Patented Dec. 8, 1936 2,063,855

UNITED STATES PATENT OFFICE

2,063,855

POLYBASIC ALIPHATIC ACID-POLYHYDRIC ALCOHOL RESIN

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No Drawing. Application December 6, 1933, Serial No. 701,181

8 Claims. (Cl. 260—8)

The present invention relates to the production of polyhydric alcohol-fatty acid resins, and more particularly of an improved resin composed of a polyhydric alcohol, maleic acid and one or more fatty acids of high molecular weight, such as can be obtained upon hydrolysis of a fatty oil, especially of a drying or semi-drying oil, or of a fat.

It is the object of the invention to produce homogeneous, fusible, soluble resins of practically neutral character and pale color by the interaction of glycerol or a polyglycerol or equivalent polyhydric alcohol, maleic acid, and a fatty acid or mixtures of fatty acids obtained by hydrolysis of drying or nondrying oils or of fats, and characterized by being substantially free of uncombined hydroxyl groups, and hence possessing rapid drying qualities.

I have found that when glycerol, maleic acid and a fatty oil acid are reacted in the manner generally practiced in the art, as by heating the three ingredients together to reacting temperatures, two separate layers are invariably formed which cannot be made to fuse together even by prolonged heating; in fact, if the mass is heated at elevated temperatures in the attempt to homogenize the mixture, the lower layer, which consists essentially of glycerol-maleic acid esters, is converted into the infusible, insoluble state and ultimately chars.

It has already been suggested to perform the condensation of glycerol, unsaturated fatty oil acids and maleic acid by first oxidizing the fatty oil acid glycerol monoester with a current of air in the presence of a drier, and then reacting the oxidized mono-ester with maleic acid. However when it is attempted to carry out such reaction, particularly with the use of linseed oil fatty acids, and oxidation of their partial ester in the presence of a drier, it will be found that two separate layers are formed which persist in spite of vigorous stirring and finally the lower layer chars. If this action is carried out with unoxidized esters, enough maleic acid being employed substantially to neutralize the partial glycerol ester, the maleic acid will go into solution, but the reaction must be stopped while the acid number is still high (80–100); if it is attempted to reduce the acid number by further heating, the mass jells and becomes infusible and insoluble in common solvents, and finally chars.

It has also been proposed to employ an excess of glycerol and thereby favor the formation of a more nearly neutral-reacting product; however, the large excess of glycerol that must be employed is highly undesirable because the resulting product contains a large proportion of free hydroxyl groups and hence dries with difficulty and is generally unsuited for the manufacture of air drying or even of baking varnishes and enamels.

I have found, however, that a homogeneous resin of low acid number and substantially free of uncombined hydroxyl groups can be obtained by first reacting the glycerol with the fatty oil acid to produce the diester of such acid, and then neutralizing the remaining free hydroxyl groups with approximately the theoretical amount of maleic acid. By such procedure the resin can be safely heated long enough to reduce its acid number to about 25 or below without danger of converting it into the infusible state; in fact, a resin having an acid number of only about 3 to 6 can readily be obtained with my improved procedure.

The present invention accordingly contemplates an improved process for the manufacture of pale, quick-drying, soluble resinous materials of low acid number by reacting a trihydric or higher alcohol, maleic acid and one or more fatty oil or fat acids in such order and in such proportions, due allowance being made for unavoidable loss of alcohol during the reaction, that first the di-acid ester of the last-mentioned acid is formed, and such ester then substantially neutralized with maleic acid, there being no quantity of remaining free hydroxyls sufficient to impair the air drying qualities of the resin when the latter is applied as a film in a suitable solvent.

The invention will be described in greater detail with the aid of the following examples which illustrate several satisfactory procedures embodying my improved process.

Example 1.—1680 grs. (approximately 6 mols) of soya bean oil fatty acids are heated to about 230–240° C. or somewhat higher with 285 grs. (approximately 3 mols) of glycerol until a glycerol diester is obtained having an acid number of about 1. There are then added 1½ gram-molecular weights of maleic acid (174 grs.) or maleic anhydride (147 grs.) and the heating is continued at a temperature of 230–240°, or somewhat lower or higher, the mass being continually stirred either mechanically or by bubbling an inert gas therethrough. After about 15 to 20 hours heating the product becomes highly viscous and has an extremely low acid number (about 4–8). The product is plastic in character at room temperatures, is soluble in mineral spirits and in varnish oils, and presents a very desirable resin because of its practically neutral character as it can be mixed with basic pigments (and of course

also with other types of pigments) for the manufacture of enamels and paints. It is also substantially free of hydroxyl groups and accordingly dries quickly both in air and on baking.

Example 2.—The same procedure as set forth in Example 1 is followed except that instead of soya bean fatty oil acid, wood oil fatty acids or linseed oil fatty acids, or mixtures of the different fatty oil acids and fat acids, or the acids obtained from cotton seed oil or perilla oil are employed. There may also be employed the acids of the following oils, either alone or in admixture: corn oil, sunflower oil, castor oil, olive oil, rapeseed oil, rubber seed oil, fish oil etc. the properties of the final product depending to some extent upon the character of the fatty oil acid used.

The mixed ester resins produced in accordance with the above-described process are soluble also in benzol, turpentine and other common varnish solvents.

The plastic resins above-obtained can be mixed with varnish oils or with varnishes and impart thereto paleness of color and superior durability and water-proofness.

Care should be taken not to use oxidized fatty oil acids, as I have found that the partial glycerol esters made from such acids have only a slight solvent power for maleic acid, so that a large part of the maleic acid can not be made to enter into reaction to form a neutral or nearly neutral product, but form rather a separate layer. In addition, oxidation of the fatty acids, especially at elevated temperatures, tends to darken the color of the product and reduces the value of the latter.

I claim:

1. The method of producing homogeneous, oil-soluble resins containing maleic acid, which comprises reacting glycerol and one or more of the acids obtainable on hydrolysis of an oil or fat in substantially the theoretical amount required to form the glycerol diester of such acid or acids until a product of low acid number is obtained, and then reacting such product with substantially the theoretical amount of maleic acid required to neutralize the same.

2. The method of producing homogeneous, oil-soluble resins containing maleic acid, which comprises reacting the glycerol diester of one or more acids obtainable on hydrolysis of an oil or fat with substantially the theoretical amount of maleic acid required to neutralize the same.

3. The method of producing homogeneous, oil-soluble resins containing maleic acid, which comprises reacting glycerol and substantially the theoretical amount of unsaturated fatty oil acid required to form the glycerol diester of such acid until a product of low acid number is obtained, and then reacting such product with substantially the theoretical amount of maleic acid required to neutralize the same.

4. The method of producing homogeneous, oil-soluble resins containing maleic acid, which comprises reacting the glycerol diester of the acids of a drying oil with substantially the theoretical amount of maleic acid required to neutralize the same.

5. The method of producing homogeneous, oil-soluble resins containing maleic acid, which comprises reacting two mols of glycerol with four mols of unsaturated fatty oil acid until a product consisting primarily of the diester of such acid and having a negligible acid number is obtained, and then reacting such diester with one mol. of maleic acid at temperatures up to about 250° C. until an oil-soluble, homogeneous product is obtained.

6. The homogeneous, oil-soluble reaction product of (1) the low acid number product obtained by reacting approximately two mols of glycerol and four mols of a fatty acid obtainable on hydrolysis of a fatty oil or of a fat, and (2) one mol. of maleic acid.

7. The homogeneous, oil-soluble reaction product of (1) the low acid number product obtained by reacting approximately two mols of glycerol and four mols of drying oil acids, and (2) one mol. of maleic acid.

8. The homogeneous, oil-soluble reaction product of (1) the low acid number, glycerol diester-containing product obtained by reacting approximately 1 mol. of glycerol with two mols of the acids on hydrolysis of a fatty oil or of a fat and (2) approximately the theoretical amount of maleic acid required to neutralize the same, said product having an acid number of 25 or below.

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