Oct. 1, 1946. D. E. EDGAR ET AL 2,408,416

SEMI-CONDUCTING COMPOSITION

Filed Feb. 18, 1944

Fig. 1

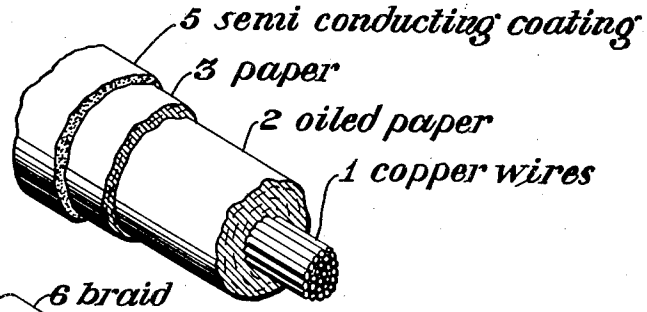


Fig. 2

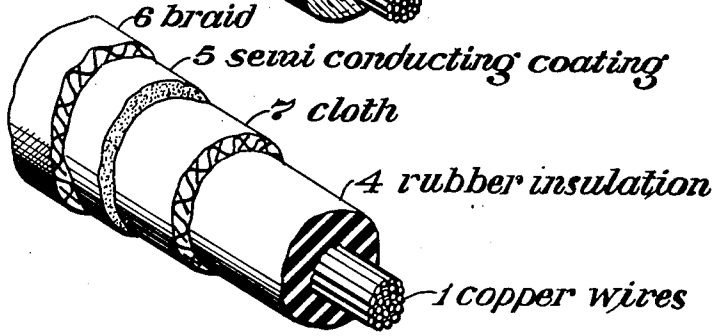


Fig. 3

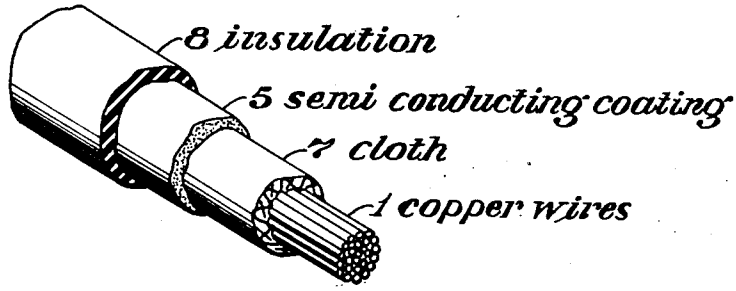


Fig. 4



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SEMICONDUCTING COMPOSITION

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15 Claims. (Cl. 174—102)

1

This invention relates to a semi-conducting coating composition, particularly adapted for coating insulated high tension electric cables and more particularly to a semi-conducting tape which maintains the voltage gradient at the surface of the insulation below a value above which harmful electrical disturbances occur.

Heretofore it has been common to dissipate high voltage charges which surround electric cables carrying very high voltages, that is of the order of 2,000 volts or more, by means of a metallic conducting shield over an insulating medium which may be in the form of oil saturated paper in combination with rubber, braid, regenerated cellulose and the like. In ordinary use it is necessary to dissipate or discharge the charges which build up on such a cable and this has been done by various means, such as surrounding the cable with the thin metallic sheath mentioned above. Metals, however, have the disadvantage that frequent bendings of the cable tend to develop air gaps because of the separation of the metal shield from the adjacent insulation. When such gaps are formed, arcing occurs which eventually causes a failure of the insulating medium. It has also been proposed to provide a shield which is more flexible than metal. Such shields have been prepared by a conducting paint, composition of rubber, or other film-forming vehicle in combination with metallic particles. None of these expedients have been entirely satisfactory due primarily to the failure of the film-forming vehicle when immersed in a liquid inimical to the vehicle, such as hot oil.

These defects in the previously available methods for dissipating static charges in insulated high tension electric cables and other non-conducting surfaces are eliminated in the practice of the present invention.

This invention has as an object the provision of an improved semi-conducting coating composition or tape carrying the coating for use over flexible electrical insulation, which effectively dissipates static charges. Another object is the provision of a semi-conducting coating or coated tape which is highly resistant to water, acids, ozone, oils and greases at low and high temperatures, thus protecting the insulation used in electric cable construction from injury and deterioration by exposure to such materials. Another object is the provision of a semi-conducting coating which is tough and elastic and which will retain its flexibility and remain intact over a wide range of temperatures without deterioration. A further and more particular object is the provision of a semi-conducting coating which is highly resistant to mineral oils and greases, even when exposed to such materials at elevated temperatures. Another object is the provision of a semi-conducting composition which does not contaminate insulating oils with decomposition products formed during normal service with resultant failure of insulating properties such as is commonly encountered with previously employed materials, for example, rubber. A further object is the provision of an improved semi-conducting tape, particularly adapted for use in the manufacture of high tension electric cables. A still further object is the provision of an insulated high tension electric cable in which the accumulation of static charge is substantially eliminated, thereby avoiding deteriorating and breakdown effects in the insulating covering over the cable. Other objects will appear as the description of the invention proceeds.

2

These objects are accomplished in accordance with the present invention by means of a semi-conducting coating composition comprising finely divided carbon black of low electrical resistivity, preferably not over about 1.0 ohm per 1" cube dispersed in a vehicle containing an alkyd resin as the essential film-forming ingredient. In the preferred embodiment a semi-conducting composition comprising an alkyd resin and acetylene black described hereinafter is applied to a fabric tape which is adapted for covering the organic insulation commonly employed in electric cable construction.

In the drawing Figures 1, 2, and 3 represent diagrammatic partial sections of a high tension cable prepared according to the present invention. Figure 4 is a section of fabric coated with a semi-conducting composition described in the examples. In Figure 1, the conductor is shown as 1 which may be a solid conductor or a number of copper wires as shown. Next to the conductor is a layer of oiled paper shown as 2. Over this is applied a semi-conducting layer applied as a tape made up of a semi-conducting coating 5 on a support which in Figure 1 is shown as paper. Figure 2 is a modification of Figure 1 in which the oiled paper is replaced by rubber insulation 4. A semi-conducting cloth layer 7 having a coating 5 is applied over the rubber insulation. The layers 5 and 7 are made up from a spirally wound tape over the rubber, the tape or cloth 7 being coated or impregnated with a semi-conducting composition 5 described in the examples. The braid 6 is provided to protect the semi-conducting layer 5. Figure 3 is a modification in which

the copper conductor 1 is wound directly with a tape made up of a cloth base 7 and a semi-conducting composition 5. Over this tape is applied a layer of rubber insulation 8.

In Figure 4 a section of the semi-conducting tape is shown having a fabric base 7 and a composition 5 which is more fully described below.

The following examples are given by way of illustration only and no limitations are intended thereby except as indicated in the appended claims.

Example 1

	Per cent by weight
Alkyd resin solution	43.8
Polyvinyl butyral resin ("Butacite")	9.8
Urea-formaldehyde resin solution	7.3
Dicapryl phthalate	4.9
Acetylene black	34.2
	100.0

The alkyd resin solution of this example consisted of a 60% solution of a 53% castor oil modified diglycerol-triphthalate resin in a volatile solvent vehicle consisting of

	Per cent by weight
Isobutyl alcohol	80
Petroleum naphthas (B. P. 135–215° C.)	20
	100

The polyvinyl butyral resin may be prepared by any of the methods well known in the art, for example, by treating polyvinyl acetate with a hydrolyzing agent such as sulfuric acid, followed by condensation with butyraldehyde to give a solid, fusible resin soluble in certain organic solvents. The resin of the example had a hydroxyl content of about 10%. The viscosity of the resin was 75 centipoises determined on a 5% solution of the resin in 2B denatured alcohol.

The urea-formaldehyde resin solution consisted of a 60% solution in butyl alcohol of a butyl alcohol modified urea-formaldehyde resin as described in Edgar et al. U. S. Patent 2,191,957.

The acetylene black which imparts semi-conducting properties to the composition may be prepared in accordance with the description contained in "Canadian Chemistry and Metallurgy," May 1933, pages 93–95. In addition to this carbon black, there are now on the market many blacks with high conducting properties. Chapter 7, page 67 of the book "Columbian Colloidal Carbons," published in 1938 by the Columbian Carbon Company, defines a suitable type of black as having an electrical resistance in ohms per 1'' cube of 0.152 to 0.217, although a somewhat higher resistance up to about 1.0 ohm per 1'' cube is satisfactory. In the claims such blacks are termed "low resistance carbon blacks."

The composition was prepared by combining the "Butacite" resin and dicapryl phthalate on differential speed conventional rubber roller mill after which the acetylene black, alkyd resin and urea-formaldehyde resin are incorporated, preferably by adding alternate portions of the acetylene black and resin solutions to the material already being worked on the rolls. The materials are milled for about 20 minutes or until a homogeneous mixture is obtained. This step in the preparation of the composition may also be carried out in a kneading machine, preferably of the heavy duty type such as a Banbury mixer. The resulting plastic stock from the roller mill was cut into small pieces and churned with xylol in the proportion of about 1 part of plastic to 0.4 part of xylol in an agitator mixer until a homogeneous solution is obtained. If the plastic is prepared in a kneading machine the solvent may be added direct with continued kneading.

The composition thus reduced to spreader viscosity with xylol was applied to a fabric base consisting of cotton sheeting weighing about 5.35 yards per pound by a conventional knife spreader coating machine. Usually three coats suffice to obtain a desired thickness of about 3 mils, although a fewer or greater number of coats may be applied if preferred. Each coat was dried at 240° F. for approximately 2 minutes in order to remove the volatile solvent and to promote the reaction between the "Butacite" resin and the insolubilizing agent, in this instance the urea-formaldehyde resin. When a cloth base is used, it is coated with about 2 to 4 ounces per square yard of the semi-conducting composition. With a suitable paper base which may be used alternatively as a support, about 1 ounce per square yard usually suffices.

The electrical resistance of the tape or an unsupported film of the semi-conducting composition of Example 1 was 300 ohms per inch square.

Samples of fabric tape coated with the composition of Example 1 were immersed in mineral oil of the type commonly employed in electrical transformers at a temperature of 180° C. After exposure under these conditions for a period of 6 months the coating was still intact and no evidence of deterioration was observed whereas tapes coated with compositions based on rubber or neoprene and exposed to the same conditions failed in less than 48 hours and after 15 days, respectively, as shown by development of porosity in the coating which allows the penetration of the mineral oil and subsequent electrical failure of the insulation surrounding the conductor. These results clearly demonstrated the great superiority of the new coating for the intended purposes.

Example 2

	Per cent by weight
Alkyd resin solution	40.3
Polyvinyl butyral ("Butacite")	9.0
Dibutyl ether of dimethylol urea solution	5.8
Dicapryl phthalate	4.6
"Spheron N" carbon black	40.3
	100.0

The alkyd resin solution and the polyvinyl butyral resin used in this composition were of the same type as described in Example 1.

The insolubilizing agent for the polyvinyl resin consisted of a 70% solution in butanol of dibutyl ether of dimethylol urea.

The "Spheron N" carbon black used in this example consisted of a special "channel" carbon black marketed by Godfrey L. Cabot, Inc., which is also characterized by low electrical resistivity.

The composition was prepared in accordance with the procedure of Example 1 and results similar to those obtained in Example 1 were also obtained in this instance.

The electrical resistance of the treated tape or unsupported film of the semi-conducting composition is usually between about 100 and 500 ohms per inch square although in some instances the tape may have a resistance of about 1,000 ohms per inch square.

Although castor oil modified alkyd resins as shown in Example 1 are preferred, other non-drying oils such as coconut and cottonseed may also be used as modifiers for the alkyd resin.

For present purposes the oil length of the modified alkyd resin is ordinarily between 30 and 60%. Drying oils are not desired because of their greater tendency to oxidize and cause embrittling in the present utility where heat and the presence of ozone promote such tendencies. Phthalic anhydride is the preferred acid radical in the alkyd resin ingredient of the improved compositions but other carboxylic acids such as succinic, malic, adipic, maleic, sebacic, etc., may be substituted wholly or in part for the phthalic anhydride, but best results may be secured when phthalic anhydride is employed as the sole acid radical or at least in preponderant amounts. Suitable alkyd resins for the new compositions may also be prepared from other polyhydric alcohols including ethylene glycol and higher homologs, diethylene glycol and other polyglycols, polyglycerols, pentaerythritol and sorbitol.

Although the use of polyvinyl butyral is shown in the examples, the invention is also applicable with other polyvinyl acetal resins including reaction products of hydrolyzed (or partially hydrolyzed) polyvinyl esters with the lower alkyl aldehydes such as formaldehyde, acetaldehyde, propionaldehyde and valeraldehyde. The polyvinyl acetal toughens and strengthens the coating and facilitates application by spreading or calendering to fabrics and other sheet material and functions also to prevent excessive penetration into such porous bases.

The butanol modified urea-formaldehyde resin shown in the Example 1 reacts with the polyvinyl acetals as a cross-linking agent for the double bonds resulting in an insolubilizing of the acetal and a reduction in plastic flow. Other agents which function in a similar manner and may be used in place of the butanol modified urea-formaldehyde condensation product shown in the Example 1 include N,N'-bis(alkoxymethyl) urons, described in co-pending application S. N. 438,949 to Maxwell, filed April 14, 1942, now Patent No. 2,373,135, dated April 10, 1945, alcohol modified melamine-formaldehyde condensation products of co-pending application S. N. 491,400 to Vaala, filed June 18, 1943 (also U. S. Patent 2,197,357), dimethylol urea and alkyl ethers of dimethylol urea as described in co-pending application S. N. 489,805 to Vaala, filed June 5, 1943, and organic complexes of the Werner type in which a trivalent chromium atom is coordinated with a carboxylic acido group having at least 10 carbon atoms such as stearate chromic acetate as disclosed in co-pending application S. N. 498,981 to Johnson, filed August 17, 1943.

The plasticizers or softeners which may be used in the present invention include conventional materials such as castor oil, blown castor oil, aryl sulfonamides, aryl and alkyl esters of phosphoric acid, dibutyl tartrate, dicyclohexyl phthalate, diethyl phthalate and the phthalate esters of the ether alcohols such as the butyl ester of ethylene glycol monomethyl ether.

In preparing the new compositions from the alternative materials suggested above, care should be taken to select those combinations which will afford maximum resistance to penetration of mineral oil such as is achieved with the specific compositions shown in the examples.

As previously indicated, the carbon black used in the present composition has low electrical resistivity of between about 0.152 ohm per 1" cube and preferably not over 1.0 ohm per 1" cube. Acetylene black (Shawinigan Black) is of particular merit in the present compositions, although "Graphon," a graphitized carbon black, prepared from natural gas and treated in accordance with U. S. Patent 2,134,950 is also representative of suitable semi-conducting carbon blacks. Other special forms of "channel" carbon black sold by Godfrey L. Cabot, Inc., under the trade names "Spheron N," "Spheron T" and "Spheron C" which have low electrical resistivities have also been found suitable for the present purposes.

These semi-conducting materials may be used in the proportion of 1 part by weight of the carbon black to between about 0.25 and 4 parts by weight of vehicle solids including the resin components and the plasticizer. A ratio of vehicle solids of between about 1 to 2 parts to 1 part of carbon black of the type defined above is preferred. If there is any substantial departure from the limits indicated, the primary objectives of the invention are not attained. If the semi-conducting carbon black is present in proportions substantially below the limits established, the desired conductance is not obtained probably due to absence of direct contact between particles and if the carbon black is incorporated in substantially greater proportions than the upper limit suggested, there are deficiencies in film properties of the coating.

Another factor which has a contributing influence on the conductance of the coating is the degree of dispersion of the semi-conducting carbon black as controlled by the grinding conditions, particularly the grinding cycle employed in dispersing the pigment in the vehicle. Extended grinding cycles apparently cause the particles of the carbon black to become surrounded with the vehicle which is relatively insulating in character, thus adversely affecting the desired conductance in the final coating.

As previously indicated, the coating may be used as a free film or coated from solution directly on to the surface of the organic insulation surrounding the conductor or alternatively and preferably the coating is applied to one or both surfaces of a suitable supporting base such as fabrics of cloth, paper, asbestos or fabric made from glass fibers and the coated support then wound spirally about the organic insulation. A suitable paper support may consist of a conventional insulating paper of between about .003 and .0035 inch in thickness. Satisfactory cloth fabric support may consist of cotton sheeting weighing about 5.35 yards per pound.

The new compositions are of general utility for purposes where a semi-conducting surface is desired. However, a specific and important use resides in the construction of high tension electric cables employed in automotive ignition systems where the coating functions as a shield to reduce or prevent the formation of static fields about the conductor which sometimes reach glow discharge or corona intensity with formation of excessive ozone and resultant rapid breakdown or failure in the electrical insulation.

The invention is characterized by a number of important advantages. In the new compositions satisfactory electrical conductance is combined with exceptionally high resistance to hot mineral oils and greases over extended periods of time. It is in this latter respect that previously available similar coatings are particularly deficient. Not only are the new compositions substantially impervious to hot oils and greases but they are also quite resistant to water, ozone and acids such as are usually encountered during service in auto-

motive ignition systems so that the electrical conductance is not impaired by exposure to such deteriorating effects. The products of the invention are further distinguished from inferior compositions previously available in that there is substantially no contamination of the insulating oils in the treated paper insulation from decomposition products so that early failure of the insulation surrounding the electric conduction is avoided. The improved coatings are tough and flexible at low and high temperatures and sufficiently elastic to conform to any curvature imparted to the cable without breaking. High tension electric cables constructed with the new compositions as a part thereof have an exceptionally long life and maintain uniform electrical conditions much longer than any heretofore in commercial use.

It is apparent that many widely different embodiments of the invention may be made without departing from the spirit and scope thereof and, therefore, it is not intended to be limited except as indicated in the appended claims.

We claim:

1. A semi-conducting coating composition particularly adapted for the manufacture of high tension electric cables comprising a resinous vehicle containing a non-drying oil modified alkyd resin, a polyvinyl acetal resin, a urea-formaldehyde resin and a carbon black having electrical resistivity of less than about 1.0 ohm per 1'' cube in the proportion of between about 0.25 and 4 parts by weight of said resinous vehicle to 1 part of said carbon black.

2. Composition of claim 1 in which the alkyd resin is a castor oil modified diglycerol triphthalate resin.

3. Composition of claim 1 in which the alkyd resin is a 30–60% castor oil modified diglycerol triphthalate resin.

4. Composition of claim 1 in which the carbon black has an electrical resistivity of between about 0.152 and 0.217 ohm per 1'' cube.

5. Composition of claim 1 in which the carbon black is acetylene black.

6. Composition of claim 1 in which the carbon black is graphitized carbon black.

7. Composition of claim 1 in which the polyvinyl acetal resin is polyvinyl butyral.

8. Composition of claim 1 in which the insolubilizing agent is a butanol modified urea-formaldehyde resin.

9. An electric cable comprising an insulated conductor having an outer layer of a composition containing the composition of claim 1.

10. A semi-conducting composition particularly adapted for the manufacture of high tension electric cables having approximately the following composition:

	Per cent by weight
53% castor oil modified alkyd resin solution (60% solids)	43.8
Polyvinyl butyral resin	9.8
Butanol modified urea-formaldehyde resin solution (60% solids)	7.3
Dicapryl phthalate	4.9
Acetylene black	34.2
	100.0

11. A new composition of matter adapted to withstand adverse conditions of moisture, temperature and mineral oil comprising carbon black having an electrical resistivity of less than 1 ohm per 1 inch cube, a non-drying oil modified alkyd resin, a polyvinyl acetal resin, and a lower monohydric aliphatic alcohol modified urea-formaldehyde resin, the electrical resistance of the said composition being between about 100 and 500 ohms per inch square.

12. A semi-conducting tape particularly adapted for the manufacture of high tension electric cables comprising a fabric base support carrying a coating containing a non-drying oil modified alkyd resin, a polyvinyl acetal resin, a urea-formaldehyde resin and a carbon black having an electrical resistivity of less than about 1.0 ohm per 1 inch cube in the proportion of between about 0.25 and 4 parts by weight of the resinous vehicle to 1 part of the said carbon black.

13. Product of claim 12 in which the tape consists of a fabric base.

14. Product of claim 12 in which the tape is paper.

15. The article of claim 12 in which the carbon black has a resistivity of between about 0.152 and 0.217 ohm per 1 inch cube.

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