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PHOSPHITE ESTERS AS ESTERIFICATION CATALYSTS

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The present invention relates to a process of esterification in which esters of phosphorous acid are employed as esterification catalysts.

The invention is applicable to the esterification of fatty acids or rosin acids with aliphatic alcohols, either monohydric or polyhydric. These catalysts can be used without causing appreciable color formation during the esterification, which is particularly troublesome with conventional catalysts, especially when unsaturated higher fatty acids are esterified. Common esterification catalysts such as strong acids cause darkening of the product during esterification. Moreover, such acid catalysts are difficult to remove. In contrast, the phosphorous esters of the present invention are volatile, and can be removed easily by vacuum distillation at the end of the reaction. Moreover, the esters which are obtained according to the present invention may have a very low free hydroxyl content, depending upon the extent to which it is desired to carry the esterification.

It is, therefore, an object of the present invention to provide a novel esterification process involving the use of phosphorous esters as esterification catalysts.

The invention is applicable to the esterification of higher fatty acids or rosin acids, or mixtures thereof. The invention may be applied to the esterification of saturated higher fatty acids, but is particularly adapted to the esterification of unsaturated higher fatty acids, since it is with these unsaturated higher fatty acids that the greatest advantages are obtained. By higher fatty acids as used herein, it is meant acids containing from 8–22 carbon atoms. These may be single isolated fatty acids or may be the whole mixed acids of a fat or oil, or any selected fraction thereof, either saturated or unsaturated. The rosin acids which may be employed in the present invention may be any of a wide variety of rosin acids which are available naturally or which have been made available by the modification of naturally occurring rosin acids. These include rosin, hydrogenated rosin, dehydrogenated rosin, polymerized rosin, tall oil, the isolated rosin acid fraction of tall oil, and many others. Moreover, the application is applicable to mixtures of fatty acids and rosin acids, as in the case of tall oil or in the case of the rosin acid fraction of tall oil, which fraction may contain approximately 30% fatty acids and approximately 70% rosin acids, with a minor amount of unsaponifiable material.

A wide variety of aliphatic alcohols may be employed including the monohydric alcohols, methyl, ethyl, propyl, butyl alcohol and the like, and also the polyhydric alcohols, such as the glycols, ethyleneglycol, diethyleneglycol, glycerol, pentaerythritol, 2,2,6,6-tetramethylolcyclohexanol and others.

The catalysts employed in the present invention are

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either aliphatic or aromatic esters of phosphorous acid. The phosphorous acid may be completely or only partially esterified. Typical of the phosphorous acid esters which may be employed are triphenylphosphite, triparacresylphosphite, tri-(2-ethylhexyl)phosphite and di-(2-ethylhexyl)phosphite.

The esterification is effected by introducing the alcohol, the esterifying acid and the catalyst into a reaction vessel, preferably together with an azeotrope such as xylene or toluene. The quantity of catalyst which may be employed may vary from 1/2–5% based on the weight of the acid being employed for esterification. Usually, however, from 1–2% is found to be a preferred range.

The temperatures employed during the esterification may vary quite widely, depending upon the nature of the materials being esterified. For example, with low molecular weight monohydric aliphatic alcohols which are quite volatile, it is preferred to operate at fairly low temperatures. Where, however, the alcohol is not appreciably volatile, as for example is the case with the glycerine, the reaction is preferably carried out at a much more elevated temperature. In preparing esters of these acids with the usual polyhydric alcohols, such as the glycols and glycerol, temperatures of from 150–250° C. are suitable. However, any temperature up to the decomposition temperature of the materials employed may be used. The time period for esterification, likewise, varies with the nature of the materials, and with the extent to which esterification is desired. It has been found, however, that the employment of the phosphorous esters appreciably reduces the time required, as compared with the same process in which no catalyst is employed.

Example 1

The following materials were placed in a three-necked round bottom flask: glycerine, 33 g., soybean oil acids, 280 g., triphenyl phosphite, 2 g., and xylene 80 cc. The flask was equipped with a mechanical stirrer, a Stark and Dean tube with condenser and a thermometer. The reaction was heated by a mantle heater. The mixture was heated rapidly to a pot temperature of 180° C., then gradually raised to a final temperature of 197–199° C. The water was removed azeotropically. The following data show the comparative speed of the above esterification and a control in which the triphenyl phosphite was left out.

Esterification Time in hours	Percent Esterification	
	Triphenyl phosphite catalyzed	No catalyst
1	61	53
2.5	84	66
4	91	77
5	95	90
6	98	92
7	98.5	94
8	99.5	96

Example 2

The following materials were refluxed in a stirred 1-liter, 3-necked flask equipped with thermometer and Stark and Dean tube with condenser: Wood rosin, 340 g. (1 mole rosin acid), pentaerythritol (pentek), 36 g. (1 equivalent of hydroxyl), 6.8 g. di(2-ethylhexyl)phosphite (catalyst), and 60 cc. xylene (azeotrope). A similar run was made with one exception that no di(2-ethylhexyl)

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phosphite was used. The water which was produced was separated and measured in the Stark and Dean tube. The data obtained were as follows:

Esterification Time		Water Eliminated		Percent Esterification on Basis of Water	
Hours	Min.	Catalyst, cc.	No Catalyst, cc.	Catalyst	No Catalyst
-----	30	8.0	5.2	44	28
1.-----	0	10.2	9.2	56	50
1.-----	45	11.6	10.7	63	58
2.-----	45	12.9	12.2	70	66
3.-----	55	14.8	13.4	81	73
5.-----	0	15.8	14.2	86	77
5.-----	50	16.5	14.8	90	81
7.-----	0	17.4	15.5	95	85
7.-----	40	17.9	16.0	98	87
8.-----	30	18.0	16.2	98	88
9.-----	35	18.3	16.8	100	91

I claim as my invention:

1. Process of esterifying an acid selected from the group consisting of higher fatty acids and rosin acids

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with an aliphatic alcohol which comprises heating the alcohol and the acid in the presence of a phosphite ester, said ester being selected from the group consisting of aliphatic and aromatic esters.

2. Process of esterifying a higher unsaturated fatty acid with an aliphatic alcohol comprising heating the alcohol and the acid in the presence of a phosphite ester selected from the group consisting of aliphatic and aromatic esters.

3. Process of esterifying an unsaturated higher fatty acid with a polyhydric aliphatic alcohol which comprises heating the alcohol and the acid in the presence of an aromatic phosphite ester.

4. Process of esterifying an unsaturated higher fatty acid with a polyhydric aliphatic alcohol which comprises heating the alcohol and the acid in the presence of phosphite aliphatic ester.

References Cited in the file of this patent

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