Patented Mar. 1, 1932

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


The present invention relates to a resino-
5 nous product and the process of making it,
and more especially to a resinoous condensa-
tion 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 in-
vvention has been developed in connection
with the production of films suitable as a
protective or decorative coating for floor cov-
erings, such as linoleum and felt base goods,
wall coverings, etc., and especially a film for
such purposes which can be set to a soap re-
sistant condition with or without heat or
prolonged stoving or baking.

When molecular proportions of a polyhy-
dric alcohol and an organic polybasic acid
are heated together, a resinos condensation
product is obtained known as an alkyd resin.
One of the more common alkyd resins is made
by condensing glycerine and phthalic anhy-
dride, and is hereinafter referred to as a
phthalic anhydride-glycerine resin. A modi-
fied 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 glycer-
ine 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 in-
creases 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 to-
gether a mixture of glycerine, phthalic anhy-
dride and fatty acids, until they react to
form a resinos 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 cover-
ings, 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 pro-
hibitive since the materials, such as linoleum
and felt base goods, cannot withstand these
higher temperatures. When lower tempera-
tures are used a fairly satisfactory film may
be obtained by long continued heating, but
this involves delay in the operation and con-
siderable expense. In cases where the film
is air-dried or heat is used simply to evap-
orate the solvent, soap resistance is not ob-
tained in a film formed of the fatty acid modi-
fied glycerine-phthalic anhydride resin.

When glycerine and phthalic anhydride
are used as the basis of the resin, it is neces-
sary 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 resinos 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 polyethylene 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. A film formed of 50 parts glycerine, 80 parts phthalic anhydride, 10 parts linseed oil fatty acids, and 15 parts Chinawood oil fatty acids. The resin formed from the glycerine-phthalic anhydride and the linseed oil fatty acids 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:

85 parts ethylene glycol; 8½ to 7½ parts di-ethylene glycol; 8 to 18 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 250° 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 250° 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 water resistance, apparently due to better esterification.

It is believed that the diethylene glycol assists in the esterification of the glycerine and ethylene glycol with the phthalic anhydride, and that such esterification is, in part at least, responsible for the soap resistant qualities imparted by the use of the diethylene glycol, and thereby forms a composition which can be air-dried to a soap resistant film. Apparently when glycerine and phthalic anhydride are combined in the formation of a resin, esterification is not complete and long continued stowing at relatively high temperatures is required to complete 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 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 diethylene glycol 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 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 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, 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 diethylene glycol and the monoethylene glycol in order to get their peculiar action 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 the amount of fatty acid required.

Triethylene glycol has effects similar to those of diethylene glycol, particularly in promoting better esterification in an alkyd resin to which it may be added. It may be substituted, at least partially, for diethylene 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:

- Ethylene glycol mono-ethyl ether, commonly known by the trade name of "Cellosolve", boiling point 128° to 137° centigrade;
- Ethylene glycol mono-methyl ether, commonly known by the trade name of "Methyl Cellosolve", boiling point 129° centigrade;
- The acetate of "Cellosolve", boiling point 154° centigrade;
- Diethylene 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;
- Solvent naphtha composed of benzol, toluol and xylol;
- A mixture of half and half solvent naphtha and ethyl acetate.

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.

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.

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.

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

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 phthalic anhydride, glycerine, 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.

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

In testimony whereof I have hereunto set
my hand.

ERNEST J. PIEPER.