film directly to a resistance or insulation base such for example as sheet asbestos. However, because of its various advantages, an epoxide-containing base film composition is preferred.

In compounding the base layer resin, I use an epoxide resin of the type formulated above, and which may be

described generally as a synthetic ester of polymeric polyhydric alcohol having alternating aliphatic chains and aromatic nuclei united through ether oxygens, the alcohol being esterified with a long chain fatty acid, typically coconut fatty acids. This ester is combined or uniformly admixed with a urea formaldehyde, phenol formaldehyde or melamine modified urea formaldehyde resin, or mixtures thereof. In the resulting mixture may be included pigments such as vermiculite, mica, antimony oxide, etc.

Satisfactory results have been obtained by using as the epoxide component of the insulative base film resin composition, Shell Chemical Corporation's Epon ester YC-3 or D-4 the former being understood to result from esterification of about 75% Epon 1007 with about 25% coconut fatty acid. Resin D-4 is similar, being the product resulting from esterification of about 60% Epon 1004 with about 40% dehydrated castor fatty acids.

For details concerning "Epon 1004," reference may be had to the Greenlee Patent No. 2,615,007 wherein the process of making the ester is described, and the ester is particularly defined as the product resulting from "reacting a mixture of p,p'-dihydroxydiphenyldimethyl methane and epichlorhydrin, the molar ratio of p,p'-dihydroxydiphenyldimethyl methane to epichlorhydrin in said mixture being between 1:1.2 and 1:1.5, with aqueous caustic soda sufficient in amount to combine with the chlorine of the chlorhydrin, at least part of the aqueous caustic soda being present in the initial mixture to convert the p,p'-dihydroxydiphenyldimethyl methane at least in part into its sodium salt, the reaction being continued with heating for a sufficient period of time to effect substantially complete reaction of the p,p'-dihydroxydiphenyldimethyl methane and epichlorhydrin to produce solid, water-insoluble resinous products having, after washing with water, softening points within the range of from about 84° C. to about 112° C. and with an epoxide equivalent within the range of from about 591 to about 1179." Epon 1007 is described as to its preparation and composition in the Greenlee Patent No. 2,615,008 and is particularly defined therein as the product "consisting essentially of a dihydric phenol free from reactive groups other than phenolic hydroxyl groups, and a low melting point epoxide resin resulting from the reaction with heating of a mixture of approximately 1 mol of dihydric phenol free from reactive groups other than phenolic hydroxyl groups with from about 1.2 to about 2 mols of a chlorhydrin selected from the group which consists of epichlorhydrin and glycerol dichlorhydrin and sufficient caustic alkali to combine with the chlorine of the chlorhydrin, said low melting point resins being polyethers of the dihydric phenols with the terminal groups of the polyethers including terminal epoxide groups, said polyethers being free from functional groups other than alcoholic hydroxyl and epoxide groups, the proportion of dihydric phenol to epoxide resin being less than that corresponding to the epoxide equivalent of the resin, whereby on heating the composition a higher molecular weight and a higher melting point epoxide resin is formed."

In compounding the insulative base film resin composition, the epoxide resin may be admixed in the stated 7 to 3 part ratio with desirably a urea or melamine formaldehyde resin, such as American Cyanamid Company's urea resin Beetle 227-8, together with a solvent and thinner which generally may be selected from individual or mixed known epoxide resin solvents, such as methyl isobutyl carbinol, methyl isobutyl ketone, toluene, xylene, and dioxane. The resin mixture is thinned sufficiently to permit even filming by spray application to the surface to be coated. The thickness of the coating may vary as desired, typically between .0025 to .02 inch. The resin mixture may range between 90 to 50 weight parts of the epoxide resin to from 10 to 50 parts of the formaldehyde resin.

For purposes of the binder component of the heating element film, I preferably use a mixture of between about

50 to 80 weight parts of Epon 1007 and between 20 to 50 parts of a formaldehyde resin of the class previously designated, though preferably Beetle 227-8. The resulting resin may be defined as a composition containing in substantial proportions a fusible urea formaldehyde or melamine modified urea resin containing active hydrogen, and a complex epoxide which is a polyether derivative of a polyhydric phenol containing epoxide groups and free from functional groups other than epoxide and hydroxyl groups, the proportions of complex epoxide and formaldehyde resin being between 5 to 9 (preferably about 7) parts by weight of complex epoxide to from 2 to 5 (preferably about 3) parts by weight of urea formaldehyde. For further details concerning resin compositions of this type, reference may be had to Greenlee Patent No. 2,528,360.

Epon 1007 is characterized in Example 1 of U. S. Patent 2,742,448 as a condensation product of a bisphenol and epichlorhydrin having an epoxy equivalent of 0.05. Additional details as to Epon 1007 are included in the publication by Shell Chemical Corporation entitled "Epon Surface Coating Resins" copyright 1948. For example, page 2 of said publication mentions that Epon 1007 has a melting point of 125-135° C., a viscosity (Gardner) of X-Z, in 40% solution in butyl carbitol and an equivalent weight of 188.

"Beetle 227-8" is identified as urea-formaldehyde resin in the publication "Annotated Comprehensive List of Trade Names of Synthetics," Research Association of British Rubber Manufacturers, circular No. 372, page 26 (October, 1949).

As in forming the base or insulative layer, the heating element layer typically is formed and deposited by spraying the resin mixture together with the later described solid particles or pigments which give the desired electrical and heating properties, thinned to a sprayable consistency using an appropriate solvent such as the solvent mixture used to thin the base layer forming resins. Typically, the epoxide and formaldehyde resin mixture may be thinned with about equal proportions of dioxane and toluene. The heating element film thickness typically may vary between about .0025 and .02 inch, and has been found to perform very satisfactorily at a thickness of about .0055.

At this point reference may be had to the accompanying drawing showing in cross-section the film layers applied to an object or surface to be heated.

The body 10 may be a metallic or non-metallic part such as an instrument housing, panel or the like, onto which is sprayed or otherwise applied at uniform thickness a layer 11 previously referred to as the insulation base layer. After application, this film may be heated to about 150° F. for around one-half hour to volatilize the solvent and cause the resins to assume solid and stable form. The heating element layer 12 is then deposited on the base layer by spray application or other means, and is then heated at around 350° F. for one-half hour so that the resins become completely polymerized and assume integrated bondage to the base layer 11. Thereafter, the heating film 12 may be surfaced with a coating 13 which preferably consists of Epon YC-3 i. e. around 75% Epon 1007 esterified with about 25% coconut fatty acid, this ester being mixed with 10% to 50% formaldehyde resin typically "Beetle 227-8," and the mixture thinned with suitable solvent for spraying.

As will be understood, electrical current may be passed between conductors c applied to the film 12 at spaced locations.

Referring further to the composition of the heating film 12, the latter contains a dispersion of the finely divided metal particles, preferably flake silver predominately under 10 microns in size, in the range of about 3 to 80 parts of metal particles to between 20 to 50 parts (solid content after evaporation of solvent) of the resins. Ordinarily it is preferred to use finely divided resistance

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particles together with the conductive metal particles, and for this purpose, I prefer to use between about 3 to 65 parts of flake graphite predominately under 10 microns in size.

The following examples are illustrative of typical heating film compositions embodying the invention and having the indicated resistance characteristics:

	Element I Resistance .05-1 ohms/sq.	Element II Resistance .6-1.2 ohms/sq.	Element III Resistance 50-100 ohms/sq.
	Parts	Parts	Parts
Antimony Oxide.....	20.2	30.1	40.1
Silver Flake.....	59.1	39.4	19.7
Graphite 200-30.....	20.2	30.1	40.1
Dioxane.....	61.9	82.3	98.8
Toluene.....	61.9	82.3	98.8
Epon 1007.....	23.1	30.8	30.8
Beetle 227-8.....	19.8	26.4	26.4
Amine.....	Trace	Trace	Trace

As previously indicated, extensive tests have shown that the resinous binders used have the highly important and distinctive advantage in heating film compositions, of restoration to an initial condition, after undergoing expansion or contraction in response to even wide temperature ranges. Tested for example as to its restorative ability after being subjected to temperatures between -70° F. to $+350^{\circ}$ F., the film was found to undergo well under 1% contractive or expansible departure from its dimension at the selected initial or reference temperature.

I claim:

1. A heating element composition comprising a mixture of finely divided electrically conductive metal particles and also graphite particles and a heat setting resinous binder consisting essentially of a formaldehyde resin of the class consisting of urea formaldehyde and melamine formaldehyde resins together with a complex epoxide which is a polyether derivative of polyhydric phenol containing epoxide groups and free from functional groups other than epoxide and hydroxyl groups, said composition containing said metal, total resins and graphite in the weight proportion of about 3 to 80 parts metal particles, 20 to 50 parts (solids basis) of resin

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(the resin itself being composed of from about 5 to 9 parts of said epoxide to from about 2 to 5 parts of said formaldehyde resin), and 3 to 65 parts of graphite.

2. A composition as defined by claim 1, in which said metal particles include finely divided silver.

3. A composition as defined by claim 1, deposited in thin hardened film form having a thickness between about 0.0025 and 0.02 inch.

4. A composition as defined by claim 1, deposited in thin hardened film form having a thickness between about 0.0025 and 0.02 inch, and in which the metal and graphite particles are predominately under 10 microns in size.

5. A composition as defined by claim 1, deposited in thin hardened film form on an electrically insulative resinous base layer.

6. A composition as defined by claim 1, deposited in thin hardened film form on an electrically insulative base layer composed of a mixture of said epoxide and formaldehyde resin.

7. A composition as defined by claim 1, deposited as a thin hardened conductive layer on an electrically insulative resinous base layer, and a thin resinous coating applied to the surface of said conductive layer.

References Cited in the file of this patent

UNITED STATES PATENTS

1,872,581	Haroldson	Aug. 16, 1932
2,177,484	Fruth	Oct. 24, 1939
2,386,095	Edgar et al.	Oct. 2, 1945
2,472,801	Barfield	June 14, 1949
2,528,360	Greenlee	Oct. 31, 1950
2,559,077	Johnson et al.	July 3, 1951
2,679,569	Hall	May 25, 1954
2,692,321	Hicks	Oct. 19, 1954

FOREIGN PATENTS

490,232	Great Britain	Aug. 11, 1938
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OTHER REFERENCES

Printed Circuits, National Bureau of Standard Circular 468, pages 6, 7, 8, 16 and 18.

Electrical Mfg. July 1949, pages 78-81, Paint, Oil and Chemical Review, November 20, 1952, pages 24-26.