

UNITED STATES PATENT OFFICE

ERNEST J. PIEPER, OF LANCASTER, PENNSYLVANIA, ASSIGNOR TO ARMSTRONG CORK COMPANY, OF LANCASTER, PENNSYLVANIA, A CORPORATION OF PENNSYLVANIA

RESINOUS PRODUCT AND PROCESS OF MAKING

No Drawing.

Application filed June 17, 1929. Serial No. 371,684.

The present invention relates to a resinous product and the process of making it, and more especially to a resinous condensation product of the type formed from the combination and condensation of polyhydric alcohols and organic polybasic acids, and particularly adapted for forming a flexible waterproof and soap resistant film. The invention has been developed in connection with the production of films suitable as a protective or decorative coating for floor coverings, such as linoleum and felt base goods, wall coverings, etc., and especially a film for such purposes which can be set to a soap resistant condition with or without heat or prolonged stoving or baking.

When molecular proportions of a polyhydric alcohol and an organic polybasic acid are heated together, a resinous condensation product is obtained known as an alkyd resin. One of the more common alkyd resins is made by condensing glycerine and phthalic anhydride, and is hereinafter referred to as a phthalic anhydride-glycerine resin. A modified alkyd or phthalic anhydride-glycerine resin may be produced by the addition of a fatty acid or acids to the polyhydric alcohol and polybasic acid mixture, or to the glycerine and phthalic anhydride mixture, during the formation of the resin.

The fatty acid or acids employed for this purpose are generally those obtained from siccative oils, such as the so-called drying oils, linseed oil and China-wood oil, and the so-called semi-drying oils, such as fish oil, soya bean oil, etc. The acids in linseed oil are principally linolic, linolenic, isolinolenic, oleic, and palmitic and stearic acids. The addition of such fatty acids softens and increases the flexibility of the resin, which is important when the resin is used as the basis for a lacquer, varnish or paint.

A modified phthalic anhydride-glycerine resin lacquer may be made by heating together a mixture of glycerine, phthalic anhy-

dride and fatty acids, until they react to form a resinous condensation product, which may be dissolved in suitable volatile solvents to form a lacquer. The solvent is evaporated, usually under heated conditions, to form a lacquer film.

It is important, particularly where the resin is applied as a lacquer to floor coverings, such as linoleum and felt base goods, that the lacquer or paint be alkali resistant because of the common practice of washing floors with soap.

It has been found that it is necessary, in order to produce a soap resistant film from a phthalic anhydride-glycerine resin formed of glycerine, phthalic anhydride and fatty acids, to heat the film after it is applied for a considerable period at about 140° to 180° Fahrenheit, or perhaps for a shorter time at higher temperatures, say, about 300° to 400° Fahrenheit. In the floor covering industry these higher baking temperatures are prohibitive since the materials, such as linoleum and felt base goods, cannot withstand these higher temperatures. When lower temperatures are used a fairly satisfactory film may be obtained by long continued heating, but this involves delay in the operation and considerable expense. In cases where the film is air-dried or heat is used simply to evaporate the solvent, soap resistance is not obtained in a film formed of the fatty acid modified glycerine-phthalic anhydride resin.

When glycerine and phthalic anhydride are used as the basis of the resin, it is necessary to employ a considerable proportion of a fatty acid or acids to soften and impart flexibility to the material. The fatty acid content commonly amounts to 50% to 75% of the resinous product. This relatively large proportion fatty acid tends to increase the solubility of the film and prevents a quick setting of the film, particularly if the fatty acid is employed in a raw or but partially oxidized condition. The continued oxida-

tion of an unsaturated fatty acid which may take place after the film is in use also tends to make the flexibility of the film less stable.

If an ethylene glycol compound, such as the mono-ethylene glycol, commonly called "ethylene glycol", or a polyethylene glycol, such as di-ethylene glycol or tri-ethylene glycol, but preferably a mixture of mono-ethylene glycol and di-ethylene glycol, be substituted for a part of the glycerine, certain desirable qualities are imparted to the resinous product which particularly adapts it for forming protective films. The film is rendered more soap and alkali resistant, and when the combination of ethylene glycol and di-ethylene glycol is employed, a film can be produced which will air-dry without continued heat to a soap resistant condition. The substitution of one or more of the ethylene glycols, i. e., mono-ethylene glycol or a poly-ethylene glycol tends to increase the softness and flexibility of the film and allows a considerable reduction in the amount of fatty acids employed, thus increasing the stability of the film and aiding in quick setting.

Some of the advantages of the invention may be seen by reference to former practice. As an example of the prior practice, reference may be had to a modified glyptal resin formed of 50 parts glycerine, 80 parts phthalic anhydride, 50 parts linseed oil fatty acids, and 15 parts Chinawood oil fatty acids. The resin formed from these constituents is dissolved in a suitable solvent and applied to form a lacquer or paint film. In order to set such film to a soap resistant condition requires from one to three day's stoving, at about 140° to 180° Fahrenheit. As contrasted with such former practice, a lacquer or paint film formed from my resin, as hereinafter described, can be set to a soap resistant condition by air-drying with the application of heat only long enough to remove the volatile solvent.

The characteristics of the materials employed and their observed behavior will now be described, together with what I believe to be the chemical reactions involved. Molecular proportions of glycerine and phthalic anhydride when heated produce a hard glossy resin film having no tackiness and having a tendency to be brittle. If sufficient fatty acid is added and condensed with the glycerine and phthalic anhydride to obtain the requisite flexibility, the film is not quick setting and has a poor soap resistance, unless it is subjected to an elevated temperature over a considerable period of time. In general, the more fatty acid used, the longer the heating time required to mature the film. Air-drying is not sufficient.

Molecular proportions of di-ethylene glycol and phthalic anhydride when heated produce a gummy balsam-like resin which is soft and tacky. It softens and imparts flexibility

to the materials to which it may be added. The film formed of the di-ethylene glycol and phthalic anhydride resin is not, of itself, inherently soap resistant.

Molecular proportions of ethylene glycol and phthalic anhydride when heated produce a resin which looks as hard and brittle and feels at first touch much the same as the glycerine phthalic anhydride resin. In reality it is not so hard and brittle but will make a slightly tacky film. It has excellent soap resistant qualities. Sufficient flexibility for film use may be secured with as low as about 5% of fatty acid, and when modified with this amount of fatty acid a highly soap resistant film is formed but one which, however, will be slightly tacky unless heat is applied to set it.

The following is a specific example of the proportions of ingredients employed in making a resin suitable for a lacquer or paint base:

35 parts ethylene glycol; 3½ to 7½ parts di-ethylene glycol; 8 to 13 parts glycerine; 105 parts phthalic anhydride and 10 to 20 parts drying oil acids, such as the acids obtained from linseed oil; Chinawood oil, etc.

This mixture is heated to about 180° to 230° centigrade until the constituents combine and condense to form the resin in its soluble form. The materials are preferably all added together in a heating vessel at one time and the temperature raised fairly rapidly to about 180° centigrade and maintained until the reaction begins. There is some tendency to foam due to the liberation of water and gases. After the reaction has proceeded for some time the temperature may be carried up to about 220° to 230° centigrade until a homogeneous condensation product is obtained. The reaction is carried to a point just under the gelation point, which point I regard as being the time at which a violent reaction sets in and the resinous material would stew up and froth over.

The resin thus produced is then dissolved in a solvent to form a lacquer or paint. The lacquer or paint gives a film which will air-dry to an alkali and soap resistant condition and which has a high flexibility and toughness.

The various constituents apparently impart the following qualities to the resin: The ethylene glycol-phthalic anhydride combination gives a tough resin but with some tendency toward tackiness. It also appears to have inherently good soap resisting qualities. The glycerine-phthalic anhydride combination tends to give a high gloss and counteracts tackiness. The di-ethylene glycol-phthalic anhydride combination gives flexibility, and its tackiness is counteracted by the glycerine-phthalic anhydride combination. While the di-ethylene

glycol-phthalic anhydride combination does not apparently have inherent good soap resisting qualities, it, in combination with the other constituents, enhances the soap and

5 water resistance, apparently due to better esterification.

It is believed that the di-ethylene glycol assists in the esterification of the glycerine and ethylene glycol with the phthalic anhydride, and that such esterification is, in part

10 at least, responsible for the soap resistant qualities imparted by the use of the di-ethylene glycol, and thereby forms a composition which can be air-dried to a soap resistant

15 film. Apparently when glycerine and phthalic anhydride are combined in the formation of a resin, esterification is not complete and long continued stoving at relatively high temperatures is required to complete

20 the esterification. I believe that the susceptibility to soap of the air-dried films as heretofore formed from the fatty acid modified glycerine-phthalic anhydride glyptal resin is due to free hydroxyl resulting from

25 incomplete esterification.

It is found that if too much glycerine is used the film is not soap resistant, and if too little is used the film is tacky. On the other hand, if too much di-ethylene glycol

30 is added to produce soap resistance, the product will be too soft. The preferred proportions given above seem to be about right for producing a tough glossy but flexible soap and alkali resistant film.

It will be noted that in the above formula the fatty acids are used in considerably less amount than is required to soften and render

35 flexible a glycerine-phthalic anhydride resin, and this is due, I believe, to the inherent flexibilizing qualities of the ethylene glycol compounds used. As above pointed out, it is of advantage to thus reduce the amount of modifying fatty acids required, particularly when an air-drying or quickly

40 setting film is desired. It may be stated in general that the smaller the amount of fatty acid used, the less time required to set the film. On the other hand, if it is desired to form a film which will not dry as quickly,

45 more fatty acid may be added, since this will require a longer time to mature. Thus, a control of the drying time of the film may be secured.

While it is preferred to use both the di-ethylene glycol and the mono-ethylene glycol in order to get their peculiar coaction in rendering the film air-drying to a soap resistant condition, one of these ethylene glycol compounds may be employed alone as a modifying or softening agent and thus reduce

50 the amount of fatty acid required.

Tri-ethylene glycol has effects similar to those of di-ethylene glycol, particularly in promoting better esterification in an alkyd resin to which it may be added. It may be

55

substituted, at least partially, for di-ethylene glycol.

In using my resinous compound as a base for lacquers and paints, there is quite a field of solvents from which to select. The particular solvent or solvents selected is determined by the conditions under which the film is applied. The solvents are selected largely with reference to their boiling points. For example, the following solvents with their boiling points noted, may be used in various combinations:

70

Ethylene glycol mono-ethyl ether, commonly known by the trade name of "Cellosolve", boiling point 128° to 137° centigrade;

75

Ethylene glycol mono-methyl ether, commonly known by the trade name of "Methyl Cellosolve", boiling point 125° centigrade;

The acetate of "Cellosolve", boiling point 154° centigrade;

80

Di-ethylene glycol mono-ethyl ether, commonly known by the trade name of "Carbitol", boiling point 186° centigrade;

The butyl "Cellosolve" or ethyl glycol mono-butyl ether, boiling point 163° to 174° centigrade;

85

Solvent naphtha composed of benzol, toluol and xylol;

A mixture of half and half solvent naphtha and ethyl acetate.

90

The dissolved resin may be used as such as a clear lacquer or varnish, or pigments may be added to form a paint. The lacquer or paint may be applied in any of the usual ways, such as by brushing or by spraying or by printing with floor covering printing machines.

95

After the lacquer or paint is applied, the film may be air-dried, such as by passing the lacquered or painted floor covering through a drying chamber, preferably heated to accelerate the evaporation of the solvent. The film as thus air-dried is not tacky and has good soap or alkali resistant qualities. The goods to which such air-drying film is applied may be immediately rolled up for shipment. In case a slower drying film is required, such for example, as an undercoat to be printed over with an oil paint, the film may be modified to increase its drying time by increasing the fatty acid modifier content, so that the resin undercoat film may require about the same length of time to dry as is required by the oil paint decoration applied over it.

100

While phthalic anhydride is the usual polybasic acid employed in making resins of this type, other polybasic acids may be employed, such, for example, as malic acid, citric acid, succinic acid, or mixtures of polybasic acids.

105

While glycerine is the preferred polyhydric alcohol used in connection with the ethylene glycol, since the glycerine counter-

110

70

75

80

85

90

95

100

105

110

115

120

125

130

acts its tackiness, other polyhydric alcohols may be substituted for the glycerine, such, for example, as the polyglycerides, erythrite, penta-erythrite, xylite, mannite.

5 While I have specifically described the preferred embodiment of my invention and have attempted to explain to the best of my understanding the properties of the constituents used and the chemical theory, it is to
10 be understood that the invention is not limited to such specific embodiments or such explanations, but that the invention may be otherwise embodied or practiced within the scope of the following claims.

15 I claim:

1. An alkyd type resin formed by the combination and condensation of a mixture containing an organic polybasic acid, glycerine, ethylene glycol, and di-ethylene glycol.

20 2. An alkyd type resin formed by the combination and condensation of a mixture containing an organic polybasic acid, glycerine, ethylene glycol, and a poly-ethylene glycol.

3. An alkyd type resin formed by the combination and condensation of a mixture containing an organic polybasic acid, glycerine, ethylene glycol, di-ethylene glycol, and
25 a fatty acid.

4. An alkyd type resin formed by the combination and condensation of a mixture containing an organic polybasic acid, a polyhydric alcohol, one of the ethylene glycols and
30 a fatty acid.

5. An alkyd type resin formed by the combination and condensation of a mixture containing phthalic anhydride, glycerine, ethylene glycol, and a poly-ethylene glycol.

6. An alkyd type resin formed by the combination and condensation of a mixture containing phthalic anhydride, glycerine, ethylene glycol, and di-ethylene glycol.

7. An alkyd type resin formed by the combination and condensation of a mixture containing phthalic anhydride, glycerine, one of
40 the ethylene glycols and a fatty acid.

8. An alkyd type resin formed by the combination and condensation of a mixture containing phthalic anhydride, glycerine, ethylene glycol, di-ethylene glycol, and a fatty
50 acid.

9. An alkyd type resin formed by the combination and condensation of a mixture containing an organic polybasic acid, glycerine and one of the ethylene glycols, and fatty
55 acid in an amount less than that required by a modified phthalic anhydride-glycerine resin of comparable softness and flexibility formed from a polybasic acid and glycerine.

10. An alkyd type resin formed by the combination and condensation of phthalic anhydride, glycerine, ethylene glycol and di-ethylene glycol, and a fatty acid modifier in
60 an amount less than that required by a phthalic anhydride-glycerine resin of comparable
65 softness and flexibility.

11. The process of producing the herein described resinous product which comprises heating a mixture containing an organic polybasic acid, glycerine, one of the ethylene glycols and a fatty acid.

12. The process of producing the herein described resinous product which comprises heating a mixture containing an organic polybasic acid, glycerine, ethylene glycol, di-ethylene glycol, and a fatty acid.

13. The process of producing the herein described resinous product which comprises heating a mixture containing phthalic anhydride, glycerine, ethylene glycol, di-ethylene glycol, and a fatty acid.

14. An alkyd type resin formed by the combination and condensation of a mixture containing an organic polybasic acid, glycerine, a poly-ethylene glycol, and ethylene glycol in an amount greater than that of either the glycerine or the poly-ethylene glycol.

15. An alkyd type resin formed by the combination and condensation of a mixture containing phthalic anhydride, glycerine, di-ethylene glycol, and ethylene glycol in an amount greater than that of either the glycerine or the di-ethylene glycol.

16. An alkyd type resin formed by the combination and condensation of a mixture containing phthalic anhydride, glycerine, ethylene glycol and di-ethylene glycol, and less than 50 per cent of a fatty acid modifier.

17. An alkyd type resin formed by the combination and condensation of a mixture containing an organic polybasic acid, a polyhydric alcohol, ethylene glycol, a poly-ethylene glycol, and a fatty acid.

18. An alkyd type resin formed by the combination and condensation of a mixture containing phthalic anhydride, glycerine, ethylene glycol, a poly-ethylene glycol, and a fatty acid.

19. The process of producing the herein described resinous product, which comprises heating a mixture containing an organic polybasic acid a polyhydric alcohol ethylene glycol a poly-ethylene glycol and a fatty acid.

20. The process of producing the herein described resinous product, which comprises heating a mixture containing an organic polybasic acid, glycerine, ethylene glycol, a poly-ethylene glycol, and a fatty acid.

21. An alkyd type resin formed by the combination and condensation of a mixture containing an organic polybasic acid, a polyhydric alcohol ethylene glycol and a poly-ethylene glycol.

22. An alkyd type resin formed by the combination and condensation of a mixture containing an organic polybasic acid, a polyhydric alcohol, ethylene glycol, and di-ethylene glycol.

23. An alkyd type resin formed by the combination and condensation of a mixture con-

taining phthalic anhydride, glycerine, a poly-ethylene glycol, ethylene glycol in an amount greater than that of either the glycerine or the poly-ethylene glycol, and a fatty acid.

5 24. An alkyd type resin formed by the combination and condensation of a mixture containing phthalic anhydride, ethylene glycol, glycerine in an amount less than that of the ethylene glycol, and a fatty acid.

10 In testimony whereof I have hereunto set my hand.

ERNEST J. PIEPER.

15

20

25

30

35

40

45

50

55

60