PROCESS OF MAKING WRINKLE VARNISHES

This invention relates to the production of coating compositions such as varnishes or paints, the films of which on drying in air at ordinary temperatures give wrinkle finish effects.

Wrinkle finishes have won an important place in the field of coatings and especially in the finishing of small items in the consumer goods group. Some of the reasons for their success are:

(I) the finish is very durable under conditions of ordinary wear;

(II) the coatings can be economically applied by electrostatic spraying or other high speed methods, and dried by modern heating equipment;

(III) because the surface will be rough, the finishing of the under surface can be less critical;

(IV) for similar reasons, the percentage of rejects because of dirt and other foreign matter in the film itself is lower;

(V) flake is reduced or eliminated;

(VI) a certain degree of sound deadening is accomplished;

(VII) the appearance is pleasing and colour when used does not vary when several different base materials are used in the same article;

(VIII) surface texture is controllable within rather wide limits.

Wrinkle finish compositions hitherto available are either oleoresinous or alkyd type the films of which form an uneven surface of regular pattern upon baking usually at 110–150°C. But as Dr. Joseph J. Mattiacci writes in his book entitled "Protective and Decorative Coatings," vol. III, 1947 edition; page 265), "the development of satisfactory air-dry wrinkling composition will do much to increase the scope of this novelty finish and make it applicable to larger objects that cannot conveniently be baked in a conveyor oven." Baking wrinkle finish compositions have only limited applications and cannot be used on metallic or wooden doors, large furniture, big pieces of and articles of fabric or leather, walls of houses, fixtures which cannot be easily detached for baking and other like surfaces.

We have discovered varnishes and paints the films of which on drying in air give wrinkle finishes of regular pattern. On account of the fact that the films of these varnishes and paints dry in air at ordinary atmospheric temperatures, these compositions can be applied to large surfaces which cannot conveniently be baked in an oven such as those mentioned in the preceding paragraph as well as to smaller objects such as scientific instruments, photographic equipment, typewriters, toys, novelty goods, beads of various kinds and the like. The present invention deals with the production of these varnishes and paints and the methods of their application on various surfaces.

The process for the production of the air-drying wrinkle finish coating compositions according to this invention consists in preparing medium or long oil length varnishes or paints derived therefrom, from mixtures of oils and resins and is characterised in that the wrinkling oils used are vegetable or animal oils which have conjugated double bond acids in their fatty acid compositions. Coating compositions prepared according to the present invention when applied in films of various thickness dry in air at ordinary temperature giving uneven wrinkled surfaces of regular pattern. Examples of suitable oils are jamaica oil from Mallotus philippinensis Muell. Arg. seeds, tung oil from Aleurites fordii and Aleurites montana seeds, oiticica oil from Licania rigida seeds, Trichosanthes anguina (chauchinda) seed oil, Monordica charantia (karela) seed oil or the like. Natural or synthetic resins may be used.

Thus medium or long oil length ester gum varnishes may be prepared. In place of ester gum other resins such as Congo copal, kaurie gum or the like can be used. The varnishes are prepared by cooking the mixture of ingredients at temperatures ranging from 175 to 280°C till a thread of 5 to 10 inches can be drawn when a drop of the cooked material is taken between the two fingers. For getting small and fine wrinkles cooking at comparatively low temperatures (not exceeding 220°C) is necessary while for medium or heavy wrinkles cooking at high temperature is required. To this material any soluble cobalt drier preferably cobalt linoleate in an amount varying from 0.1 to 1.0 per cent metal is added and the varnish is brought to the proper consistency by the addition of one or more organic solvents having boiling points between 40° to 125°C such as benzene, toluene or the like.

It has been found that when a thinner coating is desired more solvent is necessary. The wrinkling oils having conjugated double bond acids in their fatty acid compositions mentioned above can be substituted to the extent of 80 per cent by other non-wrinkling drying oils such as boiled, boiled or isolated linseed, soyabeen, dehydrated castor or fish oils or various blown, boiled or isolated oils rich in linoleic acids components as tobacco seed oil, safflower seed oil or the like.

The varnishes prepared by the process mentioned above are of dark reddish brown colour. For obtaining varnishes of pale colour which may be used for giving almost colourless films the following modification has been found of advantage. Estergum is prepared by heating a judicious mixture of pale rosin and glycerine at 200–260°C. In an atmosphere of inert gas such as carbon dioxide or nitrogen with constant stirring till the acid value falls to at least 15. The colour of the estergum so obtained is only pale yellowish brown. A similar type of product can be obtained by heating the mixture of the glycerine and rosin at 200–240°C. The estergum is filtered at 10–40 mm. mercury. Medium or long oil length varnishes are made from this estergum by heating it with the drying oil with conjugated double bond acids as components or its mixture with other oils mentioned above in an atmosphere of inert gas such as carbon dioxide.

Wrinkle finish paints can be made from these varnishes by mixing suitable pigments in the above varnishes. If oil soluble dyes are mixed in the varnishes, films of various colours can be produced. The coating can be applied by dipping, by roller or knife spreading or by spraying. Brushing is not recommended as the brush strokes tend to break the surface pattern. Spraying gives excellent results.

It has been found that for getting fine wrinkle finishes the wet film thickness of the varnish should not exceed more than 0.015 mm. The wrinkles become medium and
heavily as the film thickness is increased. To enable satisfactory wrinkles to appear on the surfaces, paints wherein heavy pigments such as lead chromate, metallic powder of copper or bronze and the like are used should have greater wet film thickness than paints containing light pigments.

No pretreatment for the application of these wrinkle varnishes and paints is required on non-absorbing surfaces such as of metals, glass and porcelain. But when the varnish or paint has to be applied on absorbent surfaces such as wood, massacre boards, brick or plastered walls, fabrics, cardboard, paper and the like, a pretreatment in order to make them non-porous and non-absorbent is necessary. The treatment consists in giving an undercoat to such surfaces of materials like estergum varnishes and paints, water glass, glue, gelatine and the like materials. It has also been found that if the varnish is applied on shining surfaces such as aluminium, nickel and silver, wrinkle finishes with golden lustre are obtained. This effect can be obtained partially on other surfaces if paints containing the powder of the above metals are used for giving an undercoat.

The films of these wrinkle finishes after about two weeks become quite hard and flexible. They are resistant to hot and cold water, organic solvents, dilute alkaline and acidic solutions.

The following examples are described in order to give a clear idea of the process described herein and do not in any way limit the scope of the invention.

Example I

100 gms. of estergum was melted in a beaker and when the temperature reached to 175° C., 150 gms. kamala seed oil heated to the same temperature was stirred in it and the temperature was raised to 200° C. in half an hour. The mixture was cooked at 200–225° C. till the run gave a thread of six to eight inches. This usually takes three to six hours. It was cooled and 500 cc. of benzene containing 1.5 gms. of cobalt linoleate was mixed. The varnish was filtered. It was sprayed uniformly in a thin film on a glass plate. Very fine wrinkles giving the appearance of a frosted glass appeared after about one hour. The film became tough dry after two hours and hard dry during two to three days. The film was quite hard and resistant to water, ordinary organic solvents, 5% alkali and acid solutions. The varnish was sprayed on a shining surface of aluminium sheet; wrinkle finishes with golden lustre were obtained. A paint containing aluminium powder was applied on a piece of long cloth. The kamala seed oil was sprayed on it and after the undercoat became absolutely dry. The film thickness was about 0.03 mm. About three hours later, yellow coloured shining wrinkles of medium size were obtained.

A coating of glue was given to a plane wooden panel. A paint consisting of the above varnish and lead chromate was sprayed on it. After about three hours the film became touch dry giving medium size wrinkles. Similar results were obtained when this paint was sprayed on a thick glazed paper.

Example II

100 gms. of estergum and 200 gms. of tung oil were separately heated to 200° C. and then mixed together. Heating was continued with stirring at 200 to 240° C. till 7–10 inches thread was obtained from the run. It took from 600 cc. of benzene and took 2.5 gms. of cobalt linoleate was added when it cooled. The varnish was filtered. An undercoat of sodium silicate (water glass) was applied to the cardboard sheet and the varnish was sprayed on it in about 0.02 mm. film thickness. After two hours the film became touch dry giving a fine regular wrinkled surface. A film after ageing for two weeks and washed off. Dilute mineral acids had no action on the film.

A mixture of equal quantities of copper powder and bronze powder was mixed thoroughly in the above varnish. The paint so prepared was applied on two sheets 4' x 6' on which an undercoat of linseed oil estergum varnish was given. The film thickness of the paint was 0.05 to 0.07 mm. After about 4 hours it became tough dry giving a thick wrinkled surface. The film of the paint became quite hard and strong after about a week and could not be scratched off by a fingernail after a month.

Example III

200 gms. of raw tobacco seed oil was heated at 270° C. in presence of two per cent of anthraquinone for five hours. The catalyst which separated on cooling was removed by centrifuging the oil and a pale brown product was obtained. 120 gms. of this isomerised tobacco seed oil was heated to 200° C. and mixed with 100 gms. of estergum, heated to the same temperature. The mixture was cooked at 230–250° C. till the run gave a thread of 7 to 10 inches length. The temperature was brought down to 200° C. and 30 gms. of kamala seed oil was mixed, and the mixture was again heated to 200–220° C. till a six to eight inches thread could be obtained. The cooked material obtained as above was cooled and diluted with 500 cc. of benzene containing 3 cc. of cobalt linoleate. The varnish prepared as above was sprayed on a glass sheet so that a film of 0.04 mm. thickness was obtained. It became touch dry after about three hours giving a medium size wrinkle pattern. The colour of the film was slightly brownish yellow. After ageing for about two weeks the film was found to be quite resistant to water (cold or hot) and organic solvents. Similar results were obtained when the films of varnish were applied on tin surfaces. Titanium dioxide and a little of carbon black were mixed in the varnish. The grey paint so obtained was applied on an iron surface. After about four hours a wrinkle pattern was obtained.

Example IV

Double boiled linseed (75 gms.) and estergum (50 gms.) heated separately to 200° C. and mixed and cooked at 230–250° C. with constant stirring till a thread of six to eight inches was obtained from the run. The temperature was brought down to 200° C. and 25 gms. of tung oil was added and cooking was resumed till a thread of about 8 inches was obtained. The material was cooled and sprayed with 300 cc. of benzene containing 1.5 gms. of cobalt linoleate was mixed with it. This varnish when sprayed on a glass plate gave medium type wrinkles after about 3 hours having reddish brown colour. 2 gms. of lamp black was mixed in 100 cc. of above varnish and a coat was applied on an iron surface. After about 4 hours black coloured wrinkles were obtained.

Example V

200 gms. of light coloured rosin and 24 gms. glycine were heated with constant stirring in a flask at 200° C. for about one hour and then for another hour at 230° C. in an atmosphere of carbon dioxide. The temperature was raised to 250° C. and heating was continued till a bead of the resin on a glass surface became transparent and an acid value 8 was obtained. This took about 3½ to 5 hours of heating. Then the mixture was cooled to about 100° C. in the atmosphere of carbon dioxide. The estergum so obtained was pale yellowish in colour and was insoluble in alcohol. Kamala seed oil varnish was prepared from this estergum as in Example I, but the whole process was conducted in the atmosphere of carbon dioxide, with constant stirring. A pale reddish brown varnish was obtained which when applied on a glass plate gave fine wrinkled surface having light yellow colour. Its titanium dioxide paint gave an ab-
2,749,247

solutely white wrinkle surface. The film after a week was quite water resistant and was also fairly resistant to organic solvents and 5% alkali and acid solutions.

In the above examples the proportions of wrinkling oil to estergum are varied from about 1.5:1 to 2:1 parts by weight.

We claim:

1. In the manufacture of wrinkle varnishes, the process which consists substantially in mixing from about 1.5 to 2 parts by weight of a wrinkling oil, whose fatty acid components contain conjugated double bonds and selected from a class consisting of kamala oil, tung oil, oiticica oil, Trichosanthes angulina seed oil and Monodora charantia seed oil, with about 1 part by weight of estergum, heating the mixture in the absence of a catalyst at a temperature ranging from about 175° to 280° until a drop of the cooled mixture gives a thread of from about 6 to 10 inches, thinning the resulting varnish base with an organic solvent having a boiling point of from about 40° to 125° C., adding a surface drier.

2. The process of claim 1 wherein the 1.5 to 2 parts by weight of oil consists of a mixture of one of said wrinkling oils with up to 80% by weight of a non-wrinkling oil selected from the class consisting of linseed oil, soyabean oil, dehydrated castor oil, fish oils, tobacco seed oil and safflower oil.

3. The process of claim 1 wherein the surface drier is cobalt linoleate which is added in amount varying from about 0.1 to 1.0 per cent by weight.

4. The process of claim 1 wherein the heating step is conducted at temperatures not exceeding 220° and a varnish producing small and fine wrinkles is produced.

References Cited in the file of this patent

UNITED STATES PATENTS

1,933,520 Bruson 1933-10-31
1,950,417 Root 1934-12-13
2,275,239 Waldie 1942-3-5
2,344,189 Waldie 1944-12-14
2,394,498 Waldie 1946-2-5
2,406,878 Whyzmus 1946-9-3
2,407,623 Waldie 1946-9-10
2,441,105 Socolofsky et al. 1948-4-5
2,443,284 Waldie 1948-6-15