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COATING COMPOSITION

John F. Socolofsky, Woodbury, and Henry G. Berger, Glen Rock, N. J., assignors to Socony-Vacuum Oil Company, Incorporated, a corporation of New York

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This invention relates generally to a method of preparing liquid coating compositions, and is more particularly concerned with liquid coating compositions of the wrinkle-finish type.

Conventional methods of preparing wrinkled paint or varnish films, generally involve the use of what are known in the art, as wrinkling oils and/or wrinkling resins. Most of the hard-drying oils and some semi-drying oils have been used in the preparation of wrinkled films and are classed as wrinkling oils. All non-drying oils are necessarily excluded from the wrinkling oil class due to the fact that oxidation plays an important part in the process of wrinkling. The wrinkling resins include congo, kauri, damar, coumarone, pontianak, manila, zanzibar, elemi, mastic, phenolic, alkyd and esters of congo, etc. Wrinkle-inhibiting resins include rosin, pyroxylin and gilsonite. Wrinkle finishes are produced by heat-bodying combinations of wrinkling oils and/or wrinkling resins at various temperatures and for varying lengths of time, depending upon the specific combination being treated. Partial bodying or what is known in the art as "under-cooking" is usually specified or implied, although much the same effect is obtained in most cases, by adding a raw wrinkling oil to a normally non-wrinkling, bodied oil-resin mixture.

Generally speaking, the ordinary paint and varnish thinners are used for dilution, although in some instances, the use of more volatile solvents is to be preferred. The use of the more volatile thinners is considered to be conducive to wrinkle formation due to the rapid surface-set which is possible when rapidly-evaporating thinners are employed.

Most of the wrinkle finishes contain also large proportions of metallic soap driers. Ordinarily, driers containing 2% by weight, of lead and 0.2% by weight, of manganese based on the oil-content, are used, and some compositions may include driers containing as much as 4% of lead and 1.4% of manganese.

The foregoing may be considered to be more or less, the standard constituents of coating compositions of the wrinkle-finish type. However, in specific cases, various other compounds are added to the main mixture, to accentuate the wrinkling or to alter the character of the wrinkling produced. Examples of these addition agents are fatty acids of drying oils, dibutyl phthalate, phthalic anhydride, specific pigments used as stabilizers, and high molecular-weight unsaturated triglycerides.

Accordingly, the liquid coating compositions of

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the wrinkle-finish type, may be stated to comprise the following ingredients:

1. Wrinkling varnish base: wrinkling oils and/or wrinkling resins.
2. Thinners.
3. Driers.
4. Additives where desired.

As is well known to those familiar with the art, various procedures on the manner of applying the films and/or diverse drying conditions have been suggested for achieving wrinkled finishes. Accordingly, it has been proposed to apply three different types of coatings, i. e., a ground coat, a design coat, and a protective coat; to use two wrinkling coats of different viscosities, the second being applied while the initial coat is still tacky; to apply a single heavy film in a somewhat uneven fashion with subsequent tilting of the coated surface so that sags or curtains occur; to use non-hiding pigments with the liquid, to furnish centers about which sagging takes place; to apply the film onto the surface with subsequent blowing of air across the surface to cause a slight flow or sagging; to subject the wet film to nitric acid fumes; to dry the film in an oxygen-rich atmosphere; to expose the film to infra-red radiation to accelerate drying; and to bake the film at various temperatures. In so far as we know, no process has been proposed whereby wrinkled finishes can be produced from drying oil-resin compositions, other than by baking the coated surface or by subjecting the film to other than atmospheric conditions during the drying process. The advantages of a coating composition that produces a film that will dry under ambient conditions, into a wrinkle finish are too manifest to merit enumeration.

We have discovered a liquid coating composition which when applied as a film onto a relatively non-porous surface, will dry under atmospheric conditions, and without baking or other treatment during or after application, to form a wrinkled and decorative finish.

We have found that wrinkling varnish bases may be produced by subjecting wrinkling oils or mixtures of wrinkling resins and wrinkling oils, to a controlled catalytic bodying treatment.

It is an object of the present invention, to provide a liquid coating composition. Another object is to provide a liquid coating composition of the wrinkle-finish type. A more specific object is to provide a liquid coating composition which when applied as a film on a relatively non-porous surface, will produce a wrinkled finish

upon drying under atmospheric conditions. A very important object of the present invention, is to afford a method of preparing a liquid coating composition capable of carrying out the foregoing objects. Other objects and advantages of the present invention will become apparent to those skilled in the art from the following description.

Broadly stated, the present invention provides a liquid coating composition of the wrinkle-finish type, which comprises a wrinkling varnish base prepared by contacting quick and hard-drying oils with a bodying catalyst under conditions of time and temperature adapted to produce a product having a specified body, and thereafter, blending a wrinkling resin in said product.

Alternatively, the wrinkling varnish base may be prepared by initially dissolving a wrinkling resin in quick and hard drying oils to yield a homogeneous mixture, and contacting the mixture with a bodying catalyst, under conditions of time and temperature adapted to produce a product having a specified body.

In accordance with our invention, any hard drying oil and some semi-drying oils may be used as the wrinkling oil. However, in the preferred embodiment of our invention, we use oiticica oil, China-wood oil, perilla oil, or dehydrated castor oil or combinations of these oils. Generally speaking, we have found that oils having a sufficient degree of conjugation in their molecular structures, and which are quick and hard drying, are best suited. Similarly, wrinkling resins generally, have been found to be suitable for our purpose. We have found, for instance, that ester gum produces a wrinkling varnish base that is satisfactory in every respect. Generally speaking, the ratio of wrinkling oils to wrinkling resins in the wrinkling varnish base of our invention, may vary within wide limits. Ordinarily and preferably, we use between 20 and 30 gallons of wrinkling oil for each 100 pounds of wrinkling resin.

The catalysts to be used in the bodying treatment, in accordance with the method of our invention, are those referred to in the art, as polymerization catalysts. Whether the bodying produced by the catalytic bodying treatment is due to polymerization, isomerization, a combination of them or some other unsuspected reaction, is not important; the common and essential characteristic of the catalysts suitable for the method of the present invention, being that they are also capable of promoting polymerization reactions. Accordingly, metal halides, synthetic and natural clays, hydrofluoric acid, and the like, are suitable bodying catalysts. We especially prefer to use anhydrous hydrogen fluoride or boron trifluoride as the bodying catalyst, and we have found that boron trifluoride may be conveniently handled, if desired, as boron trifluoride-etherate.

The amount of polymerization or in the present case, more appropriately, bodying catalyst, to be added to the wrinkling oils, varies over a wide range depending upon the catalyst used, the reactivity of the oils employed, and upon the reaction time desired. We have found, for example, that when oiticica oil is treated with boron trifluoride, concentrations of boron trifluoride on the order of 0.05–0.2%, based on the weight of the oil, will produce the desired bodying, at room temperature (70° F.), in a period of time varying between about 24 hours for 0.2% boron trifluoride, and 28 days for 0.05% boron trifluoride. The bodying of the wrinkling oil may be hastened, particularly where small amounts of boron trifluoride are employed, by heating the reaction mixtures to temperatures of up to about 300° F.

When treating oils, the desired degree of bodying corresponds to an oil body of approximately Z–5 on the Gardner-Holdt scale (=98.5 poises), and in practice, may be achieved by periodically comparing a sample of the reaction mixture with the Gardner-Holdt Standards. When an oil body of approximately Z–5 has been attained, a wrinkling resin is blended with the bodied oil, for instance, by heating to a temperature just sufficient to produce a homogeneous mixture. The homogeneous mixture constitutes the wrinkling varnish base of our invention.

When mixtures of wrinkling oils and of wrinkling resins are subjected to the catalytic bodying treatment, the wrinkling resins are first dissolved in the wrinkling oils, for example, by heating up to temperatures corresponding to the melting points of the resins employed. After complete solution is achieved, heating is discontinued, and a bodying catalyst is added to the mixture. As in the case where wrinkling oils are initially subjected to the catalytic bodying treatment, the amount of bodying catalyst to be added varies within wide limits depending upon the catalyst employed, the reactivity of the oil-resin mixtures, and the reaction time desired. We have found, for example, that when an oiticica oil-ester gum mixture is treated with boron-trifluoride, concentrations of boron trifluoride on the order of 0.15–0.30%, based on the weight of the oil, is very satisfactory, although concentrations up to 0.5% may be used to advantage, and will produce the desired bodying in a period of time varying between about 5 days and about 25 days. The bodying may be hastened, particularly where small amounts of boron trifluoride are employed, by heating the reaction mixtures to temperatures of up to about 300° F.

When treating mixtures of wrinkling oils and wrinkling resins, the desired degree of bodying corresponds to a varnish body of about B to about I on the Gardner-Holdt scale, after dilution of the product with petroleum thinners, to 60% by weight, non-volatile. In practice, this desideratum may be achieved by periodically diluting samples of the reaction mixture and noting their viscosities. Bodying proceeds slowly so that the reaction time is not critical and experience with oil-resin-catalyst reaction mixtures, will make frequent sampling and dilutions unnecessary.

The various conditions of the catalytic bodying reaction of the method of the present invention have been discussed and described to indicate clearly, the interdependency of the variables involved. It will be apparent to those skilled in the art that, in any particular instance, the most desirable conditions can be readily ascertained, the desiderata in each case having been indicated hereinbefore.

The thinners to be employed for the dilution of the wrinkled varnish base are of the fairly rapidly evaporating type. Preferably, we use thinners of the "petroleum naphtha" type such as Stoddard Solvent which has a distillation range of about 310–395° F. We particularly prefer to use a thinner of the same type but having a somewhat narrower and slightly lower boiling range, for instance, about 300–350° F. This is conducive to more rapid evaporation of the solvent during drying, and permits a relatively quick "initial set" of the wrinkling varnish film. The amounts of thinner employed in our coating composition, may vary over a wide range. Ordinarily, we prefer to

use between about three gallons and about five gallons of thinner to about five gallons of wrinkling varnish base.

Driers of the metal naphthenate type are usually added to our coating compositions to aid in the proper drying of the film. Lead drier may be added in the amounts normally used in paints and varnishes, containing lead on the order of about 0.3–1.5%, based on the weight of the oils. The lead drier acts mainly as a "through drier" for the film and is not essential for the formation of a wrinkled surface. However, the use of so-called "surface driers" such as manganese and cobalt driers is an essential part of our method of producing liquid coating compositions of the wrinkle-finish type. We have found that without the use of these "surface driers," wrinkling of the film is substantially unpredictable. For best results, a slight excess of the "surface driers," such as manganese and cobalt driers, should be added. We have found that manganese driers, in amounts to produce a manganese-content varying between about 0.03% and about 0.2%, based on the weight of the oils, and cobalt driers, in amounts to produce a cobalt-content varying between about 0.05% and about 0.2%, based on the weight of the oils, give very satisfactory results. Both the manganese and cobalt driers seem to influence the drying process in a similar manner, so that the percentage of one may be increased and the other decreased, if desired. The main object is to add a sufficient amount of one or both, to promote the proper wrinkling before the main body of the film has dried.

It must be noted that the bodying reactions caused by the presence of the polymerization or bodying catalysts in the oils or oil-resin mixtures, cease upon dilution with thinners and the addition of driers. Samples of coating compositions prepared in accordance with our invention, have been stored for over a year without any noticeable further increase in body.

The liquid coating compositions of our invention, may be applied as prepared onto surfaces to produce frosted or wrinkled films, or they may be pigmented to produce wrinkling paints or enamels. Pigments possessing good hiding-power should be used preferably, in order that complete hiding can be achieved without the necessity of a too high pigment concentration.

Varnishes and paints prepared in accordance with the present invention, may be applied directly to all types of metallic surfaces, to glass, resinous materials, etc. Before coating porous surfaces, such as wood, a priming oil or lacquer-type coating should be initially applied and allowed to dry thoroughly. This coat seals the pores and gives a continuous surface on which the wrinkling finish will dry to a satisfactory wrinkled finish.

Our coating composition may be applied by any of the methods commonly used for the application of liquid coating compositions. Brushing, spraying or dipping are equally effective methods. After the film has been applied to the surface to be coated, it should not be disturbed until dry. Conditions of the atmosphere in which the film is dried, are no more critical than those for the drying of any of the conventional oleoresinous coating compositions.

The following detailed examples are for the purpose of illustrating modes of preparing the liquid coating compositions of our invention, it being clearly understood that the invention is not to be considered as limited to the specific compositions disclosed hereinafter or to manipulations and conditions set forth in the examples. As it will be apparent to those skilled in the art, a wide variety of other liquid coating compositions within the scope of our invention, may be prepared by a suitable modification of the reactants.

Example 1

A mixture consisting of 0.18 part of boron trifluoride and 99.82 parts of oiticica oil, was placed in a closed container and allowed to react at room temperature (about 77° F.) for about 24 hours. At the end of that period, the oil had attained a body of Z–5 on the Gardner-Holdt scale. The oil was then mixed with 50 parts ester gum and heated to a temperature of 285° F. and kept at this temperature until the resin was completely dissolved. The varnish base thus produced, was then thinned with 100 parts of Stoddard solvent, and substantially, 0.75 part of lead, 0.052 part of manganese, and 0.075 part of cobalt, were added in the form of driers.

The wrinkling varnish thus prepared, had a Gardner-Holdt body of D— at 60% non-volatile. The varnish was applied to a non-porous surface and dried hard in approximately 8 hours, at atmospheric temperatures. The dried film exhibited a decorative, wrinkled and frosted appearance. The dried film possessed also excellent water resistance, a quality highly desirable in any liquid coating composition.

Example 2

33.3 parts of ester gum were dissolved in 66.6 parts of oiticica oil. 0.24 part of boron trifluoride were then added to the mixture. This corresponded to 0.36% boron trifluoride, based on the weight of the oil in the mixture. The oil-resin-catalyst mixture was allowed to react at room temperature (about 77° F.) for 6 days. The bodied product was subsequently thinned to 58% non-volatile, with 72 parts of Stoddard solvent, and 0.5 part of lead, 0.035 part of manganese, and 0.05 part of cobalt, corresponding to 0.75% lead, 0.052% manganese, and 0.075% cobalt, based on the weight of the oil in the mixture, respectively, were added in the form of driers.

The wrinkling varnish thus prepared, had a Gardner-Holdt body of E at 58% non-volatile, and when applied to a non-porous surface, it dried hard at room temperatures, in about 8 hours. The dried film exhibited a decorative, wrinkled and frosted appearance and possessed excellent water resistance.

Example 3

33.3 parts of ester gum were dissolved in 66.6 parts of oiticica oil. 0.2 part of boron trifluoride were then added to the mixture. This corresponds to 0.3% boron trifluoride, based on the weight of the oil in the mixture. The oil-resin-catalyst mixture was allowed to react at room temperature (about 77° F.) for 4 days. At the end of this time, the mixture was placed on a steam-heating radiator, temperature of 160–170° F., for 2½ hours to accelerate the bodying reaction. The bodied product was then thinned to 60% non-volatile, with 66.6 parts of Stoddard solvent, and 0.5 part of lead, 0.09 part of manganese, and 0.075 part of cobalt, corresponding to 0.75% lead, 0.13% manganese, and 0.11% cobalt, based on the weight of the oil in the mixture, respectively, were added in the form of driers.

The wrinkling varnish thus prepared, had a Gardner-Holdt body of H+ at 60% non-volatile, and when applied to a non-porous surface, it dried hard in approximately 8 hours, at atmospheric temperatures, to produce a decorative, wrinkled and frosted film. The dried film possessed excellent resistance to hot and cold water.

Example 4

33.3 parts of ester gum were dissolved in 33.3 parts of oiticica oil and 33.3 parts of China-wood oil. 0.133 part of boron trifluoride were then added to the mixture. This corresponded to 0.2% boron trifluoride, based on the weight of the oil in the mixture. The oil-resin-catalyst mixture was allowed to react at room temperature (about 77° F.) for 5 days. The bodied product was subsequently thinned to 60% non-volatile, with 66.6 parts Stoddard solvent, and 0.5 part of lead, 0.035 part of manganese, and 0.133 part of cobalt corresponding to 0.75% lead, 0.052% manganese, and 0.2% cobalt, based on the weight of the oil in the mixture, respectively, were added in the form of driers.

The wrinkling varnish thus prepared, had a Gardner-Holdt body of C+ at 60% non-volatile, and when applied to a non-porous surface, it dried hard at room temperature, in about 8 hours. The dried film exhibited a decorative, wrinkled and frosted appearance and possessed excellent water resistance.

Example 5

33.3 parts of ester gum were dissolved in 66.6 parts of oiticica oil. 0.2 part of boron trifluoride were then added to the mixture. This corresponded to 0.3% boron trifluoride, based on the weight of the oil in the mixture. The oil-resin-catalyst mixture was allowed to react at room temperature (about 77° F.), for 25 days. The bodied product was subsequently thinned to 57% non-volatile with 76 parts of the fraction of Stoddard solvent, that boils below 350° F., and 0.94 part of lead, 0.02 part of manganese, and 0.1 part of cobalt, corresponding to 1.4% lead, 0.03% manganese, and 0.15% cobalt, based on the weight of the oil in the mixture, respectively, were added in the form of driers.

The wrinkling varnish thus prepared, had a Gardner-Holdt body of E at 57% non-volatile, and when applied to a non-porous surface, it dried hard in about 7 hours at room temperature. The dried film exhibited a very pronounced wrinkled and frosted appearance and possessed excellent water resistance.

Example 6

Approximately 25 parts of Spanish red oxide were ground into 75 parts of the wrinkling varnish prepared in Example 2. A red enamel was obtained, which dried at room temperature to a decorative wrinkled finish.

Example 7

40.7 parts of titanium dioxide and 1.2 parts of carbon black were ground into 58.1 parts of the wrinkling varnish prepared in Example 4. A gray enamel was obtained, which dried at room temperature to a decorative wrinkled finish.

Example 8

3 parts of carbon black were ground into 97 parts of the wrinkling varnish prepared in Example 5. A black enamel was obtained, which dried at room temperature to an excellent wrinkled, decorative finish.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such variations and modifications are considered to be within the purview and scope of the appended claims.

We claim:

1. The method of producing decorative wrinkled films on solid surfaces, which comprises coating a solid surface with a film of a composition which includes a wrinkling varnish base prepared by contacting material selected from the group consisting of oiticica oil, China-wood oil, perilla oil, and dehydrated castor oil, with a bodying catalyst selected from the group consisting of boron trifluoride and anhydrous hydrofluoric acid, at a temperature below about 300° F. and for a time sufficient to produce a product having a body of at least about Z–5 on the Gardner-Holdt scale, a wrinkling resin selected from the group consisting of congo, kauri, damar, coumarone, pontianak, manila, zanzibar, elemi, mastic, and gum esters, a rapidly evaporating thinner and driers including at least one surface drier; and permitting said film to dry at room temperature.

2. The method of producing decorative wrinkled films on solid surfaces which comprises coating a solid surface with a film of a composition which includes a wrinkling varnish base prepared by dissolving a wrinkling resin selected from the group consisting of congo, kauri, damar, coumarone, pontianak, manila, zanzibar, elemi, mastic, and gum esters, in material selected from the group consisting of oiticica oil, China-wood oil, perilla oil and dehydrated castor oil to yield a homogeneous mixture, and contacting said mixture with a bodying catalyst selected from the group consisting of boron trifluoride and anhydrous hydrofluoric acid at a temperature below about 300° F. and for a time sufficient to produce a product having a body after dilution to 60% non-volatile, varying between about B and about I on the Gardner-Holdt scale, a rapidly evaporating thinner and driers including at least one surface drier; and permitting said film to dry at room temperature and for a period of time of at least about seven hours.

3. The method of producing decorative wrinkled films on solid surfaces, which comprises coating a solid surface with a film of a composition which includes a wrinkling varnish base prepared by contacting oiticica oil with boron trifluoride at a temperature below about 300° F. and for a time sufficient to produce a product having a body of at least about Z–5 on the Gardner-Holdt scale, an ester gum, a rapidly evaporating thinner, and driers including at least one surface drier and permitting said film to dry at room temperature and for a period of time of at least about seven hours.

4. The method of producing decorative wrinkled films on solid surfaces, which comprises coating a solid surface with a film of a composition which includes a wrinkling varnish base prepared by dissolving an ester gum in oiticica oil to yield a homogeneous mixture, and contacting said mixture with boron trifluoride at a temperature below about 300° F. and for a period of time sufficient to produce a product having a body, after dilution of 60% non-volatile, varying between about B and about I on the Gardner-

Holdt scale, a rapidly evaporating thinner, and driers including at least one surface drier; and permitting said film to dry at room temperature and for a period of time of at least about seven hours.

JOHN F. SOCOLOFSKY.
HENRY G. BERGER.

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