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METHOD OF COATING

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This invention relates to a method of coating surfaces with cellulose esters in which firm adhesion is obtained by melting the contacting layer on to the surface approximately to the point of brittleness and overcoating with a compatible flexible layer or layers.

This application is a continuation-in-part of our application Serial No. 275,485 filed May 24, 1939. That application relates to the coating of objects by melting a layer of a cellulose ester thereon. It is desirable in that method that careful control be exercised so that the cellulose ester at its juncture with the surface of the object being coated is sufficiently melted to cause good adherence but has not been heated for a length of time which will cause brittleness of the coating.

An object of this invention is to provide a process for coating objects in which firm adherence and good covering is obtained but which does not demand the degree of control necessary in the operation of the process described and claimed in our earlier application. Another object of our invention is to provide coated objects especially of metal in which the coating is substantially impenetrable by moisture and by fairly high voltages of electricity such as 4,000 volts over a distance of at least 4 inches. Other objects will appear herein.

We have found that a coating of good adherence, protecting and insulating ability and flexibility is obtained by applying to an object a thin layer of a cellulose ester having a melting point of not more than 230° C. and a char point at least 40° C. above its melting point and subsequently subjecting the object to a temperature which will melt the ester (but at least 40° C. below its char point) for a time sufficient to thoroughly soften the ester and cause at least some brittleness upon cooling and subsequently overcoating with a layer of compatible ester to give a flexible coating on the object.

We have found that in spite of the brittleness tendencies of the prime layer of our invention, the overcoating with one or more compatible flexible layers gives a coated object which may be bent or twisted without breaking the coating adhering thereto.

The cellulose esters which are most useful for the initial or prime layer which is melted onto the surface to be protected should contain sufficient higher fatty acid radicals to assure a melting point of not more than 230° C. and should be of sufficient stability to have a char point at least 40° C. above its melting point, the char

point preferably being above 260° C. The esters stabilized by the method described and claimed in Malm and Kirton application Serial No. 254,492 filed Feb. 3, 1939, are particularly adapted for use in our method. The cellulose esters of this type which have been found to be most suitable are cellulose acetate butyrate containing over 25% butyryl, cellulose acetate propionate butyrates containing over 30% of propionyl and butyryl, cellulose propionate butyrates, cellulose propionates and cellulose butyrates. The type of esters which may be used for the melt coating are those which are disclosed as suitable in our application Serial No. 275,485 referred to above. It is also true here that it is preferred that the melt coating applied to the surface to be protected be free of plasticizer, although a limited proportion may be used, and free or substantially free of resin. The disclosure concerning the composition of the material used for the layer next to the surface of the object in our application Serial No. 275,485 holds good here. Here however the prime coating is heated until it shows at least a tendency toward the brittleness upon cooling, so that less care is necessary than in the operation of the process described in our earlier application.

The application of the first or prime layers to the surface to be protected involves first contacting it with the surface such as by applying thereto a solution of the cellulose ester in a volatile solvent which may be done by spraying, spreading or dipping. Any volatile solvent which upon evaporation deposits a fairly uniform coating of the ester on the surface to be coated may be used. Solvents such as acetone, methyl ethyl ketone, methylene chloride, ethylene chloride, or their mixture with a lower aliphatic alcohol, providing they are solvents of the cellulose ester, are suitable for use. Ordinarily the coating may be applied from a solution having a ratio of 4:1 to 10:1 of solvent to solid, although this is optional.

After the solvent has evaporated the coated object is subjected to a temperature above the melting point of the ester but at least 40° C. below its char point until the coating upon cooling has at least a tendency to brittleness. At a temperature of 20°-30° C. above the melting point of the ester a time of at least 2 minutes is used. A longer time such as 3 minutes is better but times of approximately 4-5 minutes are preferred at 20°-30° C. above the melting point of the ester. The upper limit of the range of time of heating is that above which the cellulose ester begins to decompose. The range of time of heating which

should be used in every case is bounded on the lower end, by the time when the coating exhibits a tendency to brittleness upon cooling and on the upper end by a time short of that where decomposition of the coating occurs. If an ester is used having a melting point of approximately 200° C., the preferred temperature of treatment for melting the initial coating is 220-230° C.

After the initial coating has been melted on to the surface to be covered an overcoating is applied thereto. This may be applied either by spraying on, or by dipping into, a solution of a compatible cellulose ester with or without plasticizer, in a volatile solvent. On the other hand the overcoating may be the result of applying thereon a molten cellulose ester composition as described and claimed in Malm and Salo application Serial No. 275,484 filed May 24, 1939.

The overcoating composition should be compatible with the initial or prime coating. If an overcoating is desired of a cellulose ester not compatible with the prime or initial coating, the use of several intermediate layers would be necessary. Malm application Serial No. 272,353 filed May 8, 1939, teaches how the combining of incompatible layers may be accomplished and the idea therein taught can be used where the overcoating desired is not compatible with the prime coating. It is preferred that the overcoating be thin such as .001-.004 inch.

The overcoating may consist of a composition comprising a stable organic acid ester of cellulose having a butyryl content of 30-55%, a viscosity of 5-75 seconds and 1-2 free hydroxyls per 24 carbon atoms in the cellulose unit and 5-30% (based on the weight of the ester) of a stable, high boiling, low vapor pressure, moisture resistant plasticizer. An example of a suitable cellulose ester is cellulose acetatebutyrate having a butyryl content of 35-38%, hydrolyzed one-third of the way down to the diester (1½ free hydroxyls per 24 carbon atoms in the cellulose unit) and which has a char point of 280° C.

The proportion of plasticizer used in the top layer depends on the hardness which is desired therein. If extreme hardness is desired the plasticizer may be entirely omitted and a composition made up substantially entirely of the cellulose ester and the solvent may be applied. If on the other hand a molten coating is to be applied the use of at least some plasticizer is desirable to facilitate the melting of the composition. Many of the stable, high molecular weight, moisture resistant, high boiling point, low vapor pressure plasticizers which are suitable for use in the overcoating fall within the following groups:

1. Esters of organic dibasic acids and aliphatic monohydric alcohols of 4-5 carbon atoms such as dibutyl sebacate, dibutyl phthalate, diamyl phthalate.

2. Esters of aliphatic long-chain acids and lower aliphatic monohydric alcohols, such as methyl stearate, butyl stearate and methoxyethyl stearate.

3. Esters of aliphatic long-chain alcohols and lower monobasic aliphatic acids such as cetyl acetate, cetyl propionate and cetyl lactate.

4. Esters of phosphoric acid and phenols or derivatives of phenols such as triphenyl phosphate and tricresyl phosphate.

Any of the solvents mentioned above as suitable for applying the initial coating may be employed for applying the overcoating providing it is a solvent for the composition to be applied.

The coating of an object in accordance with our invention may be carried out as follows:

A solution of one part of cellulose acetate butyrate having a butyryl content of 37.5% and an acetyl content of 13%, a melting point of 200° C. and a char point of 295° C. in 10 parts of ethylene chloride was sprayed on to the surface of a copper sheet to form a thin coating thereon. After evaporating the solvent from the coating the sheet was put in an oven having a temperature of 230° C. for 5 minutes. The sheet was removed from the oven and cooled. It was found to have a tightly adhering transparent coating, however bending of the sheet caused cracking in the coating.

One part of a mixture of cellulose acetate butyrate having a butyryl content of 37.5%, and an acetyl content of 13% and 10% (based on the cellulose ester) of dibutyl sebacate was dissolved in 6 parts of ethylene chloride and was sprayed on to the melt-coated copper sheet so as to form a thin coating over the coating which had been melted on. The sheet was subjected to mild heating to drive off the solvent. Upon cooling there was a transparent, non-tacky, firmly adhering coating on the copper sheet which did not crack or break upon bending or creasing.

Instead of applying the top coating from a solution of the ester in a volatile solvent, it may be applied from a molten cellulose ester composition. For instance a composition of 100 parts of a cellulose acetate butyrate having a butyryl content of 37.5% and an acetyl content of 13%, a fundamental cuprammonium viscosity of approximately 4 centipoises and a char point of approximately 300° C. and 30 parts of dibutyl sebacate, was melted by heating to approximately 190° C. and was spread over the melt-coated copper sheet so as to form a thin coating over the coating which had been melted on. A blade was used to assure an even spread and smoothness of surface. Upon cooling it was found that the metal sheet could be bent at will without cracking the protective coating thereon.

Our invention is directed primarily to the coating of metallic surfaces due to the high degree of adherence necessary and the ease with which ordinary coatings may crack or peel off therefrom. However, the coating of other surfaces such as glass, wood or any material which is not adversely affected by moderate heat, such as is necessary in affixing the prime or initial coating, is contemplated by our invention.

The coatings of our invention are especially valuable for electrical insulating purposes due to the absence of indentations or pinholes in the basic coating layer. Our invention contemplates electrical conductors coated as described. For instance bare wire may be given a protective coating in accordance with our invention forming a uniformly insulated electrical conductor. Other metal articles, some of which are useful electrically, may be coated in accordance with our invention such as telephone relays, coils and condensers or metal strips for use in electrical work. Also brass fittings which it is desired to protect may be coated in accordance with our invention.

Metal objects which are to be used for non-electrical purposes but which may be subjected to the effect of moisture and/or oil such as fishing equipment, corset stays, marine equipment etc. may be protected in this manner with good effect. Metal surfaces exposed to weather conditions such as automobile bodies may be protected in accord-

ance with our invention. Due to the moisture and oil resistant nature of our coatings and their permanence and the protection which they afford pigment incorporated therein they are eminently suited for this purpose. To further this protection a material which filters out ultra-violet rays can be incorporated in the top layers of the coating.

We claim:

1. A method of applying a flexible, strongly-adhering coating to a surface of an object which is not affected by moderate heat, which comprises applying thereto a thin layer of a cellulose ester having a melting point of not more than 230° C. and a char point at least 40° C. above its melting point, containing not more than 20% of a non-resinous plasticizer and substantially free of resin, subjecting the layer to a melting temperature 20-30° C. above the melting point of the ester for 4-5 minutes, cooling and after the layer has hardened, applying thereto at least one overcoating of good flexibility comprising a cellulose ester compatible with the base layer.

2. A method of applying a flexible, strongly-adhering coating to a surface of an object which is not affected by moderate heat, which comprises applying thereto a thin layer of a cellulose ester having a melting point of not more than 230° C. and a char point at least 40° C. above its melting point, containing not more than 20% of a non-resinous plasticizer and substantially free of resin, subjecting the layer to a melting temperature 20-30° C. above the melting point of the ester for 4-5 minutes, cooling and after the layer has hardened, applying thereto an overcoating from a so-

lution of a compatible cellulose ester in a volatile solvent.

3. A method of applying a flexible, strongly-adhering coating to a surface of an object which is not affected by moderate heat, which comprises applying thereto a thin layer of a cellulose ester having a melting point of not more than 230° C. and a char point at least 40° C. above its melting point, containing not more than 20% of a non-resinous plasticizer and substantially free of resin, subjecting the layer to a melting temperature 20-30° C. above the melting point of the ester for 4-5 minutes, cooling and after the layer has hardened, applying thereto a layer of a molten composition essentially consisting of a stable, low melting, cellulose ester and a minor proportion of a plasticizer.

4. A method of applying a flexible, strongly-adhering coating to a surface of an object which is not affected by moderate heat, which comprises applying thereto a thin layer of a butyric acid ester of cellulose having a melting point below 200° C. and a char point at least 40° C. above its melting point, containing not more than 20% of a non-resinous plasticizer and substantially free of resin, subjecting the layer to a temperature of 20-30° C. above its melting point for 4-5 minutes, cooling and after the layer has hardened, applying thereto a coating of a stable organic acid ester of cellulose having a butyryl content of 30-55%, a viscosity of 5-75 seconds and 1-2 free hydroxyls per 24 carbon atoms in the cellulose unit and containing 5-30% of a stable, high boiling, low vapor pressure, moisture resistant plasticizer.

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