If a soap stock from the alkali refining of one of the above oils, or another oil of vegetable or animal origin, is obtained in the raw form, that is, the product obtained directly by the alkali refining process, it can readily be acidulated simply by the addition of an acid such as hydrochloric or sulfuric acid to neutralize the product or to make it slightly acidic, in which process the acidulated material is present as an oily top layer that can be recovered by decantation or other means.

The properties of typical acidulated soap stocks are listed in the following table.

Three different types of acidulated soybean soap stocks are shown in the above table to demonstrate the fact that the properties may differ from sample to sample due to slight variation in alkali refining procedures or in the oil processed.

As mentioned hereinafter, the acidulated soap stocks possess some free or available hydroxyl groups. The amount of available hydroxyl can be ascertained if desired either by trial esterification and determination of the drop in the acid value, or by a direct determination of the hydroxyl content of the acidulated soap stock. The amount of polyol which must be added in the esterification process can be adjusted accordingly.

The esterification of the acidulated soap stock can be carried out utilizing any of the various polyols. Examples of such polyols include ethylene glycol, glycerol, trimethylene glycol, tetramethylene glycol, pentamethyleneglycol, hexamethylene glycol, heptamethylene glycol, pinacol, pentaerythritol, trimethylolethane, polyallyl alcohol, sorbitol, alpha-methyl glucoside, epoxide resins containing hydroxyl groups, polyglycerol, and glycerol.

The esterification process is best carried out by heating a mixture of the acidulated soap stock and the polyol in an inert solvent or diluent such as toluene or xylene at a temperature in the range of about 150° C. to 300° C. or higher for a period of from about 1 hour to 6 hours or more. A catalyst is not necessary to effect the esterification, particularly if a relatively large amount of acid is present in the soap stock, although the time of reaction may be decreased somewhat by utilizing a conventional esterification catalyst such as lithium or toluenesulfonic acid, or the like. It is desirable to utilize a silicone anti-foaming agent in a very small amount during the esterification to prevent foaming which is likely to occur.
during the esterification of the crude acidulated soap stocks, and additionally to employ an inert gas to prevent oxidation of the double bonds of the hydrocarbon groups in the fatty acids present.

The preferred alpha, beta-ethylenically unsaturated polyesters of acrylic acid or acrylonitrile for use in modifying the acidulated soap stock esters prepared according to the procedures described in the foregoing paragraph is maleic acid. However, other acids, including furamic acid, crotonic acid, acrylic acid, itaconic acid and the like may be utilized. Alpha, beta-ethylenically unsaturated acids containing halogen or other substituent groups may also be employed, as may the anhydrides of any of the foregoing acids; in fact, the anhydrides are preferably utilized in the esterification reaction and it is intended that the terms "acid" include the corresponding anhydride.

In most instances about 2 percent to 8.0 percent of the alpha, beta-ethylenically unsaturated acid, based on the weight of the acidulated soap stock, is used. However, smaller or larger amounts may also be utilized, with the larger amounts giving somewhat improved drying properties.

The alpha, beta-ethylenically unsaturated acid is preferably added to the esterification reaction mixture after esterification of the acidulated soap stock with the polyol is substantially complete. If the unsaturated acid is added while substantial polyol is present in the reaction mixture, the acid and polyol may react to form a relatively insoluble precipitate; for example, when maleic acid and glycerol are present, glycerol maleate may be formed. It is obvious, therefore, that where the presence of such a precipitate is objectionable, the alpha, beta-unsaturated acid should not be added until most of the polyol has reacted with the acidulated soap stock.

The modified esters thus prepared can be used per se as vehicles in coating compositions. However, they do not dry as well as is desired for certain applications, probably due to the presence in the acidulated soap stocks of certain antioxidants, particularly tocopherol. Accordingly, it is another feature of this invention that the drying properties of the modified esters can be greatly improved by blowing air through the ester in a controlled manner to destroy the inhibitor, but not to oxidize the oil to any significant extent.

In the aeration process, the addition of small amounts of catalysts of oxidation and particularly catalysts such as are conventionally employed as driers in paints and varnishes is important. The catalysts include the various oxides of heavy metals such as cobalt, nickel, chromium, manganese, lead, and the like, that have at least slight solubility in the modified ester. The salts may be, for example, the oxalates, linoleates, naphthenates, resinate or the like of the foregoing metals. Soluble forms of these materials are now available. The amount of the drier is small and usually will be within a range of about .0001 to .01 percent by weight, with the preferred range being about .0002 to .0006 percent by weight. These percentages are calculated as active metal based upon the total amount of modified ester which is treated.

The temperature of treating the modified ester is preferably within a range of about 230° F. to 280° F., although higher or lower temperatures may also be utilized successfully. The aeration may be carried out in any convenient reactor.

Air constitutes the usual oxidizing agent, but it is to be understood that oxygen gas can also be utilized by appropriate adjustment of the amount and the rate of addition. The air (or oxygen) is more effective if it is thoroughly distributed in the modified ester which is undergoing treatment. Various types of agitation may be employed. For example, the air may be whipped or stirred relatively uniformly in the ester by conventional agitators or turbo-agitators. It is also possible to break up the air or oxygen as it is supplied to the ester by bubbling it into the ester through a distributor head provided with minute openings.

In most instances the total amount of air (assuming air is employed as the oxidizing agent) will not exceed 2.5 cubic feet of air per gallon of oil, with about 0.2 to 1.0 cubic foot of air per gallon of oil being preferably utilized. Considerable variation in the rate of addition of air (or oxygen) can be tolerated but usually the rate will be within the range of 0.005 to 0.02 of air or 0.001 to 0.004 of oxygen expressed in terms of cubic foot per minute per gallon of oil treated. It is to be understood that if oxygen is employed, the necessary reduction in volume to compensate for the increased concentration of the active agent should be made.

The time of aeration can be varied substantially, but in most instances will be within the range of about 2 to 6 hours, and preferably 2 to 4 hours. Excessively protracted aeration will result in increases in the viscosity of the oil, in peroxide value and of acid value which may in some instances be objectionable.

The completion of the aeration of the oil can easily be determined by conventional tests for inhibitors, for example by the well known Emmerie-Engel test. The overall inhibitor content of the ester is reduced as much as 98 percent by the aeration process.

The following examples are intended to illustrate more fully the preparation of vehicles from acidulated soap stocks in accordance with the practice of this invention.

The examples are not, however, intended to limit the scope of the invention for there are, of course, numerous possible variations and modifications.

**Example 1**

The following materials were charged into a glass lined reactor:

- Soybean acidulated soap stock, type C 20 pounds.
- Soybean acidulated soap stock, type B 20 pounds.
- Monopentenyltheritol 3.05 pounds.
- Xylene 2.0 pounds.
- Silicone anti-foaming agent 40 cc. (1% solution).

The resulting mixture was heated at a temperature within the range of about 200° C. to 235° C. for 4½ hours. One and two-tenths pounds of maleic anhydride were then added over a 10 minute period and heating was continued at about 235° C. for an additional 2 hours. The resultant product had an acid value of 9.5, a viscosity of L (Gardner-Holdt), a Gardner color of 18+ and a solids content of 95.5 percent.

The modified ester thus prepared was then aerated for about 2 hours at 230° F. in the presence of about 0.01 percent cobalt (as the naphthenate), utilizing 0.075 cubic foot of air per minute. The final product contained only 0.04 percent of tocopherol. Drying tests utilizing 6.9 cc. of a lead-cobalt drier (0.3 percent lead and 0.03 percent cobalt) per 100 grams of resin solids were made on the original and aerated samples. The original ester was tested in 320 minutes and the aerated ester in only 150 minutes.

The aerated ester prepared according to the above method was formulated into a conventional house paint and showed no appreciable checking, flaking, peeling or chalking after prolonged exposure under various climatic conditions. The paint was found to be the substantial equivalent in durability and other properties to paints utilizing a linseed oil vehicle.

**Examples II to IX**

A series of vehicles were prepared from various acidulated soap stocks as follows. The soap stock was first heated with pentacrylthritol for about 1 to 4 hours in
the same manner and substantially the same temperatures as set forth in Example I. Maleic anhydride was then added and the heating continued at about 235 °C. until an acid value of about 10 was reached. The modified ester was then secured by blowing with air for from 2 to 6 hours at about 230 °F., the air being supplied at the rate of about 0.075 cubic foot per minute. The pertinent data are recorded in the table below:

<table>
<thead>
<tr>
<th>Example</th>
<th>Soap Stock Type</th>
<th>Charge</th>
<th>Miscellaneous</th>
<th>Physical Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Soap Stock (Grams)</td>
<td>Pentaeerythritol (Grams)</td>
<td>Maleic Anhydride (Grams)</td>
</tr>
<tr>
<td>II</td>
<td>Acidulated soybean soap stocks</td>
<td>2,500.0</td>
<td>150.0</td>
<td>60.0 (5%)</td>
</tr>
<tr>
<td>III</td>
<td>Acidulated soybean soap stocks</td>
<td>2,500.0</td>
<td>210.0</td>
<td>70.0 (5%)</td>
</tr>
<tr>
<td>IV</td>
<td>Acidulated soybean soap stocks</td>
<td>2,500.0</td>
<td>180.0</td>
<td>65.0 (5%)</td>
</tr>
<tr>
<td>V</td>
<td>Acidulated soybean soap stocks</td>
<td>1,800.0</td>
<td>110.0</td>
<td>55.0 (5%)</td>
</tr>
<tr>
<td>VI</td>
<td>Acidulated corn oil</td>
<td>2,500.0</td>
<td>220.0</td>
<td>70.0 (5%)</td>
</tr>
<tr>
<td>VII</td>
<td>Acidulated corn oil</td>
<td>2,500.0</td>
<td>120.0</td>
<td>60.0 (5%)</td>
</tr>
</tbody>
</table>

The above data demonstrates conclusively that the very economically prepared vehicles of the present invention are the equivalent of the more expensive conventional vehicles. In addition the formulations based upon the vehicles of this invention give initially equally good appearance, brushability and gloss and a more positive drying than paints containing a linseed oil vehicle. Accordingly, the vehicles prepared from acidulated soap stocks can be substituted in whole or part for more expensive vehicles in both interior and exterior coating compositions, particularly in colored paints. Since the acidulated soaps stocks tend to be relatively dark, they cannot ordinarily be utilized as the sole vehicle in a white paint, but can be used in amounts up to about 50 percent in such compositions. The color of the vehicles can be somewhat improved by bleaching with a material such as sodium chlorite, NaClO₂, bleaching earths or activated carbons, although for colored coating compositions such treatment is not necessary.

**Example X**

Seven hundred eighty grams of the modified ester prepared according to the method of Example I was formulated into a varnish by heating the modified ester with 500 grams of pentaeerythritol-maleic acid-resin ester gum (prepared from 2500 grams rosin, 538 grams pentaeerythritol and 312.5 grams of maleic anhydride). The cooking log is as follows:

<table>
<thead>
<tr>
<th>Time (Minutes)</th>
<th>Temperature (°C.)</th>
<th>Viscosity at 50% Total Solids</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>200 A</td>
<td></td>
</tr>
<tr>
<td>145</td>
<td>260 B</td>
<td></td>
</tr>
<tr>
<td>165</td>
<td>280 C</td>
<td></td>
</tr>
<tr>
<td>185</td>
<td>185 D</td>
<td></td>
</tr>
<tr>
<td>215</td>
<td>215 E</td>
<td></td>
</tr>
<tr>
<td>220</td>
<td>220 F</td>
<td></td>
</tr>
</tbody>
</table>

The product thus obtained was thinned to 48.2 percent total solids (Gardner viscosity G) in a high flash aliphatic naphtha, giving a varnish having a Gardner color of 16.5. The drying rate and other properties of the varnish was equivalent to that of an analogous varnish utilizing linseed oil as the oil component.

The modified esters of the above examples may be readily bodied if desired. For example, when the ester prepared according to the method of Example I is heated...
and aerated for about 4 hours at 300° C., the resultant product has a Gardner-Holdt viscosity of Z and a Gardner color of 16.0 at 25% total solids.

The acidulated soap stocks may also be utilized to prepare alkyd resins, the drying properties of which can be greatly improved by aeration. The aeration process may be carried out upon the acidulated soap stocks, the esterified acid oil, the esterified oil modified with the unsaturated acid, or upon the alkyd resin.

From the foregoing specific examples, it is readily apparent that the vehicles prepared according to the process of the present invention constitute a novel and useful class of materials. It is also apparent, therefore, that various embodiments of the invention, in addition to those specifically disclosed, may be provided without departing from the spirit and scope of the invention as defined in the appended claims.

We claim:

1. A method of preparing a product useful as a vehicle in coating compositions, which comprises substantially completely esterifying an acidulated soap stock with a polyhydric alcohol containing from 2 to 4 hydroxy! groups at a temperature of about 150° C. to 300° C., reacting the resultant ester with about 2 percent to 8 percent by weight of the acidulated soap stock of an alpha, beta-ethylenically unsaturated polycarboxylic acid, and then blowing the reaction mixture with a member of the class consisting of air and oxygen in the presence of a metallic drier in an amount such that there is present from about 0.001 to 0.001 percent by weight of active metal, based upon the weight of the acid modified ester, for a time sufficient to remove substantially all of the antioxidants present in said reaction mixture.

2. The method of claim 1 wherein said member of the class consisting of air and oxygen is utilized in an amount such that from 0.001 to 0.004 cubic foot per minute of oxygen is utilized per gallon of ester for a period of about 2 to 6 hours.

3. The method of claim 2 wherein the alpha, beta-ethylenically unsaturated polycarboxylic acid is maleic acid.

4. A vehicle for coating compositions prepared according to the method of claim 2.

5. The method of claim 1 wherein the acidulated soap stock is a soybean oil soap stock and the polyhydroxy alcohol is pentaerythritol.

6. A method of preparing a product useful as a vehicle in coating compositions which comprises substantially completely esterifying an acidulated soybean oil soap stock with pentaerythritol at a temperature of about 150° C. to 300° C., reacting the resulting ester with from about 2 percent to 8 percent by weight of maleic anhydride at a temperature of about 200° C. to 250° C., and then blowing the reaction mixture with air for about 2 to 6 hours at about 230° F. to 250° F. and at a rate such that the reaction mixture is treated with oxygen in an amount of from about 0.001 to 0.004 cubic foot per minute per gallon of ester, in the presence of a metallic drier in an amount such that there is present about 0.0001 to 0.001 percent by weight of active metal based upon the amount of ester treated with air.

7. The method of claim 6 wherein the acidulated soybean oil soap stock is replaced by an acidulated corn oil soap stock.

8. The method of claim 6 wherein the acidulated soybean oil soap stock is replaced by an acidulated linseed oil soap stock.

9. A vehicle for coating compositions prepared according to the method of claim 1.

10. A pigmented paint composition, the vehicle thereof comprising the product of claim 9.

11. A varnish composition, the vehicle thereof comprising the product of claim 9.

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