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ELECTRICALLY CONDUCTIVE COATINGS

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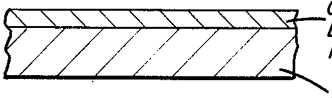

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ELECTRICALLY CONDUCTIVE COATINGS

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This is a continuation-in-part of my copending application Serial No. 56,648 filed September 19, 1960, and now abandoned.

This invention relates to electrically-conductive coatings useful as antistatic coatings on photographic films and the like, and to methods for making such conductive coatings, and to manufactures that comprise such coatings.

An object of the invention is to provide novel electrically-conductive coatings having surface resistivity less than 10^{11} ohms per square. More specifically an object is to provide such conductive coatings which comprise a film of electrically insulating binder material and dispersed through this film as a disperse phase, a metal-containing semiconductor compound.

Other objects are to provide certain novel processes for making such conductive coatings and to provide certain novel manufactures comprising such conductive coatings.

Conductive coatings of the present invention may be made in a variety of embodiments which provide a variety of advantageous properties. All of the coatings are substantially independent of humidity or moisture for their conductive property and this humidity independence is especially advantageous in applications where the conductive coating must function in a dry atmosphere or in vacuum. Many embodiments comprise substantially clear transparent conductive coatings, which properties make these coatings especially useful as transparent conductive overcoats on insulating surfaces, for example, on a photographic film, a fabric, a printed surface, and the like. Mechanical properties of the conductive coatings are more or less variable according to the specific properties of the selected film-forming binder and a suitable insulating binder material may be selected from resins and colloid binders having a wide variety of mechanical properties.

The foregoing objects and advantages as well as others will be apparent from the following detailed description of the invention.

According to the invention, novel conductive coatings are provided which comprise a metal-containing semiconductor compound dispersed in an insulating, film-forming binder and which have resistance, expressed as surface resistivity, of less than 10^{11} ohms per square. The semiconductor compound is dispersed in the insulating binder as particles ranging in size from colloidal down to molecular, generally less than 0.1 micron. In some embodiments the dispersion appears to be a solid solution, in others, a colloidal dispersion.

A preferred method of making such conductive coatings is by coating a solution containing the semiconductor compound and the binder, both solubilized in a volatile solvent which evaporates leaving film of the binder material with a dispersion of the semiconductor in the binder. A complexing agent is used to solubilize the ordinarily insoluble semiconductor compound.

From consideration of prior art coatings which comprise an insulating layer of semiconductor material dispersed in film-forming binders (i.e. silver halide-gelatin photographic emulsions, photoconductive insulating layers in electrophotographic elements, etc.) the very good conductivity of my conductive layers would not be expected. The reason for this good conductivity is not entirely understood but I believe it is related to the extremely fine

and homogeneous dispersion of semiconducting material obtained by the solution coating method, which perhaps forms a conducting lattice in the binder film as the coated solution is dried.

In various embodiments of the invention, conductive coatings will contain semiconductor compounds in concentrations ranging from as low as about 15% by volume of the finished coating up to about 80–90% by volume. Volume percentages, as expressed, are calculated from known densities of the respective semiconductor and binder components and from known weight ratios of these materials in the coating.

The minimum volume percentage needed to provide the necessary conductivity will vary, depending upon the peculiar properties of the selected semiconductor and binder components, and to a great extent upon the method of making the coating. In embodiments in which a conductive coating is made by a solution coating method minimum effective semiconductor concentrations in the finished coating may be as low as about 15% by volume. Useful conductive coatings according to my invention have surface resistivity less than 10^{11} ohms per square, as measured by the procedure described in Example I. For most applications I prefer conductive coatings having surface resistivity in the range from about 10^2 to 10^9 ohms per square.

Cuprous iodide and silver iodide are preferred metal-containing semiconductor compounds that I have selected to illustrate certain preferred embodiments of the invention in detail. However, my invention contemplates use of other metal-containing semiconductor compounds. The invention contemplates use of both ionic and electronic semiconductor compounds of both intrinsic and extrinsic semiconductor types. Examples of other semiconductor compounds contemplated for use in accordance with the invention include other cuprous and silver halides, halides of bismuth, gold, indium, iridium, lead, nickel, palladium, rhenium, tin, tellurium and tungsten; cuprous, cupric and silver thiocyanates, and iodomercurates, and other metal-containing semiconductor compounds.

These semi-conductor compounds are essentially non-hygroscopic and do not depend upon presence of moisture for their electrical conductivity.

The term "semiconductor" as used herein, defines metal-containing compounds having electrical resistivity (specific resistance) in the range from 10^{-3} to 10^9 ohm-cm., as measured by standard procedures.

The term "surface resistivity" conventionally refers to measurement of electrical leakage across an insulating surface and is usually measured on an insulating surface by procedures similar to that described in Example 1. In the present specification however, the term is used with reference to resistance of conducting films that apparently behave as conductors transmitting currents through the body of the coating of electrically conducting material. Resistivity (specific resistance) is the usually accepted measurement for the conductive property of conducting and semiconducting materials. However, in the case of thin conductive coatings, measurement of the conductive property in terms of surface resistivity provides a value that is useful in practice and involves a direct method of measurement. It should be pointed out that the dimensional units for specific resistance (ohm-cm.) and the unit for surface resistivity (ohms per square) are not equivalent and the respective measurements should not be confused. For an electrically conducting material whose electrical behavior is ohmic, the calculated resistance per square of a film of such material would be the specific resistance of the material divided by the film thickness, but this calculated resistance for a given material will not always coincide with measured surface resistivity particularly in the case of a thin coated film.

According to certain preferred embodiments of the invention, conductive coatings are prepared by solution coating methods, using a coating solution in which both the semiconductor compound and the film-forming binder are solubilized in a volatile liquid solvent.

By the term "volatile" I means capable of being readily evaporated from solution at temperature low enough to be nondestructive, usually below 150° C. The metal-containing semiconductor compounds generally are not readily soluble in most volatile solvents such as water and organic solvents that are suitable for solubilizing most electrically insulating film-forming binders. Therefore we may employ as a solubilizing agent for the semiconductor compound, a compound that will form a soluble complex with the semiconductor.

Example I illustrates a preferred embodiment of the invention in which a conductive coating is coated on an insulating film support by a solution coating method.

Example I

A solution was prepared by stirring rapidly 3.83 g. of silver iodide and 1.07 g. of potassium iodide into a mixture of 10.6 ml. acetone and 38.4 ml. of cyclohexanone. After stirring for several hours the salts were all dissolved and the solution was water white. Potassium iodide formed a colorless complex with silver iodide and this complex was dissolved by the ketone solvents. Into this solution was stirred 9 ml. of a 20% solution of poly(vinylacetate) (Vinylite AYAC) in cyclohexanone. The resulting clear solution was whirl-coated onto a sheet of Mylar polyester film and dried by evaporating the organic solvents. After drying, the residual coating was clear and consisted of a dispersion of the colorless complex of the salt in the polyvinyl acetate. The sheet was immersed in water at room temperature for 5 minutes to destroy the complex and to dissolve potassium iodide from the coating. Silver iodide remained dispersed in the coating. After the film had been washed and dried the coating was optically clear and had turned pale yellow, the color characteristic of silver iodide. Surface resistivity (ohms per square) of the coating was measured by placing 1-inch long electrodes along opposite sides of a 1-inch square on the coated surface. These graphite electrodes were formed by application of an aqueous suspension of colloidal graphite (Aquadag, Acheson Colloids Company) along opopsite sides of the square and then drying the applied suspension. Resistance was measured by a Keithley electrometer using applied potential of 3 volts D.C. Measurements were made at various relative humidities:

Relative humidity:	Surface resistivity ohms, per square (o.p.s.)
40%	1.5×10^8
15%	1.2×10^8
5%	1.2×10^8

These results illustrate that surface resistivity of the coating is essentially independent of humidity. The conductive layer was exposed to floodlamp illumination for 2½ hours to test for silver printout. No printout was observed, nor was there any apparent change in properties of the coating.

Generally alkali metal halides and ammonium halides may be used as complexing agents with silver halides, cuprous halides and with some other semiconducting metal halides such as stannous halides, lead halides and the like to form a complex that is most readily soluble in ketone solvents. Usually it is preferable to remove the solubilizing agents, as illustrated in Example 1 by washing in water, but in some embodiments the dispersion of the complex salt will provide sufficient conductivity. In these latter cases, the complex is, itself, a semiconductor compound. Examples of volatile ketone solvents suitable for dissolving these complexes are acetone, methylethylketone, 2-pentanone, 3-pentanone, 2-hexanone, 2-heptanone, 4-heptanone, methylisopropylketone, ethylisopropylketone, diisopropylketone, methylisobutylketone, methyl t-butylketone, diacetyl, acetyl acetone, acetonyl acetone, diacetone alcohol, mesityl oxide, chloroacetone, cyclopentanone, cyclohexanone, acetophenone and benzophenone. A mixture of ketone solvents may be used, as in the above example, or in some embodiments a single ketone solvent may be used. In some embodiments, other volatile solvents may be used in mixture with the ketone solvent to facilitate solubilizing of the binder material. Examples of organic solvents suitable for such use in mixture with a ketone are volatile alcohols, ethers, esters, Cellosolve solvents, paraffinic, cyclic and aromatic hydrocarbons, etc. In some cases, when using an alkali metal halide or an ammonium halide as a complexing agent, a solution can be prepared by using a film-forming polymeric binder that contains a ketone group in the polymeric molecule, and using a solvent that is not a ketone. In other cases, espectially when lithium iodide and sodium iodide are used as complexing agents, some solvents which are not ketones may be used to dissolve the iodide complex. Certain solvents such as methyl acetate, ethyl acetate, n-propyl acetate, isopropyl acetate, n-butyl acetate, iso-amyl acetate, tetrahydrofuran, dimethylformamide, methyl Cellosolve, methyl Cellosolve acetate, ethyl acetate, and some others may be effective to dissolve the iodide complex without need for a ketone solvent or a ketone polymer.

A suitable film-forming binder for the conductive layer may be selected from a number of available natural and synthetic electrically insulating polymeric materials according to the particular properties wanted. Suitable film-forming binders for a wide range of uses may be selected from among the following binders and resin classes: gelatin, poly(vinyl alcohol), poly(vinyl acetate), carboxylated poly(vinyl acetate), poly(vinyl acetal), poly(vinyl chloride), poly(vinylphthalate), poly(vinyl methyl ether-maleic anhydride), poly(methylmethacrylate), poly(vinyl acetal phthalate), poly(styrene-butadiene-acrylonitrile), poly(styrene-maleic acid), poly(vinylidene chloride-acrylonitrile), poly(methylmethacrylate - methacrylic acid), poly(butyl methacrylate-methacrylic acid), cellulose acetate, cellulose acetate-butyrate, cellulose acetate-phthalate, cellulose ethylether phthalate, methylcellulose, ethylcellulose, poly(methylacrylate - vinylidene chloride-itaconic acid), poly-2-vinyl pyridine, celluloseacetate diethylamino - acetate, methylcellulose, diethylamino acetate, poly(vinyl methyl ketone), poly(vinyl acetophenone), poly(vinyl benzophenone), poly(vinylmethylacrylate-methacrylic acid), poly(vinyl acetate maleic anhydride), poly(acrylonitrile-acrylic acid), poly(styrene-butadiene), poly(ethylene-maleic acid), poly(-4-vinyl pyridine), carboxylic esters of resin lactones, polystyrene, cellulose nitrate, polyurethane resins, polyamide resins, phenolic resins, urea resins, melamine resins, ethyl cellulose diethylamino acetate, other basic polymers, polybasic acid polymers, polyesters, epoxy resins, alkyds, etc.

The present invention is not limited to any particular means for applying the coating solution and any suitable means may be used such as whirl coating, either with or without heat, dip coating, spray coating, bead application on continuous coating machines, wick application to a continuously moving web, hopper coating, etc. Drying of the coated solution to remove the volatile solvents may be effected at room temperature or at elevated temperatures. In some cases, drying at elevated temperatures or subsequent heating of the dried coating will improve conductivity.

The coatings in Example 1 were prepared using a mixture of ketone solvents. Example 2 illustrates an embodiment using a single ketone solvent with an alkali metal halide complexing agent and further illustrates an embodiment of the invention in which the coating is suitably conductive before the complexing agent is removed.

Example 2

Coatings were prepared and tested as in Example 1, using the same weights of solid constituents, but using 25 ml. of acetone, and no cyclohexanone. Surface resistivity of the unwashed coating was 7.0×10^6 ohms per square at 29% R.H., while the washed coatings gave a value of 4.6×10^9 ohms per square at 29% R.H. Likewise, coatings were prepared using cyclohexanone as the only solvent and similar results were observed.

Example 3

The following ingredients were mixed, coated and tested as in Example 1: 1.4 g. of silver iodide, 0.45 g. of potassium iodide, 40 ml. of methylethyl ketone, 8 ml. of ethyl alcohol, 20 ml. of benzene and 1.0 g. of polyvinyl phthalate. Because this binder is soluble in Aquadag, a graphite dispersion, DAG No. 2412, in mineral spirits was used to make electrodes for testing. Surface resistivity of the coating after the water wash treatment was 5.4×10^7 o.p.s. at 15% R.H. Another solution containing diethyl ketone, n-propanol and n-heptane as the solvent mixture was made and, when coated, gave similar results.

Example 4

Illustrating preparation of a conducting layer in which no ketone is present: A coating solution was prepared containing 0.75 g. of silver iodide, 0.25 g. of sodium iodide, 50 ml. of methyl Cellosolve, 10 ml. of n-propanol, and 0.5 g. of polyvinyl formal (Formvar 12/85, Shawinigan Resins Company). The solution was whirl-coated on Mylar film, cured at 125° C. for 10 minutes, then washed in water for 10 minutes at room temperature. A clear coating resulted which had surface resistivity of 3×10^8 o.p.s. measured at 15% R.H.

In addition to the alkali metal halides and ammonium halides, other metal halides such as halides of metals from Groups 2A and 3A of the Periodic Table may be used as complexing agents for solubilizing silver iodide and some other semiconductor compounds in solutions preferably containing ketone solvent. Hydrogen iodide may be used to solubilize silver iodide in ketone solvents, and hydrogen iodide has the advantage that it is removed by evaporation as the coated solution dries. Thus the complexing agent is removed without need for a separate water-wash step.

Silver iodide, 0.5 g., 0.75 ml. of 50% hydrogen iodide (aqueous), 5 ml. of acetone, 55 ml. of methyl ethyl ketone were mixed and agitated until the silver iodide was dissolved and 0.25 g. of poly(methyl methacrylate was added. The solution was filtered, and whirl-coated on polyethylene terephthalate film support. The coating was heated at 80° C. for 20 minutes. The surface resistivity was 2.0×10^8 ohms per square at 45% R.H., and 2.3×10^8 ohms per square in a high vacuum.

Quaternary ammonium iodide compounds may be used as solubilizing agents for silver iodide. For example, N-methyl-N, N, N-tridodecyl ammonium iodide and N, N-dimethyl-N, N-didodecyl ammonium iodide are useful for complexing silver iodide.

Another especially preferred semiconductor compound useful for making conducting coatings according to the present invention is cuprous iodide which can be solubilized by alkali metal halides and ammonium halides, hydrogen iodide and other hydrogen halides in ketone solvents, as well as by other complexing agents in various solvents.

Conducting coatings according to the invention may be prepared from a completely aqueous solvent system involving a suitable complexing agent. The following example, illustrates use of a thiosulfate complex of cuprous iodide in aqueous solution with a water soluble binder.

Example 5

A solution was prepared consisting of 1.5 g. of cuprous iodide, 0.6 ml. of ammonium thiosulfate, 1.0 g. of cellulose acetate (16.7% acetyl, water soluble), and 60 ml. of distilled water. The solution was whirl-coated on Mylar film base and cured at 150° C. for 5 minutes. Surface resistivity was measured as 2.7×10^5 o.p.s. at 15% R.H. Other film-forming binders suitable for use with aqueous solvent systems include polyvinyl alcohol, polyvinyl methyl ether maleic acid, polyethylene-maleic acid, methyl cellulose, carboxymethylcellulose, and gelatin. Suitable conducting coatings may also be prepared by mixing an aqueous solution of the semiconducting compound with an aqueous solution of a latex such as a styrene-butadiene latex (Dow Latex 512R) and coating and drying the mixture. Conductivity of this coating may be improved by curing at elevated temperature (about 150° C.) for a few minutes.

Example 6 illustrates an embodiment wherein a semiconductor compound is solubilized by a nitrile solvent. Volatile nitrile solvents may serve as both complexing agent and solvent for the complex and may be used for solubilizing cuprous iodide, copper iodomercurate and the like.

Example 6

Cuprous iodide (1.4 g.) was dissolved with stirring in 53 ml. of acetonitrile and 7 ml. of a 5% solution of cellulose acetate butyrate in acetonitrile was added. The solution was filtered and then whirl-coated on a Mylar film and cured at 100° C. for 10 minutes. After drying, the coating was clear and had a surface resistivity of 6.9×10^4 ohms per square. After 24 hours at room temperature, the surface resistivity was measured as 9.0×10^3 ohms per square. After 9 months, surface resistivity of the same coating was 8.5×10^3 ohms per square at 37% R.H. and 7.7×10^3 ohms per square in high vacuum (1.5×10^{-5} mm. Hg).

Example 7 illustrates use of a mixed solvent system to solubilize a binder that is not readily soluble in the volatile nitrile liquid complexing agent.

Example 7

Cuprous iodide (0.6 g.) was dissolved with stirring in 31 ml. of acetonitrile, and 23 ml. of ethylene chloride was added slowly with stirring. Then 6 ml. of 5% solution of poly(vinyl chloride acetate) (VMCH) in ethylene chloride was added slowly with stirring. The solution was filtered and then whirl-coated on Mylar film and when dry was cured at 100° C. for 10 minutes. After aging overnight at room temperature, the coating had surface resistivity 8.5×10^3 ohms per square.

Other nitrile solvents that could be substituted for acetonitrile in Examples 6 and 7 are propionitrile, and other volatile nitrile liquids.

Another class of complexing agents for cuprous and silver halide is the class of volatile trialkyl phosphites, in which the alkyl constituents contain 1 to 5 carbon atoms. The complexes formed by these agents generally are soluble in a range of organic solvents somewhat broader than the range of organic solvents useful with the complexes described above. Ketone solvents are suitable as well as chlorinated hydrocarbons, Cellosolve solvents and the like. The preferred trialkyl phosphites complexing agents are volatile and can be separated from the complex and removed by evaporation from the coating as the solvents are evaporated. Therefore no washing step is necessary to remove these complexing agents.

Example 8

Cuprous iodide (0.7 g.) was added to 50 ml. of methylethylketone and 1.5 ml. of trimethyl phosphite and the mixture was stirred until substantially all of the solids had dissolved. Then 10 ml. of a 5% solution of a terpolymer, poly(acrylonitrile - vinylidene chloride - acrylic acid), in methylethylketone (90%) and cyclohexanone (10%) was added. The solution was heated with stirring to about 40° C., filtered and whirl-coated on Mylar film. After coating, the film was cured at 105° C. for 10 minutes and was essentially clear. Surface resistivity of the coating was 9.1×10^5 o.p.s. After 24 hours surface resistivity was 1.4×10^5 ohms per square and, after 2 months, surface resistivity was 2.0×10^5 o.p.s.

Example 9

Cuprous iodide (0.6 g.) was dissolved in a mixture of 52 ml. of methyl Cellosolve containing 1.0 ml. of trimethyl phosphite and 8 ml. of a polyvinyl formal solution. (5% Formvar 12/85 in methyl Cellosolve.) The solution was filtered and then whirl-coated on Mylar film and after drying was cured at 105° C. for 10 minutes. Surface resistivity after curing was 3.7×10^6 o.p.s. and 24 hours later was 5.8×10^5 o.p.s.

Example 10

Silver iodide (1.5 g.) was added to 50 ml. of methylethylketone and 1.0 ml. of trimethyl phosphite and the mixture was stirred until all the solids had dissolved. Then 10 ml. of a 5% solution of poly(methyl methacrylate) (Lucite 41) in methylethyl ketone was added. The solution was whirl-coated on Mylar film and a clear coating resulted. Surface resistivity was 2.0×10^8 o.p.s.

Diethyl sulfide is still another complexing agent for solubilizing cuprous iodide. Other dialkyl sulfides containing 1 to 5 carbon atoms in each alkyl group may be used and the complexes formed are soluble in several organic solvents such as chlorinated hydrocarbon solvents, etc.

Example 11

Cuprous iodide (0.7 g.) was added to 50 ml. of ethylene chloride and 1.5 ml. of diethyl sulfide and the mixture was stirred until substantially all the solids had dissolved. Then 10 ml. of a 5% solution of a polyester adhesive (Du Pont 49,000) in ethylene chloride was added and the solution was whirl-coated on Mylar film. The coating was cured at 125° C. for 10 minutes, after which the coating was clear and surface resistivity was 6.5×10^9 o.p.s. After 24 hours at room temperature, surface resistivity of the coating was 3.6×10^6 o.p.s. Volatile primary, secondary and tertiary alkyl amines having alkyl groups contain 1 to 5 carbon atoms and may be used as solubilizing agents for cuprous iodide, silver iodide and other semiconductor compounds. Complexes formed with such amines are generally soluble in volatile ketone solvents.

Example 12

Cuprous iodide was dissolved with stirring in 50 ml. of methyl ethyl ketone containing 5.5 ml. of triethylamine. Then 10 ml. of a 5% terpolymer solution, poly(methyl acrylate-vinylidine chloride-itaconic acid) in 90% methyl ethyl ketone and 10% cyclohexanone was added. The solution was filtered and then whirl-coated on Mylar film. Immediately after preparation, the clear uncured coating had surface resistivity of 3×10^7 ohms per square. After 3 days, surface resistivity was 1.3×10^6 o.p.s. When a freshly prepared coating was cured at 105° for 10 minutes, the surface resistivity was 3×10^5 ohms per square. After 3 days this sample had surface resistivity of 5.2×10^4 o.p.s.

Example 13

Silver iodide (1.5 g.) was dissolved with stirring in 25 ml. of acetone, 25 ml. of acetone, 25 ml. of methyl ethyl ketone and 4.0 ml. of n-butylamine. Then 10 ml. of 5% polyvinyl acetate (Vinylite AYAT) solution in acetone was added. The solution was filtered and then whirl-coated on Mylar film with heat applied from above with a heat lamp and a hair dryer. After drying, the film was cured at 105° C. for 10 minutes and the surface resistivity was measured at 7.6×10^9 ohms per square.

A conductive coating of the present invention might be substituted for the conductive film coated under a photoconductive layer in an electrophotography element of the kind described in U.S. Patent 2,833,675 patented May 6, 1958 to P. K. Weimer. A transparent coating according to my invention can be substituted for the graphite conductive overcoat on an electron sensitive photographic plate of the kind described in U.S. Patent No. 2,797,331 patented June 25, 1957 to H. B. Law et al., or can be substituted for the conductive metal overcoat on an electron recording plate of the kind described in U.S. Patent 2,748,288 patented May 29, 1956 to T. A. Saulnier, Jr. As a conductive undercoat my conductive coatings may be substituted for those described for use in facsimile recording papers of the kind described in U.S. Patent No. 2,555,321 patented June 5, 1951 to H. R. Dalton et al. An insulating support coated with my conductive coating may be substituted for the conducting support described in U.S. Patent No. 3,075,859 patented January 29, 1963 to E. B. Relph et al. My conductive coating is useful as the transparent conducting layer in recording mediums of the kind described in U.S. Patent 3,118,787 patented January 21, 1964 to Arthur Katchman.

In some embodiments the conductive coating may comprise a binder that is alkali soluble so that the coating is removable, as for instance by alkaline photographic developer solutions. Instead of, or in addition to, use of an alkali soluble binder, the conductive coating may be made removable by providing a water-soluble or alkali-soluble stripping layer between the film support and the conductive coating. For example, a one percent aqueous solution of polyvinyl methyl ether-maleic acid was found to be especially suitable for making such an alkali-soluble stripping layer.

Extremely thin conductive coatings of suitable surface resistivity have been made according to the invention with measured thicknesses as low as only 200 Angstrom units.

As antistatic coatings for photographic films, the conductive coating may be coated either as a surface coating or as a subsurface coating and may be coated on the side of the support with the sensitive material or on the back side, opposite the sensitive material.

As shown by the preceding examples, several various complexing agents, semiconducting compounds, solvents and binders may be used for making conducting layers and use of these materials in various combinations have been shown to illustrate versatility of the invention. My invention comprises use of a broad variety of such materials and is by no means intended to be limited only to those preferred embodiments that I have described in detail.

Conductive coatings may be made permanent or may be made to be removable by processing solutions in various embodiments of the invention. Conductive coatings may be used to provide antistatic, electrically conductive surfaces or subcoatings on a variety of supports, and especially to provide a conductive surface coating on an insulating support. For example, the conductive coatings may be applied as a subcoating to serve as an electrode on an insulating support, providing a conductive base for electrophoretic application of subsequent coatings. Metal plating can thus be applied to the surface of articles made of insulating synthetic resins. Conductive coatings may be used as thin conductive electrodes in making electrical condensers, resistors, and other electrical and electronic manufactures.

In some embodiments the conductive coating may be used as an antistatic coating for phonograph records or magnetic recording tapes. The conductive coating may be used as an antistatic coating for synthetic fibers and filaments, fabric webs, carpets and the like.

Supports on which conductive coatings according to the present invention may be applied usually, but not necessarily, will be insulating surfaces. The binder for the conductive coating may be selected for particular adhesive properties to provide good adhesion to the support surface and in some cases solvents may be selected which are active to soften or partially dissolve the support surface in order to improve adhesion. In some cases a subbing layer or a protective layer may be necessary or advantageous between the support surface and the conducting surface. Some special treatment of the support surface may be advantageous to improve adhesion in some embodiments.

Example 14

Cuprous iodide (2.4 g.) was dissolved in a mixture of 200 ml. methylethyl ketone and 4.0 ml. of trimethyl phosphite, then 40 ml. of a 5% solution of a terpolymer, poly(methylacrylate-vinylidene-chloride-itaconic acid) in 90% methylethyl ketone and 10% cyclohexanone, was added. The filtered solution was machine-coated by bead application on a subbed polyester film support to give a coverage of 5 mg. of copper per square foot. The coating was dried at 110° C. and then cured at 120° C. for 10 minutes. The coating was clear and surface resistivity was 1.7×10^5 ohms per square. A protective layer of Vinylite VMCH was solution-coated from a ketone solvent over the conducting layer. This protective coating was dried at 95° C. and cured at 100° C. for 4 minutes. This layer serves as a barrier between the cuprous iodide layer and the silver halide photographic emulsion layer. Over the protective layer a thin subbing of cellulose nitrate (from a 1.4% solution in methanol) was applied to improve adhesion. A gelatin subbing layer and a gelatin-silver halide photographic emulsion of the Lippman type were coated over this subbing layer. Despite the fact that the conducting coating was covered by four layers of insulating material, surface resistivity at the outer surface was still considerably less than 10^{11} o.p.s. Without the conductive coating, surface resistivity on the outer coated surface would be more than 10^{11} ohms per square. This film is especially suitable for direct electron recording, which is usually done in vacuum. An example, of such use is as a recording film in an electron microscope. Low surface resistivity prevents accumulation of electrons and consequent image distortion during electron beam exposure. A polyester film support (e.g. Mylar) is preferred for direct electron recording because of its exceptional stability in vacuum. In making films for use in vacuum it is advantageous to thoroughly remove solvents from each successive coating. Residual volatile material can cause film damage when the film is used in vacuum.

Alternatively, a photographic film may be prepared as in Example 14 but with the subbing and photographic emulsion layers coated on the side of the support opposite the conductive coating. Thus the conductive coating serves as an antistatic backing on the photographic film. The barrier layer may be omitted in such embodiments, but is useful to protect the conductive layer from processing solutions. A thin protective layer (e.g. 1–2 microns) over the conductive coating will not interfere with the antistatic function even though this overcoat is of an insulating material.

The support with conductive layer and with or without the protective overcoat as made in Example 14 may also be used as a conductive base for an electrophotographic element. Thus a photoconductive insulating layer such as a dispersion of photoconductive zinc oxide or photoconductive organic compound in an insulating resin binder may be coated on the conductive base of Example 14 to make a photoconductive recording element.

Example 15

A direct electron recording film having a conductive layer coated over the sensitive emulsion layer is illustrated as follows.

A subbed polyethylene terephthalate film support was coated with a fine grain, high resolution, low gel silver bromoiodide emulsion composition containing 80 grams of gelatin per mole of silver, a Saponin coating aid, muchloric acid gelatin hardener and a preservative at a coverage of 252 mg. silver per square foot. This sensitive layer was overcoated with a hardened gelatin layer containing 90.8 mg. gelatin per square foot. A conductive coating consisting of 7.5 g. of cuprous iodide, 0.75 g. of Gelva C3V20 binder and 491.7 grams of acetonitrile was coated over the hardened gelatin layer at a coverage of 5 mg. of cuprous iodide per square foot (a dry thickness of about 0.1 micron). The coating was dried at ambient air temperature. The outer coating was conductive and was essentially clear and transparent. Gelva C3V20 is a copolymer of poly(vinyl acetate) and crotonic acid. The outer conductive coating is effective in preventing accumulation of static charge during exposure of the film to a direct electron beam. The conductive coating is permeable by photographic developing and fixing solutions. The subbing on the Estar support is a terpolymer of vinyl methacrylate, vinylidine chloride and itaconic acid.

Example 16

A transparent electrostatic recording film is prepared as follows.

A 5 mil polyethylene terephthalate film support was coated with a coating solution containing 1 gram of Formvar 7/70, 3.3 grams of Mondur CB–75 and 6 grams of cuprous iodide dissolved in 242 grams of acetonitrile. Formvar 7/70 is a poly(vinyl formal) resin containing 5–7% poly(vinyl alcohol) and 40–50% poly(vinyl acetate), made by Shawinigan Resin Co. Mondur CB–75 is a poly isocyanate crosslinking agent containing 75% solids having about 13% isocyanate and 1% free tolylene diisocyanate in ethyl acetate, made by Mobay Chemical Company. The solution was coated at a coverage of 5 mg. per square foot and dried in air at room temperature leaving a conductive coating on the film support. This conductive coating was then overcoated at a coverage of 0.4 gram per square foot with a solution of 10 grams Butvar B–76 resin in 90 grams of toluene and the solvent was evaporated in the air at room temperature leaving a high dielectric coating. Butvar B–76 is a poly(vinyl butyral) resin containing 9–13% poly(vinyl alcohol), 2.5% poly(vinyl acetate) and 84.5–88.5% poly(vinyl butyral) made by Shawinigan Resin Co. This overcoat is sufficiently insulating to prevent leakage of electrostatic charge through the overcoat to the conducting layer. This film is useful in electrostatic printing processes such as those described in U.S. Patent No. 2,933,556 to C. W. Barnes, Jr. patented May 13, 1957, U.S. Patent No. 2,919,170 to Herman Epstein patented December 29, 1959, U.S. Patent No. 2,931,688 to F. T. Innes et al. patented December 30, 1954, etc.

It will be understood that modifications and variations may be made within the scope of the invention as described above and as defined in the following claims.

I claim:

1. A method of making an electrically conductive coating having surface resistivity in the range from 10^{-2} to 10^{11} ohms per square and comprising a metal-containing semiconductor compound dispersed in an electrically insulating film-forming binder material, said method comprising the steps of solubilizing said semiconductor compound by means of a complexing agent that forms a soluble complex with the semiconductor compound and dissolving the solubilized semiconductor compound in a volatile liquid solvent, dissolving said binder material in said solution, coating the solution onto a support, evaporating the volatile solvent from the coated solution, and removing the complexing agent from the coating to leave a residual continuous film of said insulating binder material having dispersed therein particles of size less than 0.1 micron of said semiconductor compound.

2. A method of making an electrically conductive coating having surface resistivity in the range from 10^{-2} to 10^{11} ohms per square and comprising a metal-

containing semiconductor compound dispersed as a complex in an electrically insulating film-forming binder material, said method comprising the steps of solubilizing said semiconductor compound by means of a complexing agent that forms a semiconducting complex with the semiconductor compound and dissolving the complexed semiconductor compound in a volatile liquid solvent, dissolving said binder material in said solution, coating the solution onto a support, and evaporating the volatile solvent from the coated solution to leave a residual continuous film of binder material having dispersed therein particles of size less than 0.1 micron of the semiconducting complex formed by the complexing agent with the semiconductor compound.

3. The method of claim **1** wherein said complexing agent is removed from the coating with said solvent by means of evaporation.

4. The method of claim **1** wherein, after the solvent has been evaporated, said complexing agent is removed from the coating by means of a selective solvent for the complexing agent which is not a solvent for the binder and semiconductor compound.

5. The method of claim **1** wherein said semiconductor material is silver iodide.

6. The method of claim **2** wherein said semiconductor material is silver iodide.

7. The method of claim **1** wherein said semiconductor material is cuprous iodide.

8. The method of claim **2** wherein said semiconductor material is cuprous iodide.

9. The method of claim **3** wherein said complexing agent is a liquid volatile solvent for the complex which it forms with the semiconductor compound.

10. The method of claim **9** wherein said complexing agent is a volatile liquid nitrile compound.

11. The method of claim **1** wherein said complexing agent is a member selected from the group consisting of alkali metal halides, ammonium halides, and hydrogen halides and said volatile liquid solvent comprises a volatile ketone liquid.

12. The method of claim **2** wherein said complexing agent is a member selected from the group consisting of alkali metal halides and ammonium halides and said volatile liquid solvent comprises a volatile ketone liquid.

13. A manufacture comprising a support and coated thereon a conductive coating having surface resistivity in the range from 10^2 to 10^{11} ohms per square, said conductive coating comprising a film-forming binder material having dispersed therein at least 15 volume percent of a semiconductor compound dispersed as particles of size less than about 0.1 micron.

14. A manufacture comprising a support and coated thereon a conductive coating having surface resistivity in the range from 10^2 to 10^{11} ohms per square, said conductive coating comprising a film-forming binder material having dispersed therein at least 15 volume percent of silver iodide dispersed as particles of size less than about 0.1 micron.

15. A manufacture comprising a support and coated thereon a conductive coating having surface resistivity in the range from 10^2 to 10^{11} ohms per square, said conductive coating comprising a film-forming binder material having dispersed therein at least 15 volume percent of cuprous iodide dispersed as particles of size less than about 0.1 micron.

References Cited by the Examiner

UNITED STATES PATENTS

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FOREIGN PATENTS

586,322	3/1947	Great Britain.

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