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LOW TEMPERATURE PREPARATION OF ALKYD RESINS FROM LONG CHAIN FATTY ACIDS

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This invention relates to a method of making an alkyd resin, and more particularly to a method of making an alkyd resin suitable for use as a paint vehicle. Still more particularly, it describes a method whereby alkyds made from long chain fatty acids may be prepared at lower temperatures and without loss of material.

It is known to react long chain fatty acids with polyhydric alcohol and dibasic acids to form alkyds of varying oil length. For example, the formation of an alkyd from tall oil fatty acid, pentaerythritol, and phthalic acid or anhydride has been thoroughly explored in the art.

The use of isophthalic acid in place of the phthalic acid or anhydride has also been described. However, isophthalic acid calls for more stringent reaction conditions. Thus, the usual manner of preparing the alkyds is simply to mix together the requisite amounts of long chain fatty acid, polyhydric alcohol, and isophthalic acid, heat the mixture to a temperature of at least about 290° C., and maintain the temperature at that high level until the desired acid number is obtained. Although such a procedure produces an excellent alkyd resin, there is an unavoidable loss of isophthalic acid and pentaerythritol due to entrainment, or sublimation, or other similar mechanism.

It is the primary object of the present invention to present a process whereby such losses are avoided. It is a further object of the present invention to present a process whereby reaction between a long chain fatty acid, a polyhydric alcohol, and isophthalic acid may be accomplished at temperatures substantially lower than those previously found necessary.

These objects have been accomplished in a surprisingly effective manner. The invention contemplates reacting a long chain fatty acid with pentaerythritol in the ratio of about 1.0 to 2.2 equivalents of fatty acid to about 4 equivalents of alcohol. The isophthalic acid is then added to this partial ester at a temperature in the range of about 220°–260° C. and in an amount of about 0.5–1.5 equivalents of isophthalic acid per 4 equivalents of polyhydric alcohol. Thereafter the balance of the long chain fatty acid is reacted with the product.

The long chain fatty acids contemplated for use in the process of the present invention are those obtained from drying, semidrying, or nondrying oils. Exemplary of the oils from which the fatty acids are obtained are soy bean, linseed, cottonseed, castor, dehydrated castor, corn, perilla, tall, coconut, and tallow oils. The long chain fatty acids are those known to be present in such oils, as for example, stearic, eleostearic, palmitic, oleic, linoleic, linolenic, ricinoleic, and often lauric. The various isomers of these acids such as are found in some processed oils are also suitable. The styrene or vinyl toluene modified siccative oils may be used as total or partial replacements for the fatty acids. These products are prepared by reacting styrene or vinyl toluene with a bodied drying

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or semidrying oil, preferably in the presence of a catalyst to produce a modified oil generally having an oil length of about 60%.

The polyhydric alcohol to be used in the present process must contain four hydroxy groups. Should the alcohol contain less than the requisite four hydroxy groups, as for example glycerine with three, the resulting alkyd does not possess sufficient molecular weight to serve the role intended.

The dibasic acid used in the present invention is isophthalic acid.

The invention contemplates reacting initially a portion of the total of the long chain fatty acids with the pentaerythritol. The relative amounts of the fatty acid and the polyhydric alcohol in the initial reaction must be maintained within fairly narrow limits if the isophthalic acid is to react swiftly on subsequent addition. On an equivalent basis, the ratio is about 1.0 to about 2.2 equivalents of fatty acid to about 4 equivalents of alcohol. On a mole basis, about 1–2 moles of fatty acid are reacted with about 1 mole of pentaerythritol. It can readily be seen that the goal in general in this initial reaction is to form the fatty acid-pentaerythritol diester. One of the surprising features of the present invention is that the initial reaction should not produce a compound substantially varying from the diester, otherwise the isophthalic acid will not dissolve in the reaction product at the relatively low temperatures contemplated by the present process. In fact, it has been found that if in the initial reaction about 2.4 equivalents of the fatty acid are reacted with about 4 equivalents of the polyhydric alcohol, the subsequent addition of isophthalic acid will not produce a reaction within a reasonable time at the temperatures contemplated by the present invention.

The conditions of the initial reaction of the long chain fatty acid and the pentaerythritol are in accordance with usual alkyd practice. The initial reaction may be carried out at a temperature in the range of about 150°–250° C., and preferably at about 220° C. At this latter temperature, the reaction generally takes about 3 hours, during which times substantially all the fatty acid reacts. It is preferred that the acid number be brought down to 3–10.

When the initial reaction is complete, the isophthalic acid is added and the reaction mixture is raised to a temperature of between about 220°–275° C., and preferably about 250° C. The amount of isophthalic acid to be added will be greater than 0 and less than 2 equivalents per 4 equivalents of the polyhydric alcohol. Generally speaking, the amount of isophthalic acid will range between 0.5–1.5 equivalents, and preferably about 1.1 equivalents.

The unexpected advantages of the present process become apparent on the addition of the isophthalic acid. The isophthalic acid readily dissolves in the diester. If, on the other hand, an attempt had been made in accordance with usual practice to mix the long chain fatty acid, the pentaerythritol, and the isophthalic acid, and heat the mixture to a temperature of about 250° C., it would be found that the isophthalic acid could not be made to go into solution. It would be necessary instead to raise the temperature to about 290° C. in accordance with known practice involving isophthalic acid; this practice, however, produces losses due to volatilization or entrainment of the pentaerythritol and isophthalic acid, as explained earlier.

By adding the isophthalic acid to a reaction mixture comprising substantially a diester of the fatty acid and polyhydric alcohol, however, the isophthalic acid swiftly

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goes into solution, usually taking ½–1 hour to do so. Additional reaction time may be utilized if desired.

Once the isophthalic acid has dissolved, the balance of the long chain fatty acid may be added to the mixture. In accordance with the amounts given above, this amount of long chain fatty acid will be about 0.3–2.5 equivalents per 4 equivalents of polyhydric alcohol. The temperature should be maintained in the range of about 220°–275° C., and preferably at about 250° C., until the desired extent of reaction has taken place. Where the alkyd resin is to be used as a paint vehicle, it is preferred that the acid number of the final product be in the range of about 5–10.

Varying the relative amounts of ingredients within the ranges listed above will produce alkyd resins having slightly different properties in accordance with precisely what is desired. For instance, increasing the amount of isophthalic acid within the above-listed ranges gives a tougher paint film, higher solvent resistance, quicker cure, and tends to yield a paint vehicle that gives a heat-cured film as opposed to an air-cured film. In accordance with usual alkyd practice, the total carboxylic acid equivalents should be about equal to the total hydroxyl equivalents in the reactants; a 5% excess of hydroxy equivalents is preferred.

The following examples illustrate several embodiments of the invention. All parts are by weight unless otherwise stated.

Example I

To an alkyd reactor equipped with agitator, reflux condenser, water trap, and CO₂ inlet tube there was added 453 parts Acintol FA-1 (tall oil fatty acids, 1% rosin), which was then heated to 200° C. To the fatty acids was added 105 parts technical pentaerythritol, sold under the name "Pentek," and the reaction mixture was maintained at 200° C. for 2 hours and then 220° C. for 3 hours. The mixture was then raised to a temperature of 250° C., whereupon there was added 83 parts isophthalic acid, and the mixture was maintained at 250° C. for ½ hour. There was then added an additional 110 parts of fatty acid. The resultant mixture was maintained at 250° C. for 2 hours to an acid number of 8.

The resultant alkyd was an excellent paint vehicle.

Example II

A mixture of 755 parts of vinyl toluene treated tall oil fatty acids having an average molecular weight of 475 and an oil length of 65% plus 98 parts "Pentek" was heated for 2 hours at 220° C. To the heated diester was added 53 parts isophthalic acid and the temperature raised to 250° C.

After 1 hour at the 250° C. temperature, an additional 163 parts of the vinyl toluene modified tall oil fatty acid was added. The mixture was maintained at 250° C. for 4½ hours to an acid number of 5.

Example III

A mixture of 386 parts vinyl toluene modified fatty acid of 70% oil length wherein the fatty acid consisted of 90% tall oil fatty acids and 10% dehydrated castor oil fatty acids, plus 66 parts "Pentek," was heated to 220° C. for 2 hours. There was then added 23 parts isophthalic acid, and the mixture raised to 250° C. and maintained at that temperature for ½ hour. At the end of the ½ hour, the solution had cleared; the isophthalic acid had completely dissolved. There was then added 224 parts of the vinyl toluene modified tall oil described above and the mixture was maintained at 250° C. for 7 hours to an acid number of 4.76.

Example IV

A mixture of 465 parts of vinyl toluene modified tall oil (65% oil length) plus 75 parts "Pentek" was heated

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to 220° C. for 2 hours. There was then added 38 parts "Pentek" and the mixture was heated to 250° C. for 1 hour. At the end of the hour, the solution was clear. There was then added 157 parts of the vinyl toluene modified tall oil fatty acids described above, and the mixture was maintained at 250° C. for 7 hours to an acid number of 4.15.

Example V

To determine the solubility of the isophthalic acid in the diester at various temperatures, 3 runs were made. A mixture of 375 parts pentaerythritol-tall oil fatty acid diester, plus 50 parts isophthalic acid was heated in separate containers to temperatures of 190° C., 220° C., and 250° C., and maintained at those temperatures for 5 hours, after which the acid number was obtained. The acid numbers were 158, 63, and 9, respectively, showing that the isophthalic acid dissolves to a significant extent only in a temperature in the range of at least about 220°–250° C.

Example VI

To show the effect of the ratio of reactants in the initial reaction on the solution of the isophthalic acid, five runs were made using 63 parts (4 equivalents) pentaerythritol and varying amounts of tall oil fatty acids. 50 parts isophthalic acid was then added and the mixture was maintained at 250° C. for 2½ hours. The appearance of the mixture was then noted. Following are the results:

Hydroxyl Eqs.	Fatty Acid Eqs.	Acid No.	Appearance 2½ Hours After Addition of Isophthalic Acid
4	2.5	4	Cloudy; batch filled with undissolved isophthalic acid.
4	2.2	4	Very slight cloudiness.
4	2.0	3	Batch cleared after 55 minutes.
4	1.5	3	Do.
4	1.3	3	Very slight cloudiness.

Example VII

A mixture of 340 parts (2.5 equivalents) tall oil fatty acids, 63 parts (4 equivalents) pentaerythritol, and 50 parts (1.4 equivalents) isophthalic acid was heated to 250° C. and maintained at that temperature for 2½ hours. The acid number was 24, and the mixture remained very cloudy with undissolved isophthalic acid.

I claim:

1. The method of making an alkyd resin comprising reacting at a temperature in the range of about 150°–250° C. a long chain fatty acid obtained from an oil selected from the group consisting of drying oils, semi-drying oils, nondrying oils, and mixtures thereof with pentaerythritol in the ratio of about 1.3 to 2.2 equivalents of fatty acid to about 4 equivalents of pentaerythritol to form fatty acid-pentaerythritol diester, dissolving in said diester at a temperature in the range of about 220°–260° C. about 0.5–1.5 equivalents of isophthalic acid, and reacting with the resulting product about 0.3–2.5 equivalents of said long chain fatty acid.

2. The method according to claim 1 wherein said long chain fatty acid comprises a tall oil acid.

3. The method according to claim 1 wherein said fatty acid comprises a vinyl toluene modified fatty acid of a drying oil.

4. The method according to claim 1 wherein said diester has an acid number in the range of about 3–10.

5. The method according to claim 1 wherein the final alkyd resin product has an acid number in the range of about 5–10.

6. The method according to claim 1 wherein said fatty acid comprises a mixture of tall oil fatty acid and dehydrated castor oil fatty acid.

References Cited in the file of this patent

UNITED STATES PATENTS

1,889,923	Kienle -----	Dec. 6, 1932
2,071,313	Saunders -----	Feb. 16, 1937
2,527,057	Canfield -----	Oct. 24, 1950
2,627,508	Lum -----	Feb. 3, 1953
2,731,430	Brunner -----	June 17, 1956

FOREIGN PATENTS

316,914 Great Britain ----- Aug. 6, 1929

OTHER REFERENCES

Isophthalic, Paint, Oil and Chemical Review, February 10, 1955, pages 10-17.