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RESINOUS COATING

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This invention relates to resinous coatings and has for its object to provide an improved coating of this type and process for applying the same, which is cheaper and which does not involve the expense for equipment and time for getting rid of volatile solvents, yet which is capable of providing a product which at the same time is both flexible without being greasy and hard to the touch without being brittle.

The ideal characteristics for a resinous coating for paper and other foundations have long been known and such an ideal coating should possess a high gloss, transparency, be colorless, have a smooth surface which is both hard and flexible throughout the natural temperature range, should not penetrate a fibrous or porous foundation but yet should adhere tightly to it, should be waterproof, grease-proof and moisture-proof, should be odorless, strong, permanent and not likely to contaminate whatever is next to it, should be heat-sealing, should not cause curling of the foundations, and should have good dielectric properties.

Commercial coatings for paper have for years reached the closest approach to this ideal by means of resinous coatings containing a cellulose material applied with a volatile solvent. The cellulose material was desired in order to give the coating hardness. Most of the cellulose materials had melting points higher than the temperature at which paper chars, so that a volatile solvent was customarily used in applying the coating to a foundation. All such solvent applied coatings generally penetrated the foundation and required considerable expense not only for the volatile solvent but also for the necessary coating and drying machinery and the space necessary therefor. Complete removal of the solvent to prevent contamination was also difficult, if not impossible. Volatile solvent applied coatings generally cause a curling of the foundation on drying.

Efforts have been made to apply resinous coatings by means of heat and without the use of volatile solvents. One general objection applies to most of these efforts and that is that the coating is either too soft and tacky if flexible, or else if hard is brittle and not flexible at normal temperatures. The use of plasticizers of various kinds did not help because if the material were rendered flexible it also lost its hardness. The use of cellulose compounds to render the material hard could not be resorted to because of their high melting points and because many of the cellulose materials burned or charred before reaching their melting temperature. A material like ethyl-cellulose, which does not burn, made the material too viscous to be easily applied.

In short, there has been a lack of resinous materials which might occupy a mid position between softness with flexibility, on the one hand, and hardness with brittleness, on the other.

Shellac is a natural resinous material which occupies such a mid position, being both hard to the touch and flexible. Suggestions have been made for applying shellac to a foundation with the aid of heat and without any volatile solvent. However, there have been enough objections to shellac to prevent its ever having become commercial as a coating for packaging paper and analogous uses.

One difficulty is that shellac polymerizes quickly, making it hard to handle and if shellac is fully polymerized it is not heat-sealing. Tackiness at the higher natural temperatures is another objection to the widespread use of shellac as a coating for the purposes mentioned.

An effort was made to combine ethyl-cellulose with shellac to raise the blocking point and make it less tacky. This has been successful in eliminating the tackiness of shellac and has provided a coating which was both flexible and hard yet not brittle nor tacky. The ethyl-cellulose was found to inhibit or retard polymerization of the shellac, but this suggestion has possessed another difficulty in that it raised the viscosity to such an amount that the material became very difficult to apply.

In an effort to find a better material for use with shellac, resort was had to vinyl-acetate to retard polymerization and harden the shellac, without success. The next effort involved mixing the shellac with one of the synthetic resins comprising the reaction products formed by the esterification of turpinene-maleic anhydride with a polyhydric alcohol such as a suitable glycol and known on the market as Petrex #5. Owing to the necessity for using a plasticizer to avoid brittleness, the expedient was not found satisfactory because too tacky.

The next expedient tried was the elimination of shellac by the use of Petrex #5 with a softer material which was also a synthetic resin comprising the reaction products formed by the esterification of the turpinene-maleic anhydride with polyhydric alcohols such as a suitable glycol and known in the trade as Petrex #7.

A mixture of about 10 parts by weight of Petrex #7 with about 90 parts by weight of Petrex #5 was found to give a good practical coating. It

was found that this mixture occupied a mid position with shellac between flexibility and hardness and was both flexible and hard, the Petrex #7 apparently functioning as a plasticizer for the Petrex #5. This mixture was found to be in the nature of a synthetic shellac without possessing some of the disadvantages mentioned above for shellac as a coating. This mixture of the two Petrexes is easier to handle because it does not polymerize as rapidly as does shellac. Another advantage is that its blocking point is above that of shellac. It is lighter in color, that is, more nearly colorless, and practically odorless whereas shellac is not, even though it may have been commercially purified.

To make the foregoing mixture of the Petrexes more fluid for application by heat about 0 to 10 parts of almost any wax will be found desirable, such as carnauba, beeswax, paraffin wax, etc. Many of these waxes will also assist in enhancing the moisture-proof character of the coating. A little paraffin, for example, or carnauba wax will raise the blocking point of the material, i. e., elevate the temperature at which the material becomes tacky. To further enhance the heat-sealing character of the material, that is, its adhesiveness at elevated temperatures, some shellac may be added in quantity from 0 to 40 parts by weight.

Another composition for a desirable coating includes 10 to 30 parts by weight of Petrex #7, 70 to 90 parts by weight of Petrex #5 and about 5 parts by weight of paraffin or carnauba wax.

The addition of shellac to this foregoing formula will also be found useful where the best heat-sealing characteristics are desired and with the same proportions about 0 to 40 parts by weight of shellac can be added.

Another example of an almost ideal coating comprises 20 parts by weight of Petrex #7, 80 parts by weight of Petrex #5, 20 parts by weight of a purified shellac, free from arsenic, wax, dirt and other impurities, 5 parts by weight of carnauba wax, 5 parts by weight of paraffin wax and 5 parts by weight of stearic acid.

For example, either the last mentioned formula or the first, in which the coating consisted of 10 parts by weight of Petrex #7 and 90 parts by weight of Petrex #5, as well as the other mentioned coatings coming within this invention, include a number of advantages that make the coating of this invention close to the ideal coating. These possess a sharp melting point which means that when the melted material is applied to a fibrous foundation, like paper, it does not penetrate the foundation yet adheres and sets quickly before there has been substantial penetration; especially when a substantial amount of shellac is used the coating material may be heat-sealing at about 175° F. to 200° F. and at 280° F. the seal is such that a paper foundation will be ruptured when an attempt is made to separate the foundation from the coating. These coatings are flexible, hard, have blocking points above ordinary temperatures, are simple and inexpensive, and do not cause the foundation to curl because there is no wetting of the fibres in the foundation as occurs when a volatile solvent is used in the application of resinous coatings.

Instead of the waxes mentioned many other waxes, such as ceresin, candelilla, etc., may be used to enhance the fluidity of the material at the time of application by heat. The material possesses a higher gloss than do resinous coatings applied with the aid of volatile solvents.

Lowering the amount of Petrex #7 in the mixture reduces its flexibility whereas if the amount of Petrex #7 is greatly increased the material becomes tacky. Lowering the amount of Petrex #5 makes the material less brittle whereas increasing it has the opposite effect.

Paper or other fibrous foundations coated under this invention will possess a high gloss or sheen, and the coating will be transparent and colorless and have a smooth, hard surface. The coating is waterproof, moistureproof, and greaseproof, possesses substantial strength and flexibility, is odorless, has a satisfactory high blocking point, is stable or permanent, does not contaminate any materials placed next to it, does not have any residual odor, nor does it promote corrosion. While its dielectric properties have not yet been determined, it is believed they are satisfactory.

Due to the viscosity of this coating material it can be applied most readily with the aid of a coating machine using heated pressure rolls and a heated smoothing roll moving in the opposite direction as and at about half the linear speed of the foundation. This smoothing roll should be located close to the pressure rolls on account of the quick setting character of this coating material.

Instead of mixing the Petrex #5 with the Petrex #7 in the quantities specified, a single product equivalent in character to the mixture of Petrex #5 and Petrex #7 can be made by esterifying the turpinene-maleic anhydride with the two alcohols present in the proportion required. Where the appended claims refer to a mixture of Petrex #5 and Petrex #7, such an expression is intended to include also the single equivalent esterification product.

The exact composition of Petrex #5 and of Petrex #7 is unknown and can not be readily determined by analysis at this time. The packages containing such materials bear the Patent Numbers 1,993,027 and 1,993,032, but such patents are believed to include many other materials than the Petrex #5 and the Petrex #7. The manufacturer of the Petrexes has refused to disclose the composition or process of making either Petrex #7 or Petrex #5.

This invention should not be confused with a coating material like that described in the patent to Weingand, et al., 1,988,099, dated January 15, 1935. In order for the material of Weingand to be applied in the ways described it is necessary to use a great deal of wax because the cellulose compounds make the material otherwise too viscous. Such large quantities of wax cause more penetration of the foundation and give the coating a greasy feel. Weingand had no base product which is both flexible and hard. He used cellulose to try and bring his product into a mid ground position but in doing so acquired the disadvantages referred to. His #2 sample should be dark and not colorless and the high percentage of wax makes his coating more like a wax than like a resinous coating because, for example, it can be smoothed after being set, whereas the coating of this invention can not, but a wax coating can.

If the coating material of this invention is heated substantially above 320° F. the viscosity becomes so low that considerable penetration of the foundation occurs. The paper being coated can be run as high as 500 feet per minute and immediately wound up without blocking, which

gives an idea of how rapid is the cooling and setting and how sharp the melting point.

A specimen coating comprised of 10 parts by weight of Petrex #7, 90 parts by weight of Petrex #5, 20 parts by weight of shellac and 10 parts by weight of carnauba wax has been tested with the following results:

Softening range	137–233° F.
First indications of softening	137° F.
Drop falls from thermometer bulb at (melting point)	233° F.
Fluidity range	233–300° F.

Fluidity range based on viscosity determinations made by allowing a 10 millimeter steel ball to drop through five inches of the molten resin at temperatures as follows:

Temperature	Time for ball to drop
°F.	*Seconds*
230	135
240	113
250	37
275	11
300	2

The foregoing data indicate that the softening or blocking point for the coating tested is 137° F. The difference in viscosity of fluidity between 240° F. and 300° F. shows the comparative sharpness of the melting point.

Where the addition of parts of wax or shellac is mentioned, it is intended that there shall be one hundred parts by weight of the synthetic resin comprising the reaction products formed by the esterification of turpinene-maleic anhydride with polyhydric alcohols as is indicated in the examples given.

I claim:

1. The process of providing a high gloss thin surface film firmly adhering to a porous flexible foundation which includes melting a synthetic resin comprising the reaction products formed by the esterification of turpinene-maleic anhydride by polyhydric alcohols which is flexible, hard and non-blocking at normal temperatures, applying and smoothing the resin while melted to a surface of the flexible foundation at a temperature below that at which the fluidity of the resin is high enough to cause substantial impregnation of said foundation, and quickly solidifying the resinous film substantially entirely by cooling before the film has substantially impregnated said foundation.

2. The process of providing a high gloss thin surface film firmly adhering to a porous flexible foundation which includes melting a synthetic resin comprising the reaction products formed by the esterification of turpinene-maleic anhydride by polyhydric alcohols, which is flexible, hard and non-blocking at normal temperatures, has a blocking or softening point above about 120° F., does not polymerize with heat as rapidly as does shellac, is heat sealing at elevated temperatures, is fluid enough to be thinly applied to said foundation at below 320° F., and has a relatively sharp melting point, applying and smoothing the resin while melted to a surface of the flexible foundation at a temperature between about 250° F. and 320° F., solidifying the resinous film substantially entirely by cooling, and maintaining said film on the surface of said foundation without substantial impregnation during application by keeping the temperature of the melt below that at which its viscosity is low enough to cause substantial impregnation of the foundation and by means of the sharp melting point characteristic of the film.

3. The process of providing a high gloss thin surface film firmly adhering to a porous flexible foundation which includes melting not over about ten parts of a suitable wax and a synthetic resin comprising the reaction products formed by the esterification of turpinene-maleic anhydride by polyhydric alcohols, which is flexible, hard and non-blocking at normal temperatures, has a blocking or softening point above about 120° F., does not polymerize with heat as rapidly as does shellac, is heat sealing at elevated temperatures, is fluid enough to be thinly applied to said foundation at below 320° F., and has a relatively sharp melting point, applying and smoothing the resin while melted to a surface of the flexible foundation at a temperature between about 250° F. and 320° F., the fluidity of the material for application by heat having been raised by the addition of said wax, solidifying the resinous film substantially entirely by cooling, and maintaining said film on the surface of said foundation without substantial impregnation during application by keeping the temperature of the melt below that at which its viscosity is low enough to cause substantial impregnation of the foundation and by means of the sharp melting point characteristic of the film.

4. The process of providing a high gloss thin surface film firmly adhering to a porous flexible foundation which includes melting not over about forty parts of shellac, a synthetic resin comprising the reaction products formed by the esterification of turpinene-maleic anhydride by polyhydric alcohols, which is flexible, hard and non-blocking at normal temperatures, has a blocking or softening point above about 120° F., does not polymerize with heat as rapidly as does shellac, is heat sealing at elevated temperatures, is fluid enough to be thinly applied to said foundation at below 320° F., and has a relatively sharp melting point, applying and smoothing the resin while melted to a surface of the flexible foundation at a temperature between about 250° F. and 320° F., said material having its heat sealing character at elevated temperatures enhanced by the addition of said shellac, solidifying the resinous film substantially entirely by cooling, and maintaining said film on the surface of said foundation without substantial impregnation during application by keeping the temperature of the melt below that at which its viscosity is low enough to cause substantial impregnation of the foundation and by means of the sharp melting point characteristic of the film.

5. The process of providing a high gloss thin surface film firmly adhering to a porous flexible foundation which includes melting not over about ten parts of a suitable wax with not over about forty parts of shellac and with a synthetic resin comprising the reaction products formed by the esterification of turpinene-maleic anhydride by polyhydric alcohols, which is flexible, hard and non-blocking at normal temperatures, has a blocking or softening point above about 120° F., does not polymerize with heat as rapidly as does shellac, is heat sealing at elevated temperatures, is fluid enough to be thinly applied to said foundation at below 320° F., and has a relatively sharp melting point, applying and smoothing the resin while melted to a surface of the flexible founda-

tion at a temperature between about 250° F. and 320° F., said material having its fluidity and heat sealing character at elevated temperatures enhanced by the addition of said wax and shellac, solidifying the resinous film substantially entirely by cooling, and maintaining said film on the surface of said foundation without substantial impregnation during application by keeping the temperature of the melt below that at which its viscosity is low enough to cause substantial impregnation of the foundation and by means of the sharp melting point characteristic of the film.

6. The combination with a porous flexible foundation, of a high gloss thin film of synthetic resinous material firmly adhering thereto and without substantially penetrating the foundation, said film comprising reaction products formed by the esterification of turpinene-maleic anhydride by polyhydric alcohols, which is hard, flexible, has a blocking point not below about 120° F., is more slowly polymerized with heat than is shellac, and is capable of being applied to said foundation by heat without the aid of a solvent, at least one of said reaction products functioning as a plasticizer for another.

7. The combination with a porous flexible foundation, of a high gloss thin film of synthetic resinous material firmly adhering thereto, said film comprising reaction products formed by the esterification of turpinene-maleic anhydride by polyhydric alcohols which is hard, flexible, has a blocking point not below about 120° F., is capable of being applied to said foundation by heat without the aid of a solvent and of solidifying solely by cooling and has such an approximate sharp melting point that at about 250° F. a steel ball of 10 millimeters diameter takes about 37 seconds to drop 5 inches in the same resinous material as the film and takes about 2 seconds at 300° F. to drop through the same distance in the same material.

8. The combination with a porous flexible foundation, of a high gloss thin film of synthetic resinous material firmly adhering thereto, said film comprising reaction products formed by the esterification of turpinene-maleic anhydride by polyhydric alcohols which is hard, flexible, has a blocking point not below about 120° F., is adapted to polymerize more slowly with heat than is shellac, is capable of being applied to said foundation by heat without the aid of a solvent and of solidifying solely by cooling, and has such an approximate sharp melting point that at about 250° F. a steel ball of 10 millimeters diameter takes about 37 seconds to drop 5 inches in the same resinous material as the film and takes about 2 seconds at 300° F. to drop through the same distance in the same material.

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