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PREPARATION OF ALKYD RESINS INVOLVING THE ACIDOLYSIS OF TRIGLYCERIDE OILS, ISOPHTHALIC AND TEREPHTHALIC ACIDS

Earl F. Carlston, El Cerrito, Calif., assignor to California Research Corporation, San Francisco, Calif., a corporation of Delaware

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The present invention relates to the preparation of oil-modified alkyd resins, and more particularly to an improved process of alkyd preparation involving the acidolysis of a triglyceride and a phthalic acid in which the carboxyl groups are separated from each other by at least three carbon atoms, e.g., isophthalic acid or terephthalic acid.

As employed herein, the term "oil-modified alkyd resin" denotes generically polymeric polyesters of polyhydric alcohols having more than two hydroxyl groups, e.g., glycerol, and the resinifying polycarboxylic acids comprising phthalic acids in which the carboxyl groups are separated from each other by at least three carbon atoms, such as isophthalic acid and terephthalic acid, and in which a portion of the polycarboxylic acid is replaced by a fatty acid from vegetable or marine oils, to produce an oil-modified alkyd resin. As is known in the art, oil-modified alkyd resins are made with drying, semi-drying, or non-drying oils.

One way of preparing oil-modified alkyd resins is by the so-called process of "alcoholysis." According to this procedure, the first stage involves heating with catalyst, litharge or other metallic oxides and hydroxides, the oil containing monocarboxylic fatty acids in the form of triglycerides with a polyhydric alcohol, in order to produce a mixture of partial esters of polyhydric alcohols and monocarboxylic fatty acids. In the second stage this mixture of partial esters is condensed with a polycarboxylic acid or anhydride, e.g., phthalic anhydride, to a substantially completely esterified alkyd resin of low acid number. Resins of varying oil length, i.e., short, medium, long, and very long, can be produced depending on the relative oil content or oil length calculated as triglyceride in percent by weight of the final resin.

The preparation of alkyd resins as above described has associated therewith certain problems, which although troublesome, are nevertheless tolerated for lack of a solution therefor. To illustrate, in the preparation of the oil-modified glyceryl phthalate resins, the reaction product of the dibasic acid phthalic anhydride, trihydric alcohol, glycerol, modified with either a drying or non-drying oil, following the alcoholysis of the triglyceride and polyhydric alcohol, the phthalic anhydride may be added in either of two ways: The resin kettle is opened, and the anhydride added directly to the contents; or anhydride in fluid state may be pumped into the closed kettle. The first alternative, opening of the hot kettle or reactor for the addition of anhydride, gives rise to the issuance of undesirable vapors comprising steam, acrolein, and anhydride, which in addition to creating a fire hazard are regarded as industrial toxicants. The second alternative of pumping and transmitting molten anhydride involves costly corrosion-resistant equipment. When isophthalic or terephthalic acids are used instead of phthalic anhydride, a costly solids handling system would be required to minimize the hazards in opening the hot kettle. It has, accordingly, been proposed to change the sequence of steps involved in the esterification reaction by first reacting the triglyceride with the polybasic acid, a prodecure known as "acidolysis," followed by the addition of the glycerol. While alcoholysis results in a mixture of partial esters of polyhydric alcohols and monocarboxylic acids, "acidolysis" produces fatty acids and half-esters of the triglyceride oil and the dibasic acid. It has been ascertained, however, that the procedure of acidolysis to be successful requires the observance of certain unpredictable requirements ragarding both the materials employed and the conditions under which the process is carried out. For example, it has been observed that the simple variation in the order of addition of reactants to the alkyd vessel, i.e., heating to temperature of phthalic anhydride and triglyceride oil, followed by addition of glycerol, a known non-corrosive and easily pumpable material, does not produce the desired results, inasmuch as the acidolysis reaction of the phthalic anhydride with the oil does not occur, and gelation interferes with the course of reaction. Successful acidolysis employing phthalic anhydride is covered in copending application Serial No. 762,922, filed September 24, 1958. Similarly, when using a phthalic acid other than o-phthalic acid or phthalic anhydride, such as isophthalic acid, which does react with triglyceride oil, it is desirable that existing equipment for alkyd preparation be capable of utilization without extensive modification when employing the technique of acidolysis. Equipment customarily employed in alkyd manufacture is sometimes limited with respect to the temperature that can be achieved or allowed, with the result that temperatures substantially in excess of 535° F. are frequently impracticable. While, as indicated above, the acidolysis reaction of phthalic anhydride with triglyceride oil cannot now be effected irrespective of temperature, the acidolysis reaction of phthalic acids of the type of isophthalic acid with triglyceride oil can be completed in a few minutes provided that high temperatures of the order of 575° F. (300° C.) are employed. The rate of acidolysis is slower as the temperature of reaction is lowered. Thus, when lower temperatures in the range of 500–535° F. are employed, due to the inability of the alkyd resin cooking equipment to operate at higher temperatures, an impracticable long time is required to obtain the desired degree of acidolysis. But since the high temperatures required are those outside the range characterizing conventional alkyd equipment, it is apparent that the complete acidolysis of phthalic acids of the type of isophthalic acid is not so feasible or practicable as might be desired.

Accordingly, an object of the present invention is to provide a process for the acidolysis of phthalic acids of the isophthalic acid type which employs sufficiently low temperatures as to permit the acidolysis reaction in equipment customarily employed in alkyd manufacture.

Another problem encountered in the acidolysis procedure of making alkyds from isophthalic and terephthalic acids is that while the acidolysis reaction is conducted at high temperatures up to 575° F., the polyhydric alcohol, e.g., gylcerol, is added at a much lower temperature in the range of 400–450° F., preferably 420° F. or below, causing a loss of time while waiting for the reaction mixture to cool; and the time of waiting varies according to the capacity of the cooling facilities of the kettle. If the glycerol or other polyhydric alcohol is charged to the kettle at too high a temperature, explosive evolution of water occurs.

Accordingly, another object of the invention is to eliminate the cooling requirement and to save the time lost by such a procedure.

Broadly, the present invention is predicated on the discovery that alkyd resins can be prepared from glycerol, a triglyceride oil, and isophthalic acid by the procedure of acidolysis employing a temperature capable of being readily attained with the ordinary equipment, i.e., around 500° F.–535° F. by heating a mixture of the triglyceride and isophthalic acid to a temperature within the range 500° F.–535° F., maintaining this temperature during the addition of the glycerol to the aforesaid mixture at a con-

trolled rate to allow acidolysis to proceed simultaneously with esterification, thus avoiding the formation of gels. Since the esterification reacting with subsequent evolution of water is endothermic in nature, care is exercised that the rate of addition of the glycerol does not overbalance the input of heat to produce a precipitous drop in temperature, thus preventing acidolysis. Following addition of the glycerine, the whole is then further heated to continue esterification and produce a bright resin of desired acid number, generally below 25, and preferably below 10. The temperature employed in the final heating treatment will depend on the degree of acidolysis achieved during the addition of glycerine, the temperature varying inversely with the degree of acidolysis, and being sufficiently high to effect esterification and inhibit or prevent gel formation, whereby a bright, gel-free resin is produced.

This procedure, which allows acidolysis to occur simultaneously with esterification and also trans-esterification, is free from gel formation because the isophthalic acidolyzed oil and the liberated fatty acids react with glycerol to form compatible products in contrast to the incompatible triglyceride oil and gelable glycerol isophthalate mixture.

It is apparent that the acidolysis temperatures of 500–535° F. are operable with a considerable quantity of alkyd cooking equipment that cannot be used above this range of temperature in a practicable manner. The procedure of adding glycerol in a controlled manner to achieve rapid and complete acidolysis can be used successfully at any temperature of 500° F. or above. At temperatures lower than 500° F., the rate of the acidolysis reaction diminishes so that at 480° F. for example, the rate is so slow that a completely homogeneous and bright alkyd resin cannot be made by this procedure without extending the time of glycerol addition to an impractical value.

As above indicated, the satisfactory addition of the glycerol or polyol to the heated mixture of isophthalic acid and glyceride oil to produce bright alkyd resins free from cloud, haze, or other evidence of gel structure is related to the acidolysis reaction, and while it has heretofore been thought that complete acidolysis, either by use of high temperature or an impracticably long time at lower temperatures, had first to be effected prior to the addition of the glycerol or polyol, I have now found that acidolysis need not be complete prior to charging of the glycerol. Accordingly, I have discovered that if acidolysis is effected beyond a certain critical minimum, the glycerol can be subsequently added as one charge and esterification effected in conventional manner. Suitable criteria in ascertaining a satisfactory degree or extent of acidolysis is by determination of the amount of oil converted to acid product, that is, partial ester and free fatty acid, or a measurement of the acid number of the acidolysis product. In general, when the acidolysis product possesses an acid number of at least 100, acidolysis has proceeded to a sufficient extent to permit dumping in all the glycerol at 420–400° F. in the conventional manner and esterifying at any suitable temperature, for example, 425° F.–480° F. Acid numbers of the products of acidolysis can be determined in conventional fashion, that is, by diluting a hot sample with about five volumes of toluene, followed by filtering to remove the unreacted isophthalic acid, which is insoluble in the hot (around 200° F.) toluene solution, the filtrate is boiled to remove the toluene, and the resulting oil, which is a mixture of fatty acid, isophthalic half-ester, and unreacted triglyceride oil, is titrated with 0.1 KOH in ethanol, acid number being defined as mg. of KOH required to neutralize 1 gram of oil.

It has been found that even a lesser degree of acidolysis, expressed in terms of acid number as above described, is required if the acidolysis of the triglyceride oil is effected in the presence of a fatty acid. For example, when a mixture of isophthalic acid and triglyceride oil is heated in the presence of a mole of fatty acid per mole of triglyceride oil to a reaction product mixture having an acid number of 75, subsequent addition of all of the glyceryl produces a bright, gel-free resin. In this connection, it should be pointed out that since fatty acid is present at the start of the reaction in the amount indicated, the actual acid number derived from the acidolysis of the triglyceride oil is only about 27, compared with an acid number of about 100 when oil alone is used.

In proceeding, as above described, gelation during reaction is inhibited or prevented, whereby the simultaneous acidolysis and esterification reactions are permitted to go to completion smoothly and in the shortest time. In addition, clear and bright solutions are produced at the end as compared with the hazy or cloudy solutions obtained by alcoholysis. In the alcoholysis procedure, the resin solutions are cloudy or hazy because of catalyst residues, and require pressure filtration to produce bright and clear solutions. In contrast thereto, filtration is not required in the instant process.

The following examples are given to illustrate the invention, but are not to be construed as limiting the invention thereto.

Example 1

A mixture of 1375 g. (1.55 moles) safflower oil and 915 g. (5.51 moles) isophthalic acid is heated to 480° F. To the heated mixture there is added 414 g. (4.50 moles) glycerol (anhydrous basis) over a period of 1 hour 8 minutes, the temperature being maintained at 480° F. during the addition of the glycerol. Following the addition of glycerine, the mixture is heated at 480° F. for an additional 45 minutes. Gel formation occurs, and the resin is cloudy. The example shows that a temperature of 480° F. is insufficiently high to effect a satisfactory degree of acidolysis.

Example 2

A mixture of 1375 g. (1.55 moles) safflower oil and 915 g. isophthalic acid (5.51 moles) is heated to a temperature of 500° F., whereupon 414 g. (4.50 moles) of glycerol (anhydrous basis) is added over a period of 1 hour, 5 minutes, while maintaining the temperature at about 500° F. The temperature is then lowered to 480° F. and the mixture heated or cooked at 480° F. for an additional one hour. The resulting resin is cloudy, indicating that acidolysis to the desired extent had not been achieved.

Example 3

A mixture of 1375 g. (1.55 moles) safflower oil and 915 g. isophthalic acid (5.51 moles) is heated to 500° F. 414 g. (4.50 moles) glycerol (anhydrous basis) is then added to the heated mixture over a period of time of 1 hour, 19 minutes, the mixture being heated all the while to maintain the temperature at 500° F. After the addition of all of the glycerol, the mixture is heated at 500° F. for an additional 41 minutes, thus providing for a total cooking time of 2 hours. The final resin is clear and bright and has an acid number of 10.

Example 4

A mixture of 1375 g. (1.55 moles) alkali refined soybean oil and 915 g. (5.51 moles) isophthalic acid is heated to a temperature of 518° F., whereupon 414 g. (4.50 moles) glycerol (anhydrous basis) is added, while slowly cooling to a temperature of 500° F., over a period of 59 minutes. At this point, a satisfactory degree of acidolysis has been reached for lowering of the temperature to 480° F. and cooking for an additional time of one hour produces a bright and clear resin having an acid number of 10.

Example 5

A mixture of 1375 g. (1.55 moles) safflower oil and 915 g. (5.51 moles) terephthalic acid is heated to 500° F. Glycerol in an amount of 414 g. (4.50 moles) is then added to the heated mixture at a uniform rate over a

period of 1 hour and 54 minutes, and the whole further heated at 500° F. to provide a total heating time at 500° F. of 4 hours. There results a clear and bright resin having an acid number of 10.

Example 6

A mixture of 1375 g. safflower oil and 915 g. isophthalic acid is heated to 518° F. (270° C.) and held at 518° F. for 3 hours. At the end of this time a small sample is diluted with toluene and filtered hot to separate the oil from unreacted isophthalic acid. The filtrate, after removal of toluene, is found to have an acid number of 108. After cooling to 400° F., 414 grams of glycerol (anhydrous basis), less the small amount required to react with the sample that was taken for acid number, is added, and heating is continued to a final temperature of 480° F., where it was held until the acid number of the resin was 10. The resin is bright with no evidence of gel structure.

Example 7

Example 6 is repeated except that acidolysis is effected for 1 hour to produce an acidolysis product having an acid number of 58. An unsatisfactory resin is obtained, as evidence by a slight amount of gel formation.

Example 8

Example 6 is repeated except that acidolysis is carried out for one-half hour, or to an acid number of 36. The resin is unsatisfactory, as evidenced by the presence of a large quantity of insoluble sand-like gel particles.

Example 9

Example 6 is repeated, except that the oil is soybean oil, and the acidolysis is carried out for one hour at 536° F., to produce an acidolysis product with an acid number of 101. The resin is bright, with no evidence of gel structure.

Example 10

A mixture of 1375 g. safflower oil and 915 g. isophthalic acid is heated to a temperature of 575° F. (300° C.), and the heat is then turned off. When the temperature has dropped to 550° F. the heat is turned on, and 414 g. glycerol (anhydrous basis) is added over a period of 21 minutes, after which the temperature is 445° F. Heating is continued at 480° F. for a total cooking time, exclusive of up-heat time, of 2¼ hours. The resin is bright, with no evidence of gel structure.

Example 11

A mixture of 1043 g. (1.18 moles) linseed oil, 915 g. (5.50 moles) isophthalic acid, and 338 g. (1.18 moles) fractionated tall oil fatty acids is heated to 518° F. and held at 518° F. for 30 minutes and then cooled to 410° F. A sample of the batch is diluted with toluene, filtered, and the acid number of the oil-fatty acid product is found to be 80. Since the acid number of the oil-fatty acid mixture before heating was 48, the acid number due to acidolysis of the oil is 32. Glycerol, 451 g. (4.90 moles) less the amount required to react with the sample that was removed, is added at once, after which the temperature of the batch is about 360° F. Heating is resumed and esterification carried out for a period of 2½ hours. The resulting resin is clear and bright.

Example 12

Example 11 is repeated except that the time of heating at 518° F. is reduced to 15 minutes, and the acid number of the oil-fatty acid product is about 75. The resulting resin is bright.

Example 13

Example 11 is repeated except that the time of heating at 518° F. is reduced to 2 minutes and the acid number of the oil-fatty acid product is 60. The resin has considerable gel lumps.

Example 14

A mixture of 1043 g. (1.18 moles) safflower oil, 338 g. (1.18 moles) fractionated tall oil fatty acids, and 915 g. isophthalic acid is heated to 465° F. and 451 g. (4.90 moles) glycerol (anhydrous basis) is then added at 465° F. to the mixture over a period of 86 minutes, and beating continued, all at 465° F., for an additional 1⅓ hours. The resulting resin is clear and bright.

Example 15

Example 14 is repeated with terephthalic acid instead of isophthalic acid, except that the temperature is 500° F. and the time for addition of glycerol is 72 minutes. After further heating at 500° F. for 1⅔ hours the resin is clear and bright.

In preparing the resins of the invention, it is advantageous to employ an excess of glycerol, and an amount of glycerine, expressed in terms of the isophthalic employed, of 10 to 25% over and above that required stoichiometrically to react with the isophthalic acid will be found satisfactory. In other words, for each equivalent of isophthalic acid there can be employed 1.1 to 1.25 equivalents of glycerol. By then varying the amounts of triglyceride employed in the acidolysis reaction, the oil length of the resin, defined as the percent by weight of the glyceride content based on total resin weight, may be adjusted to any percent, but preferably within the range of 20% to 90%. The whole operation of making the partial ester of isophthalic acid and triglyceride followed by esterification with the glycerol can be effected in conventional cooking vessels or kettles of any suitable size, equipped with adequate heating and stirring means, openings for charging the ingredients, sampling the product and, if it is desired to exclude oxidative effects of the air, provided with inlets and outlets for the passage of an inert gas. Following the addition of the glycerol cooking is continued to a point until a resin of the desired acid number is achieved. In general, a resin of low acid number is desirable, and resins of acid numbers below 25, and preferably below 10, are highly desirable.

While the invention has been exemplified in terms of the specific materials employed, other equivalent materials may replace these in part or in whole. Thus, in addition to isophthalic acid and terephthalic acids as such, mixtures of these two acids may be used. Moreover, there can be used substituted isophthalic and terephthalic acids containing substituents inert under the conditions of reacting, such as 5-tertiary butyl isophthalic acid and 2-methyl terephthalic acid. These materials, as hereinbefore indicated, may be characterized as phthalic acids in which the carboxyl groups are separated from each other by at least 3 carbon atoms of the benzene ring.

Similarly, the glycerine may be replaced in while or in part by other polyhydric alcohols including glycols, such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol; and polyols, such as trimethylolpropane, pentaerythritol, dipentaerythritol, mannitol, sorbitol, and the like.

The glyceride employed in the acidolysis reaction may be derived from various sources, and include those of marine and vegetable origin. They may be of nondrying, semi-drying, or drying oil type. Thus, in addition to the safflower oil employed in the examples, there may be mentioned such oils as castor, corn, cocoanut, cottonseed, linseed, oiticica, perilla, rapeseed, poppyseed, sunflower, tall oil, tung, and the marine oils, herring, menhaden, and sardine.

In the event is is desired to employ a fatty acid in the acidolysis reaction, any fatty acid derived from the hydrolysis or saponification of the foregoing glycerides can be employed. These include such acids as caproic, caprylic, capric, lauric, myristic, palmitic, stearic, arach-

idic, behenic, oleic, ricinoleic, tall oil fatty acids, linoleic, linolenic, and licanic.

I claim:

1. Process for the preparation of an oil-modified alkyd resin which comprises heating to a temperature within about the range 500° F. to 535° F. a mixture of triglyceride and a phthalic acid in which the carboxyl groups are separated from each other by at least three carbon atoms, then adding slowly and continuously a saturated aliphatic polyhydric alcohol to the mixture and heating the mixture throughout the addition of the polyhydric alcohol to maintain the mixture at a temperature within the above-specified range, whereby incompatible gel formation is avoided, and then continuing heating to effect esterification and to produce a resin of acid number below 25, the polyhydric alcohol being employed in an amount sufficient to react with all the carboxyl groups up to 25% stoichiometric excess over the phthalic acid, and the glyceride being present in an amount within the range of 20% to 90%, based on total resin weight.

2. Process according to claim 1 wherein the phthalic acid is isophthalic acid.

3. Process according to claim 1 wherein the trihydric alcohol is glycerine.

4. Process according to claim 3 wherein the phthalic acid is isophthalic acid.

References Cited in the file of this patent

UNITED STATES PATENTS

1,888,849	Dawson	Nov. 22, 1932
2,627,508	Lum	Feb. 3, 1953
2,884,390	Carmody	Apr. 28, 1959

OTHER REFERENCES

Ellis: The Chemistry of Synthetic Resins, pages 921 and 930, vol. II, published 1935, Reinhold Publishing Corporation, New York, New York.