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[54] **METHOD OF TREATING NON-CONDUCTING AND POORLY CONDUCTING FILM**

[76] Inventors: **Hiroshi Sakai,** 23 Hakuraku, Kanagawa-ku, Yokohama-shi, Kanagawa-ken; **Kazuo Igarashi,** 128 Suwacho, Hachioji-shi, Tokyo; **Takuji Yamamoto,** 195 Fujimicho, 6-chome, Tachikowa-shi, Tokyo; **Norimichi Matsuo,** 16-25 Shiyoan, 3-chome, Suginami-ku, Tokyo, all of Japan

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[56] **References Cited**

UNITED STATES PATENTS

3,620,840	11/1971	Schroeder	117/227
3,514,326	5/1970	Stow	117/227
3,475,213	10/1969	Stow	117/227

Primary Examiner—Alfred L. Leavitt
Assistant Examiner—M. F. Esposito
Attorney, Agent, or Firm—Jay M. Cantor

[57] **ABSTRACT**

The disclosure relates to an applied film of a non-conducting lacquer comprising a mixture of non-conducting or weakly conducting metallic powder with a lacquer base wherein the mixture is changed into a good conductor by applying a conductivating agent in the presence of a solvent. The method lends itself to the manufacture of plate electrodes for batteries, conducting yarn, conducting nets, electrical circuits, heating elements, charge accumulation prevention shields, radio wave shields, etc. from films of a non-conducting or weakly conducting lacquer.

33 Claims, No Drawings

METHOD OF TREATING NON-CONDUCTING AND POORLY CONDUCTING FILM

This invention relates to a method of treating a non-conducting or weakly conducting film of applied lacquer comprising a lacquer base to which a non-conducting or weakly conducting metallic powder is added, so that said film becomes an excellent conductor. The invention also relates to methods for manufacturing products by means of the above described treating method.

The method of making a conductive lacquer by mixing gold, silver, or carbon powder, the surface of which is free from oil, grease or dust etc. is well known in the art. The high cost of gold and silver, prohibits the large quantity commercial use of this type of conductive paint, and such paint is therefore limited to special uses. Carbon powder is low in cost, however, it has the drawback of requiring large amounts thereof in the mix to obtain good conductivity. This results in a thick film prone to cracking or peeling with vibration and mechanical shocks, which results in a loss in conductivity. Furthermore, this dense lacquer is difficult to apply, particularly when fine lines are required. In accordance with the present invention there is provided a new and novel method free from the above described defects.

Briefly, in accordance with the present invention, an applied film of a non-conducting lacquer comprising a mixture of non-conducting or weakly conducting metallic powder with a lacquer base is changed into a good conductor by applying a conductivating agent in the presence of a solvent. The method lends itself to the manufacture of, plate electrodes for batteries, conducting yearn, conducting nets, electrical circuits, heating elements, charge accumulation prevention shields, radio wave shields, etc., from films of a non-conducting or weakly conducting lacquer.

It is therefore an object of this invention to provide a simple method of making conductive film of lacquer which comprises a lacquer base mixed with a non-conducting or weakly conducting low cost metal powder and which when applied is non-conducting or weakly conducting.

It is another object of this invention to provide a method of fabricating parts for electrical appliances such as plate electrodes for batteries, conducting yarn, conducting nets, electrical circuits, heating elements, charge accumulation preventive shields, radio wave shields and the like by applying a non-conducting or weakly conducting lacquer containing non-conducting or only weakly conducting metallic powder, to form a film or films, and thereafter making the film into an excellent conductor by a simple conductivating process.

The above objects and still further objects of this invention will immediately become apparent to those skilled in the art after consideration of the following preferred embodiments thereof, which are provided by way of example and not by way of limitation.

The lacquer used in this invention comprises a mixture of a suitable binder, a solvent and metallic powder. The metallic powder is in the state in which it was produced, and has a film of oxide, sulfide and other films formed by contamination of the metal which make the metallic powder totally non-conducting or only weakly conducting. Thus, the lacquer and the lacquer film are made non-conducting or only weakly conducting.

The methods for teating the film in the presence of a solvent with a conductivating agent such as: acids containing halogens, halogenides, halogen gases, phosphates, carboxylic acids, comprise the following:

1. A method of painting the film with a conductivating liquid consisting of a solution of the conductivating agent mixed with a solvent.
2. A method of treating the film only or the film applied to a base plate by dipping in a solution of the conductivating agent mixed with a solvent.
3. First softening and swelling the film by treating with a solvent and then placing the film in the gaseous atmosphere of the conductivating agent.

In the above methods, the film is softened and swelled by the introduction of the solvent while at the same time the conductivating agent enters into the film. Alternatively, the conductivating agent is applied to the surface which has been softened and swelled by the solvent, mixes with the solvent and penetrates the film surface. The conductivating agent is thus able to react with the non-conducting film formed on the metallic powder surface to remove this film and thereby render the metallic powder conductive. The solvent in the film is dried off and the film hardened. This hardening process compresses the now conducting metallic powder to increase the conductivity and forms an outside coating to protect the metallic powder from the atmosphere, thus preventing the formation of non-conducting films on the powder surface and serving to stabilize the conductivity of the film. The process whereby the metallic powder is rendered conductive has not yet been theoretically clarified.

When a non-conducting film with a specific resistance of 10^8 to 10^{11} ohm-cm is rendered conductive the specific resistance becomes 10^{-5} to 10^2 ohm-cm, and the specific resistance shows hardly any change caused by ageing. It is desirable to coat the film surface with a protective plastic coating or an electro-plated metal film in order to isolate the film from the atmosphere and moisture.

The metallic powder used is in the state in which it was produced, and has a non-conducting or weakly conducting film of oxide, sulfide, and other films, which renders the powder non-conducting or only weakly conducting. The metallic powder size is of from 20 to 400 mesh, and may be copper, brass, phospher bronze, other copper alloys, nickel, tin, zinc, lead, iron, aluminum, etc. The powder can be of a single metal or a mixture of two or more different metals. Metallic powder in flake form exhibits better conductivity characteristics.

The binders used to form the lacquer are synthetic rubbers such as SBE, NBR, Neoprene etc., or plastics such as polyvinyl alcohol, polyvinyl chloride, polyethylene, polypropylene, polyvinyl acetate, polyimide, polyamide, polyester, polyurethane, nylon, polyvinylchloride-polyvinylacetate copolymer, etc. or acethyl cellulose etc. These are used singly or with two or more mixed together.

The solvents used for these binders are organic solvents such as methylethylketone, toluene, ethylacetate, tetrahydrofuran, dimethylacetoamide, methylene chloride, acetone, methanol, ethanol etc., and these are used singly or with two or more mixed together.

The ratio for mixing the metallic powder, the binder, and the solvent is within the range of 40 to 5, 45 to 5 and 90 to 15 respectively. The amount of solvent is

controlled to enable the formation of a film with a thickness of from 5 to 3000μ.

The conductivating agents are halogenic acids such as hydrochloric acid, hydrobromic acid, hydroiodic acid etc., halides such as aluminum chloride, chlorosulfonic acid, monochloraecetic acid, silicon tetrachloride, etc., halogen gases such as, chlorine gas, bromine gas, hydrogen bromide gas, hydrogen iodide gas, etc., phosphoric acids such as, orthophosphoric acid, pyrophosphoric acid, meta phosphoric acid, phosphorus trioxide, phosphorus tetraoxide, phosphorus acid, hypophosphorus acid, etc., or carboxylic acid represented by the formula $C_nH_{2n+1}COOH$ where preferably n=1 to 4, such as, formic acid, acetic acid, propionic acid, butyric acid, valeric acid, methylethyl acetic acid, trimethylacetic acid etc.

The conductivating agent is used singly or with two or more of the same group in a mixture. The concentrations of the acids are not specified, however, a concentration for saturation or close to saturation is recommended for easy handling and quick time for the reaction.

The solvents suitable for the conductivating agents such as halides, phosphoric acids, carboxylic acids, are, for example, organic solvents which soften and swell the binder of the lacquer such as, methylethylketones, acetone, tetrahydrofuran, ethanol, benzene, toluene, methanol, etc. These are used singly or with two or more in a mixture. Water or water mixed with a detergent can be used as another solvent. The amount of conductivating agent mixed with the solvent is not specified and depends on the properties of the binder and the metallic powder. A preferable ratio, however is a concentration of from 0.5 to 10 mols. When the quantity of solvent is lessened, the length of time required for the conductivating reaction becomes longer and it becomes difficult to obtain an even distribution of the conductivity. The time required for the reaction depends on the process conditions, the properties of the metallic powder, of the binder and of the solvent. The time required ranges from 1 second to 10 hours, however, for most cases from 5 seconds to 1 hour is sufficient. When halogen gases are used, the time ranges from 3 seconds to 8 hours and for most cases from 3 seconds to 1 hour. When the reaction is made to take place under heated conditions where the temperature is raised to from 50° to 100°C., the reaction time is shortened considerably.

The following description explains how applications of this invention such as, electrode plates for batteries, conductive yarn, conductive nets, and electrical circuits can be fabricated.

In fabrication of electrode plates for batteries, the base plates for electrodes are formed of molded plastics such as polyethylene, polypropylene, polyester, polyvinyl chloride, polystyrene, nylon, etc. The shape is of the well known type, for instance grid-like base plates, or box-like base plates. The metallic powder mixed with the lacquer which is applied to the base plate should be of one kind or a mixture of several metallic powders of the same family from the stand-point of electrolysis of the metal. Furthermore, it should be of the same metal or of the same family of metals as the metal used for electroplating the outside surface. The amount of metallic powder mixed in the lacquer should be from 20 to 40 percent by volume. The metallic powder should be mixed with the binder and solvent to a viscosity where when dipped in the lacquer a coat of from 100 to 500 gr/cm^2 will adhere to the base plate. The lacquer film adhering to the base plate is dried and hardened after which it is treated by the afore-described conductivating agent to become a conductive film with a specific resistance of from 10^{-2} to 10 ohm-cm.

In fabrication of conductive yarn and conductive nets, the base yarn is made of natural fibers, artificial fibers, synthetic resin fibers, glass fibers or mineral fibers, either spun into yarn or composed of single strand fibers or flat fibers of plastic etc.

The base net can be made by weaving the afore-described base yarn, by molding plastics, by punching out plastics, plastic films, foam plastic sheets, non-woven cloth, or kraft paper etc. to form nets.

The lacquer is applied to the base yarn to form a film with a thickness of from 50 to 400μ and is applied to the base net to form a film with a thickness of from 100 to 500 gr/m^2.

The lacquer film applied to the base yarn and base net is dried and hardened after which it is treated by the liquid conductivating agent to make the film conductive. The resistance of the yarn is from 10^{-2} to 10^2 ohm/meter whereas the resistance for the net is from 10^{-2} to 10^{-1} ohm/5cm. × 20cm. These conductive yarns and nets are used as anti-static shields, radio radiation shields, heating elements, yarn for electroplating, nets for electro-plating, etc.

In the fabrication of electrical circuits, the required circuit is printed on various kinds of plastic film or sheets, woven cloth, non-woven cloth, papers etc., by known printing methods such as photo-gravure printing, silk-screen printing, etc. The thickness of the lacquer film which forms the circuit can be changed according to the current requirements of the circuit and should be from 10 to 200 μ when dried. After drying and hardening, the printed lacquer film is rendered conductive by the afore-described conductivating liquid. The specific resistance of the circuit should be from 10^{-5} to to 10^{-2} ohm-cm. Such conductive circuits can be used as heating elements, static charge preventive shields, underlays for electro-plating, circuits for various electrical appliances, etc.

The following is a description of several example applications of this invention:

EXAMPLE 1

A lacquer consisting of metallic copper powder of 200 mesh, 25 percent by volume, mixed with synthetic rubber SBR, 25 percent by volume, and toluene 50 percent by volume, is coated to a thickness of 80 μ on a sheet of insulating material, after which it is dried and then dipped for 5 seconds in a conductivating liquid consisting of hydrochloric acid 10 percent by weight, toluene 40 percent by weight and ethyl alcohol 50 percent by weight. The film, after drying for 30 minutes at 80°C., has a specific resistance of 3 × 10^{-4} ohm-cm. The film had a specific resistance of 6 × 10^8 ohm-cm before it was treated.

EXAMPLE 2

A lacquer consisting of metallic brass powder of 150 mesh, 10 percent by volume, mixed with saturated polyester plastic 20 percent by volume, and methyethylketone 70 percent by volume is coated onto a sheet of insulating film to a thickness of 75 μ, and after dry-

ing is painted with a liquid conductivating agent, described hereinbelow, to a thickness of 10g/m², after which it is heated to 120°C. for 10 minutes and dried. The conductivating agent consists of hydrofluoric acid 7 percent by weight, and methylethylketone 93 percent by weight. The specific resistance of the applied conductive lacquer film is 5×10^{-5} ohm-cm. whereas, before conductivating, the specific resistance of the lacquer film was 2×10^{9} ohm-cm.

EXAMPLE 3

A lacquer consisting of metallic copper powder of 350 mesh, 15 percent by volume, mixed with metallic zinc powder of 200 mesh, 10 percent by volume, polyamide plastic 25 percent by volume and dimethylacetamide 50 percent by volume, is coated on to an insulating film to a thickness of 100 μ and dried. A conductivating liquid consisting of, chlorosulfonic acid 5 percent by weight and methylethylketone 95 percent by weight, is applied to the above lacquer film at the rate of 50 g/m², then is dried by exposing to the room atmosphere (20°C. for 2 hours). The resistance of the conductive film is 8×10^{-5} ohm-cm. whereas before treatment the film had a specific resistance of 3×10^{10} ohm-cm.

EXAMPLE 4

A lacquer consisting of metallic tin powder of 250 mesh, 20 percent by volume, mixed with cellulose acetate plastic, 20 percent by volume, and acetone 60 percent by volume, is coated onto an insulating film to a thickness of 80 μ and dried. A conductivating liquid consisting of silicon tetrachloride, 3 percent by weight, and acetone 97 percent by weight is prepared, and the above insulating film with the lacquer is dipped therein for 15 seconds, after which it is dried at 150°C. for 20 minutes. The specific resistance of the film is 7×10^{-4} ohm-cm. whereas before treatment the film showed a specific resistance of 2×10^{10} ohm-cm.

EXAMPLE 5

A lacquer consisting of, metallic copper powder of 150 mesh, 7 percent by weight volume, metallic copper powder of 250 mesh, 8 percent by volume, urethane plastic, 35 percent by volume, tetrahydrofuran, 50 percent by volume, is coated on to an insulating film to a thickness of 120 μ and dried. After the film is dried, ethyl alcohol is applied to the surface at the rate of 200 g/cm², after which hydrobromic acid is applied at the rate of 20g/cm². After drying at 30°C. for 25 minutes, the specific resistance of the film was 2×10^{-5} ohm-cm. The film showed a specific resistance of 7×10^{8} ohm-cm before treatment.

EXAMPLE 6

A lacquer consisting of metallic copper powder of 100 mesh, 12.5 percent by volume, vinyl chloride plastic, 12.5 percent by volume, and tetrahydrofuran, 75 percent by volume, is coated to a thickness of 3 mm on the surface of a peelable sheet of paper and after drying, the paper is removed. Then the film is treated with a conductivating fluid consisting of aluminum chloride, 15 percent by weight, tetrahydrofuran, 85 percent by weight, by dipping in the fluid for 15 seconds, after which it is dried at 80°C. for 45 minutes. The dried film shows a specific resistance of 8×10^{-6} ohm-cm whereas before treatment the specific resistance was 8×10^{9} ohm-cm.

EXAMPLE 7

A lacquer consisting of metallic copper powder mesh of 200 mesh, 10 percent by volume, mixed with metallic tin powder of 200 mesh, 10 percent by volume, saturated polyester plastic, 30 percent by volume, toluene, 35 percent by volume, and methylethylketone 15 percent by volume, is applied to a sheet of peelable paper to a thickness of 250 μ, and, after drying, the paper-backing is peeled and the resultant film is dipped in a conductivating fluid. The conductivating fluid consists of hydrochloric acid, 10 percent by weight, and methylethylketone 90 percent by weight. After dipping in the fluid for 10 seconds, the film is removed and dried for 20 minutes at a temperature of 100°C. The resultant specific resistance is 4×10^{-4} ohm-cm. whereas before treatment, it was 6×10^{9} ohm-cm.

EXAMPLE 8

A lacquer consisting of metallic copper powder of 150 mesh, 8 percent by volume, mixed with polyvinylchloride, 18 percent by volume, and tetrahydrofuran, 74 percent by volume, is coated on to an insulating film to a thickness of 120 μ. After drying, the entire surface is treated by coating with a solvent consisting of ethyl alcohol, 90 percent by weight, and water 10 percent by weight, at a rate of 20g/m². After treating with the solvent, the film is exposed to chlorine gas at 20°C. for 15 minutes and then dried at 50°C. for a period of 10 minutes. The specific resistance of the treated film was found to be 5×10^{-4} ohm-cm., whereas for the untreated film, it was 3×10 ohm-cm.

EXAMPLE 9

A lacquer consisting of metallic copper powder of 250 mesh, 15 percent by volume, mixed with saturated polyester, 25 percent by volume, toluene, 40 percent by volume, and methylethylketone 20 percent by volume, is coated on to an insulating film to a thickness of 6 μ. After drying, the film is treated with a conductivating liquid consisting of orthophosphoric acid, 98 percent by weight, and water, 2 percent by weight, by dipping therein for 5 minutes, after which it is removed and dried at 110°C. for 45 minutes. The specific resistance after treatment is 6×10^{-4} ohm-cm, whereas the specific resistance before treatment was 5×10^{9} ohm-cm.

EXAMPLE 10

A lacquer consisting of metallic brass powder of 150 mesh, 20 percent by volume, mixed with synthetic rubber SBR, 25 percent by volume and toluene, 55 percent by volume, is coated on to a sheet of insulating material to a thickness of 100μ and dried. A conductivating fluid consisting of phosphorus acid, 10 percent by weight, and toluene, 90 percent by weight, is applied to the entire surface at a rate of 25g/m². The treated film is dried at 50°C. for 50 minutes. The specific resistance of the dried film is found to be 4×10^{-4} ohm-cm, whereas for the untreated film it was 7×10^{9} ohm-cm.

EXAMPLE 11

A lacquer consisting of 200 mesh copper powder, 10 percent by volume, 200 mesh brass powder, 10 percent

by volume, 250 mesh zinc powder, 5 percent by volume, mixed with vinyl chloride plastic, 25 percent by volume and tetrahydrofuran, 50 percent by volume, is coated on to an insulating sheet to a thickness of 50 μ, and dried. A conductivating fluid consisting of tetrahydrofuran is applied at the rate of 20g/m^2 after which another coating of metaphosphoric acid is applied at the rate of 2g/m^2. After drying under room conditions (20°C.) for 2 hours, the specific resistance is found to be 5×10^{-3} ohm-cm, whereas before treatment the specific resistance was 9×10^9 ohm-cm.

EXAMPLE 12

A lacquer consisting of copper powder, 10 percent by volume, 200 mesh copper powder, 10 percent by volume, saturated polyester plastic, 20 percent by volume and methylethylketone, 60 percent by volume, is coated on to a sheet of peelable paper to a thickness of 250 μ. After the applied coating is dry, the paper backing is removed. A conductivating fluid consisting of orthophosphoric acid, 10 percent by weight, and methylethylketone, 90 percent by weight, is prepared and the film is dipped in this fluid for 30 seconds after which it is dried at 120°C. for 30 minutes. The specific resistance of the film was found to be 3×10^{-4} ohm-cm after treatment, whereas before treatment the specific resistance was 8×10^8 ohm-cm.

EXAMPLE 13

A lacquer consisting of 150 mesh copper powder, 20 percent by volume, mixed with vinylchloride, 20 percent by volume and tetrahydrofuran 60 percent by volume is applied to a insulating sheet to a thickness of 50 μ and dried. A conductivating fluid consisting of, phosphoric acid, 90 percent by weight and water, 10 percent by weight, is applied at a rate of 35g/m^2 over the entire film surface. After drying at 110°C. for 30 minutes, the specific resistance was found to be 8×10^{-4} ohm-cm. whereas before treatment the specific resistance was 2×10^9 ohm-cm.

EXAMPLE 14

A lacquer consisting of 200 mesh powder, 15 percent by volume, 350 mesh phosphor bronze powder, 10 percent by volume, synthetic rubber NBR, 25 percent by volume, and toluene, 50 percent by volume, is applied on a sheet of insulating material to a thickness of 80 μ and dried. A conductivating fluid consisting of isopropyl alcohol is coated at the rate of 20g/m^2, after which propyonic acid is applied at the rate of 3g/m^2. After drying at 80°C. for 45 minutes, the specific resistance of the film was 3×10^{-3} ohm-cm whereas the specific resistance of the film before treatment was 6×10^9 ohm-cm.

EXAMPLE 15

A lacquer consisting of 150 mesh copper powder, 5 percent by volume, 300 mesh brass powder, 15 percent by volume, 200 mesh tin powder, 5 percent by volume, saturated polyester plastic, 20 percent by volume and methylketone, 55 percent by volume, is applied to a sheet of peeelable paper to a thickness of 500 μ, and removed from the paper after drying. The removed film is dipped for a period of 10 seconds in a conductivating fluid bath consisting of acetic acid, 50 percent by weight and methylethylketone 50 percent by weight. After drying at 120°C. for 45 minutes the specific resistance of the film was found to be 5×10^{-3} ohm-cm, whereas before treatment the specific resistance was 5×10^{10} ohm-cm.

EXAMPLE 16

A lacquer consisting of 100 mesh copper powder, 5 percent by volume, 200 mesh copper powder, 10 percent by volume, polyamide plastic, 25 percent by volume, and dimethyl acetoamide, 60 percent by volume, is applied to a peelable sheet of paper to a thickness of 250 μ. After drying, the paper is removed from the film. A conductivating fluid bath is prepared by mixing valeric acid, 80 percent by weight and tetrahydrofuran, 205 percent by weight, in which the film is dipped for 8 seconds. After natural drying (2 hours at 20°C.) the film was found to have a specific resistance of 5×10^{-4} ohm-cm, whereas the specific resistance before treatment was 6×10^9 ohm-cm.

EXAMPLE 17

A battery electrode base plate, stamped out of polyvinylchloride, 100mm × 150mm in size, 1 mm thick with vertical and horizontal grids of 1 mm × 1mm section, spaced 5mm × 10mm, is coated with lacquer consisting of 200 mesh lead powder, 25 percent by volume, polyvinylchloride, 25 percent by volume, and methylethylketone 50 percent by volume, by means of a brush at the rate of 150g/m^2. After the coating is dried and hardened, it is treated by dipping in a conductivating fluid bath consisting of hydrochloric acid, 10 percent by weight, and methylethylketone, 90 percent by weight for a period of 10 seconds at room temperature. After drying, the specific resistance of the battery electrode plate was 0.2 ohm-cm. A coating of metallic lead is applied to this conductive film to a thickness of 50 μ, by electroplating to complete the battery plate.

EXAMPLE 18

A battery electrode base plate, injection molded with polyethylene plastic, 100mm × 150mm in size, 2mm thick and with vertical and horizontal grids of 2mm × 2mm cross section, spaced 1mm × 1mm, is coated by dipping in a lacquer consisting of 200 mesh copper powder, 15 percent by volume, tin powder, 10 percent by volume, polyester, 30 percent by volume, and tetrahydrofuran, 45 percent by volume. The amount of lacquer applied to the grid is 200g/m^2. After drying, a conductivating fluid consisting of acetic acid, 50 percent by weight, and tetrahydrofuran, 50 percent by weight, is applied to the lacquer coating at a rate of 50g/m^2 and the coating is dried at room temperature. The resultant specific resistance of the coated plate is 0.1 ohm-cm at this stage, and a lead coating of 100 μ is applied by electroplating to complete the battery plate.

EXAMPLE 19

A battery electrode base plate stamped from polypropylene, 100mm × 150mm in size, 2mm thick, with vertical and horizontal grids of 2mm × 2mm cross section, spaced 2mm × 2mm is dip coated with lacquer consisting of 250 mesh brass powder. 30 percent by volume, polyethylene, 20 percent by volume, and dimethyl acetamide, 50 percent by volume, to be coated at a rate of 300g/m^2. After the lacquer coating is dried and hardened, it is treated by immersing in a conductivating fluid consisting of orthophosphoric acid, 20 percent by weight, and acetone, 80 percent by weight,

for 15 seconds. The specific resistance measured after the coating was dried and hardened at room temperature was 0.5 ohm-cm. This coating is electroplated with lead to a thickness of 50 μ to complete the battery plate.

EXAMPLE 20

Cotton yearn of size No. 20 (with a specific resistance of over 10^8 ohm-cm) is coated by a brush with lacquer consisting of 200 mesh copper powder, 25 percent by volume, polyvinyl chloride, 25 percent by volume, and methylethylketone, 50 percent by volume, to form a film with thickness of 200 μ. After drying, the coated yarn is dipped for 5 seconds in a bath of conductivating fluid consisting of hydrochloric acid, 10 percent by weight, and tetrahydrofuran, 90 percent by weight. The treated yarn is dried at room temperature and the coating is hardened. The specific resistance is 2×10^1 ohm-m, whereas the specific resistance of the untreated yarn was over 10^6 ohm-m.

EXAMPLE 21

Flat woven tape of polyethylene with a width of 7mm, weave 900 denier, and resistance of over 10 ohm-m, is dip coated with a lacquer consisting of 250 mesh brass powder, 10 percent by volume, 200 mesh copper powder, 10 percent by volume, 200 mesh nickel powder, 5 percent by volume, polyester, 25 percent by volume, and toluene, 50 percent by volume, by dipping in a bath of the lacquer to form a coating at the rate of 1.5g/m^2. After the coating is dried, a conductivating fluid consisting of phosphorus tetraoxide, 30 percent by weight and toluene, 70 percent by weight, is applied at the rate of 0.5g/m^2 and is dried by passing through a stream of air heated to 30°C. The resistance of the coated tape on drying is 6 ohm/m whereas it was 10^6 ohm/m before treatment.

EXAMPLE 22

A single strand yarn of nylon with a size of 2000 denier and a resistance of 10^{12} ohm/m is coated with lacquer consisting of 200 mesh tin powder, 20 percent by volume, synthetic rubber NBR, 25 percent by volume, toluene, 55 percent by volume, by a spraying machine to an average thickness of 100 μ, then dried. A conductivating fluid bath consisting of formic acid, 90 percent by weight, and water, 10 percent by weight, is prepared and the coated yarn is dipped in the bath for 10 seconds and dried by a stream of 50°C. heated air. The treated yarn has a resistance of 7 ohm/m whereas the untreated had a resistance of 10^6 ohm/m.

EXAMPLE 23

A net injection molded out of polypropylene plastic, 300 cm × 100 cm in size with vertical and horizontal grids — with 1 mm × 1mm cross section, spaced 10 mm × 16 mm, is dip coated with lacquer consisting of 350 mesh phosphor bronze, 10 percent by volume, 250 mesh zinc powder, 15 percent by volume, polyamide, 30 percent by volume, and dimethylacetamide, 45 percent by volume, to form a coat with a weight to area ratio of 3g/100cm^2. After the coating is dried and hardened, the coated yarn is dipped for 15 seconds in a conductivating fluid consisting of chlorosulfonic acid, 5 percent by weight, and methylethylketone, 95 percent by weight, and dried at room temperature. The resultant net has a resistance of 0.3 ohm/ 5cm × 20cm, whereas the net prior to treatment had a resistance of 10^{12} ohm/ 5cm × 20 cm.

EXAMPLE 24

A net woven to a mesh size of 5mm × 5mm with (monofilament) nylon yarn, 2000 denier in size, is coated with lacquer consisting of 150 mesh brass powder, 15 percent by volume, polyester, 25 percent by volume, and methylethylketone, 60 percent by volume, by brushing to apply a coat with a thickness of 150 μ. After the coating is dried, a conductivating fluid coating consisting of, acetic acid, 50 percent by weight, and methylethylketone, 50 percent by weight is applied at the rate of 3g/100cm^2, and it is dried at room temperature until the coating is hardened. The resistance of the treated net is 0.2 ohms/ 5cm × 20cm.

EXAMPLE 25

Injection molded polyethylene net with a mesh of 8mm × 8mm, thread diameter of 0.3mm, is coated with a lacquer consisting of 200 mesh copper powder, 15 percent by volume, 200 mesh brass powder, 15 percent by volume, polyethylene, 30 percent by volume, and tetrahydrofuran 40 percent by volume, by dipping in the lacquer to apply a coating at the rate of 3g/100cm^2. After the coating is dried, a conductivating fluid consisting of orthophosphoric acid, 20 percent by weight, a toluene, 80 percent by weight, is prepared and the coated net is dipped for 10 seconds in a bath of this fluid after which it is dried in a stream of air heated to 40°C. The resistance of the treated net is 0.1 ohm/ 5cm × 20cm, whereas the resistance before treatment was 10^8 ohms/ 5cm × 20cm.

EXAMPLE 26

An ink for photo-gravure printing consisting of 200 mesh copper powder, 10 percent by volume, 200 zinc powder, 10 percent by volume, 200 mesh brass powder, 5 percent by volume, polyester, 25 percent by volume and methylethylketone, 50 percent by volume, is used to print lines of 2mm width and thickness of 20 μ spaced 2mm to 3mm apart in circuit form, to a total length of 100 meters, on a polyester sheet 35 μ in the thickness by the well known photo-gravure printing process. After the printed pattern is dried, it is coated with a conductivating fluid consisting of acetic acid, 25 percent by weight and tetrahydrofuran, 75 percent by weight, at a rate of 175g/m^2 after which the coating is dried with an air stream heated to 50°C. The resistance of the total length of the printed conductor is 100 ohms. Lead wires are attached to the ends of the conductive pattern, and a protective insulating coating is applied over the entire surface to form a printed heater element. The resistance of the printed pattern was 10^{10} ohms prior to treatment.

EXAMPLE 27

An ink for photo-gravure printing consisting of 250 mesh copper powder, 25 percent by volume, polyethylene, 25 percent by volume, and toluene, 50 percent by volume, is used to print a pattern comprising 5 lines of width 3mm, length 1 meter and thickness 20 μ spaced 1 cm apart, on a film of polypropylene with a thickness of 25 μ, by the photo-gravure process. After the printed pattern is dried, a conductivating fluid consisting of hydrochloric acid, 5 percent by weight, and methylethylketone, 95 percent by weight, is prepared

as a bath, in which the coated film is dipped for a period of 5 seconds after which it is dried at room temperature. The resistance of one single conductor is 5 ohm whereas prior to treatment it was over 10^{10} ohm. The product when completed constitutes a flat cable.

EXAMPLE 28

An ink suitable for silk-screen printing, prepared by mixing, 200 mesh copper powder, 20 percent by volume, 200 mesh brass powder, 10 percent by volume, polyester, 20 percent by volume, and methylethylketone, 50 percent by volume, is used to silk-screen print a circuit pattern with a thickness of 40 μ and circuit conductor widths of from 1 to 2mm, on a hard phenol resin plastic board with a thickness of 1mm. After the pattern is dried, the entire printed board is dipped in a conductivating fluid bath consisting of orthophosphoric acid, 20 percent by weight, and dimethylacetamide 80 percent by weight, for a period of 10 seconds, and after drying in a stream of air heated to 40°C, the treated circuit pattern has a specific resistance of 4×10^{-5} ohm-cm, whereas before treating the specific resistance was over 10^{8} ohm-cm.

Though the invention has been described with respect to specific preferred embodiments thereof, many variations and modifications will immediately become apparent to those skilled in the art. It is therefore the intention that the appended claims be interpreted as broadly as possible in view of the prior art to include all such variations and modifications.

We claim:

1. A method of treating an electrically non-conductive or substantially non-conductive film of lacquer containing highly conductive metallic powder particles therein having their surfaces contaminated with a compound of the metal so as to impart to the film the electrically non-conducting or substantially non-conducting property, comprising the steps of:

rendering said film electrically highly conductive by applying to the film a conductivating agent which reacts with the particles to remove the compound therefrom and a solvent for the lacquer, and then drying said film.

2. A method as set forth in claim **1** wherein said conductivating agent is applied to said film as part of a mixture with said solvent.

3. A method as set forth in claim **2** wherein said conductivating agent is taken from the class consisting of acids containing halogens, halides, halogen gases, acids containing phosphorous and carboxylic acids represented by the formula $C_nH_{2n+1}COOH$ where n is in the range of about 1 to 4.

4. A method as set forth in claim **1** wherein said film is dipped in a fluid comprising said solvent and said conductivating agent.

5. A method as set forth in claim **4** wherein said conductivating agent is taken from the class consisting of acids containing halogens, halides, halogen gases, acids containing phosphorous and carboxylic acids represented by the formula $C_nH_{2n+1}COOH$ where n is in the range of about 1 to 4.

6. A method as set forth in claim **1** wherein said film is initially softened and swelled by the application of said solvent thereto, said conductivating agent then being applied to said film while in the softened and swelled condition.

7. A method as set forth in claim **6** wherein said conductivating agent is taken from the class consisting of acids containing halogens, halides, halogen gases, acids containing phosphorous and carboxylic acids represented by the formula $C_nH_{2n+1}COOH$ where n is in the range of about 1 to 4.

8. A method as set forth in claim **1** wherein said lacquer also includes a binder and a solvent, the range of metallic powder being about 40 to about 5 percent by volume, the range of binder being from about 45 to about 5 percent by volume and the range of solvent being from about 90 to about 15 percent by volume.

9. A method according to claim **1,** wherein the step of applying the conductivating agent to the film is carried out in an ambient temperature of between 50° to 100°C.

10. A method according to claim **1** followed by the step of drying the film.

11. A method according to claim **10** including, after the step of drying, the further step of applying to the film a protective coating which is impervious to moisture and the atmosphere.

12. A method according to claim **11** wherein the coating is a plastic material.

13. A method according to claim **11** in which the coating is metallic.

14. A method according to claim **13** in which the metallic coating is applied by electro-plating.

15. A method as set forth in claim **1** wherein said solvent is taken from the class consisting of methylethylketone, toluene, ethyl acetate, tetrahydrofuran, dimethylacetoamide, methylene chloride, acetone, methanol, ethanol and combinations thereof.

16. A method as set forth in claim **15** wherein said lacquer also includes a binder and a solvent, the range of metallic powder being about 40 to about 5 percent by volume, the range of binder being from about 45 to about 5 percent by volume and the range of solvent being from about 90 to about 15 percent by volume.

17. A method as set forth in claim **1** wherein said metallic powder particles includes a film of at least one of the metallic oxide and sulfide thereon, the powder size being in the range of 20 to 200 mesh, said metal being from the class consisting of copper, brass, bronze, copper alloys, nickel, tin, zinc, lead, iron, aluminum and mixtures thereof.

18. A method as set forth in claim **17** wherein said solvent is taken from the class consisting of methylethylketone, toluene, ethyl acetate, tetrahydrofuran, dimethylacetoamide, methylene chloride, acetone, methanol, ethanol and combinations thereof.

19. A method as set forth in claim **13** wherein said lacquer also includes a binder and a solvent, the range of metallic powder being about 40 to about 5 percent by volume, the range of binder being from about 45 to about 5 percent by volume and the range of solvent being from about 90 to about 15 percent by volume.

20. A method as set forth in claim **1** wherein said film is applied to one of electrical boards formed from plastic, natural fibers, synthetic fibers, plastic fibers, yarn produced by combining natural, synthetic and plastic fibers, stranded yarns, flat woven tape of plastic yarn, monofilaments of plastic cloth, net produced by weaving said fibers or by molding or stamping plastic material, plastic sheets, plastic film and cloth or nets made from paper.

21. A method as set forth in claim 20 wherein said solvent is taken from the class consisting of methylethylketone, toluene, ethyl acetate, tetrahydrofuran, dimethylacetoamide, methylene chloride, acetone, methanol, ethanol and combinations thereof.

22. A method as set forth in claim 20 wherein said metallic powder particles includes a film of at least one of the metallic oxide and sulfide thereon, the powder size being in the range of 20 to 200 mesh, said metal being from the class consisting of copper, brass, bronze, copper alloys, nickel, tin, zinc, lead, iron, aluminum and mixtures thereof.

23. A method as set forth in claim 22 wherein said solvent is taken from the class consisting of methylethylketone, toluene, ethyl acetate, tetrahydrofuran, dimethylacetoamide, methylene chloride, acetone, methanol, ethanol and combinations thereof.

24. A method as set forth in claim 1 wherein said conductivating agent is taken from the class consisting of acids containing halogens, halides, halogen gases, acids containing phosphorous and carboxylic acids represented by the formula $C_nH_{2n+1}COOH$ where n is in the range of about 1 to 4.

25. A method as set forth in claim 24 wherein said solvent is taken from the class consisting of methylethylketone, toluene, ethyl acetate, tetrahydrofuran, dimethylacetoamide, methylene chloride, acetone, methanol, ethanol and combinations thereof.

26. A method as set forth in claim 24 wherein said lacquer also includes a binder and a solvent, the range of metallic powder being about 40% to about 5% by volume, the range of binder being from about 45% to about 5% by volume and the range of solvent being from about 90% to about 15% by volume.

27. A method as set forth in claim 24 wherein said metallic powder particles includes a film of at least one of the metallic oxide and sulfide thereon, the powder size being in the range of 20 to 200 mesh, said metal being from the class consisting of copper, brass, bronze, copper alloys, nickel, tin, zinc, lead, iron, aluminum and mixtures thereof.

28. A method as set forth in claim 27 wherein said solvent is taken from the class consisting of methylethylketone, toluene, ethyl acetate, tetrahydrofuran, dimethylacetoamide, methylene chloride, acetone, methanol, ethanol and combinations thereof.

29. A method as set forth in claim 28 wherein said lacquer also includes a binder and a solvent, the range of metallic powder being about 40 to about 5 percent by volume, the range of binder being from about 45 to about 5 percent by volume and the range of solvent being from about 90 to about 15 percent by volume.

30. A method as set forth in claim 24 wherein said film is applied to one of electrical boards formed from plastic, natural fibers, synthetic fibers, plastic fibers, yarn produced by combining natural, synthetic and plastic fibers, stranded yarns, flat woven tape of plastic yarn, monofilaments of plastic cloth, net produced by weaving said fibers or by molding or stamping plastic material, plastic sheets, plastic film and cloth or nets made from paper.

31. A method as set forth in claim 30 wherein said solvent is taken from the class consisting of methylethylketone, toluene, ethyl acetate, tetrahydrofuran, dimethylacetoamide, methylene chloride, acetone, methanol, ethanol and combimations thereof.

32. A method as set forth in claim 30 wherein said metallic powder particles includes a film of at least one of the metallic oxide and sulfide thereon, the powder size being in the range of 20 to 200 mesh, said metal being from the class consisting of copper, brass, bronze, copper alloys, nickel, tin, zinc, lead, iron, aluminum and mixtures thereof.

33. A method as set forth in claim 32 wherein said solvent is taken from the class consisting of methylethylketone, toluene, ethyl acetate, tetrahydrofuran, dimethylacetoamide, methylene chloride, acetone, methanol, ethanol and combinations thereof.

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