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HYDROGENATION OF STRUCTURALLY MODIFIED ACIDS AND PRODUCTS PRODUCED THEREBY

Robert M. Peters, Cincinnati, Ohio, assignor to Emery Industries, Inc., Cincinnati, Ohio, a corporation of Ohio

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This invention relates to fatty acids which have been structurally modified to change their physical and chemical characteristics.

Fatty acids are found in nature as the glyceryl esters and occur in chain lengths ranging from C8 to C24. The most common fatty acids are those of C16 and C18 chain lengths. The acids of these chain lengths are of two types, fatty acids which are liquid and those which are solid at normal temperatures. This difference in physical characteristics is also accompanied by a difference in chemical constitution. The liquid acids are unsaturated, that is, they contain one or more double bonds in their chain. Typical examples are oleic acid containing one unsaturated bond, and linoleic acid containing two unsaturated bonds. The solid acids are saturated, that is, contain no double bonds, typical examples being palmitic acid containing 16 carbons and stearic acid containing 18 carbons.

Both the solid and the liquid acids are widely used in industry. The solid acids and their derivatives, such as the alkali metal and alkaline earth soaps, are generally higher melting and less soluble than the corresponding liquid acid derivatives. For example, even 2.0% of the sodium soap of stearic acid forms a heavy gel when dissolved in water at room temperature, while up to 15% of the sodium soap of oleic acid yields a fluid solution.

In addition to the physical differences between the solid and liquid acids and their derivatives, there are also differences in chemical reactivity due to the presence of unsaturation in the liquid acids. In some cases chemical reactivity is a desirable feature as additional chemical groups may be attached at the double bond, but in many cases the greater reactivity is evidenced by instability to atmospheric oxidation and the development of undesirable odors or color darkening.

The user of fatty acids who desired the greatest degree of stability in his product has been forced to use solid acids and compensate for any undesirable features resulting from their use as best he could. On the other hand, the user who could not sacrifice solubility, fluidity, or some similar property has had to use liquid acids and accept a degree of chemical instability.

It is the purpose of this invention to provide fatty acids having the physical characteristics of liquid acids but the chemical stability of solid acids. Otherwise expressed, it is the purpose of this invention to provide saturated liquid fatty acids.

We have found in effecting the polymerization of unsaturated fatty acids for the production of 36 carbon dibasic or dimer acids, that a secondary reaction occurs concurrently which results in a modification of the structure of a portion of the unsaturated acids to a degree which does not permit further polymerization.

We have further found that the unsaturation remaining in the structuraly modified acids, which apparently is not sufficiently active to further polymerize, can, however, be hydrogenated to yield saturated acids. These acids

which are almost completely saturated, as evidenced by very low iodine values, surprisingly have been found to be liquid at ordinary temperatures. They have the appearance of ordinary oleic or linoleic acids, but containing practically no unsaturation, they are as resistant to atmospheric oxidation and color degradation as commercial grades of solid acids having equivalent iodine values.

The structure of the modified acids has not been completely determined. Partial evidence, however, indicates that during the process of polymerization, in which the principal reaction is the linking of two or more molecules of unsaturated acids, other reactions take place. These side reactions appear to involve isomerization of the unsaturated fatty acid chains including shifting of the double bonds, probably towards the carboxyl end of the chain, formation of ring structures and/or the introduction of side chains. These reactions may occur to a greater or lesser extent depending upon the conditions, time and severity of the polymerization treatment. It is likely, therefore, that the coproduct of the polymerization treatment does not consist of a single individual compound, but rather of a series of related compounds which have been isomerized to varying degrees. In the case of mild or incomplete polymerizations some of the unsaturated acids may remain essentially in their original form or may have been so slightly isomerized that upon hydrogenation they are converted into solid acids. In addition, most commercially available unsaturated acids contain appreciable amounts of saturated acids. It may be necessary, therefore, to separate these solid acids from the liquid structurally modified acids in order to obtain the latter in a sufficient degree of purity to exhibit their characteristic properties.

The structurally modified acids are formed to a greater or lesser degree as coproducts of all thermal methods of polymerizing unsaturated fatty acids. The amount produced is not constant, but to a degree is inversely proportional to the efficiency of the polymerization process. In other words, the more unsaturated acid which reacts to form polymer the less remains to become structurally modified.

The process of United States Patent No. 2,482,761, in which polyunsaturated acids are heated in the presence of a small amount of water to prevent decarboxylation yields structurally modified acids which are essentially the same as those produced by the process of my copending application Serial No. 475,005, now Patent No. 2,793,219, issued May 21, 1957. In this process oleic acid is polymerized by heating in the presence of catalyzing amounts of a true clay mineral and water. This process, when applied to polyunsaturated acids as described in my copending application Serial No. 475,006, now Patent No. 2,793,220, issued May 21, 1957, likewise yields structurally modified acids having physical and chemical characteristics almost identical with those produced by the thermal method. Neither the nature of the initial raw material nor the process used greatly affects the characteristics of the final product.

The hydrogenated structurally modified acids, therefore, are obtained by the following steps: An unsaturated fatty acid or mixed fatty acids containing an unsaturated fatty acid is subjected to a polymerization process adapted to polymerize the unsaturated acids present. The polymerized acids are separated from the unpolymerized portion. This is usually accomplished by distillation, the polymerized acids remaining as a still residue while the unpolymerized portion is obtained as distillate. The distillate will contain any saturated acids present in the original fatty acids, possibly small amounts of unchanged or only slightly modified unsaturated acids

and structurally modified acids which still contain double bonds. This mixture of acids is then hydrogenated using the conventional nickel catalysts and hydrogen under pressure. The unchanged or only slightly modified unsaturated acids are converted to solid acids mainly stearic. The double bonds in the structurally modified acids become saturated, but these acids remain liquid. The hydrogenated mixture is then processed to separate the solid and liquid acids. For this step the conventional methods used to separate stearic and oleic acids may be employed, for example, by the use of solvents as described in United States Patent No. 2,293,676.

The resulting hydrogenated structurally modified acids are light yellow fluid oils. The iodine value will range from 3 to 10, depending upon the completeness of the hydrogenation step. The titre will range from 3 to 15° C., depending upon the efficiency of the separation step. The acids differ from normal fatty acids of C16 to C18 chain length and 3 to 10 iodine value, such as commercial stearic acid, which are hard white solids melting only at temperatures in the range of from 50° to 70° C.

As previously stated, the structure of the modified acids is not definitely known. They are not shorter chain acids produced by cracking as their combining weights are in the C16–C18 range. It is thought that isomerization has resulted in the formation of acids containing side chains or ring structures. It is also probable that the variety of similar isomers produced contributes to the fluidity of the product by the mutual depression of the freezing point of each isomer by the others present.

The structurally modified acids are, therefore, best described in terms of the method by which they are produced; that is, they are the monomeric structurally modified acids obtained as coproducts of the polymerization of unsaturated acids.

These products have utility in various industrial fields where both fluidity or solubility and stability are required. They may be compounded into textile oils either as the free acids or derivatives. They are much more compatible with other compounding ingredients than solid acids, but are more resistant to oxidation than oleic acid which is commonly used for this purpose.

The absorption of oxygen by a fatty acid may be used as a measure of stability against atmospheric oxidation. In a standard test carried out at 60° C. and under atmospheric pressure it required over 120 days for a 25 gram sample of the hydrogenated structurally modified acids to absorb 10 cc. of oxygen from the air. Under similar conditions it required only 45 days for a 1.0 gram sample of oleic acid to absorb 10 cc., while a 25 gram sample of stearic acid required 120 days. This test demonstrates that the structurally modified hydrogenated acids, although liquid, possess stability of the same order as commercial stearic acid.

When the sodium soaps are tested for solubility in water, it is found that whereas 15% concentrations of both hydrogenated modified acids and oleic acid give clear fluid solutions at room temperature, even 2% of stearic acid soap gives a viscous cloudy solution. The soaps of the hydrogenated structurally modified acisd, therefore, possess solubilities very similar to oleic acid soaps.

The methods for the production of the hydrogenated modified acids are more fully explained in the following examples:

Example 1

One-hundred parts of tall oil fatty acids and 2 parts of water were heated in an autoclave to a temperature of 370° C. at a pressure of 550 lbs. per sq. in. for 90 minutes. The mixture of polymerized and unpolymerized acids was subjected to distillation under vacuum. 23.5 parts of polymerized acids remained in the still as a residue and 76.5 parts of distillate was obtained. The distillate had a titre of 18° C. and an iodine value of 87.0.

The distillate was hydrogenated with a Raney nickel catalyst until the iodine value had decreased to 6.6. At this point the hydrogenated product was found to have a titre of 42° C.

The light-colored, semi-solid acids were separated into solid and liquid components by dissolving in 90% acetone and chilling to precipitate the solid acids which were removed by filtration. The liquid acids which were recovered by evaporation of the solvent amounted to 33.6 parts having a titre of 13.0° C. and an iodine value of 10.1.

Example 2

One-hundred parts of the fatty acids from tall oil were heated at 230° C. for 3 hours in the presence of 2 parts of water and 2 parts of true clay mineral. The product was distilled under vacuum, and 42.5 parts of polymerized acids remained in the still and 57.5 parts of distillate having a titre of 33° C. and an iodine value of 103 were obtained. The distillate was hydrogenated in the presence of a Raney nickel catalyst, the iodine value was reduced to 7.8 and the titre increased to 48.3.

Upon separating by solvents and distilling a yield of 23.8 parts of hydrogenated structurally modified acids having a titre of 11.0° C. and an iodine value of 11.2 were obtained.

Example 3

One-hundred parts of oleic acid were heated in an autoclave to 230° C. for 3 hours in the presence of 2 parts of water and 4 parts of clay (Filtrol). Upon distillation, 48.2 parts of polymerized acids remained in the still and 51.8 parts of distillate was obtained. The distillate had a titre of 25.1° C. and an iodine value of 61.3.

The distillate was hydrogenated with .5% Raney nickel catalyst under hydrogen pressure until the iodine value had been reduced to 5.8. During the hydrogenation the titre increased to 33.3° C.

The hydrogenated product was separated to yield 37.5 parts of liquid acids having a titre of 7.6° C. and 7.8 iodine value.

Having described my invention, I claim:

1. In a method of producing structurally modified liquid acids by heating unsaturated fatty acids of 18-carbon chain lengths to polymerize a substantial portion thereof and distilling the unpolymerized acids to remove them from the polymerized acids, the improvement which comprises treating the distilled unpolymerized acids with hydrogen under pressure in the presence of an hydrogenation catalyst to reduce the iodine value to the range of about 3–10, dissolving the hydrogenated acids in a solvent, chilling the solvent to precipitate the solid saturated acids, removing them by filtration and recovering saturated 18-carbon fatty acids which are liquid at room temperature by evaporation of the solvent.

2. A new composition of matter comprising structurally modified fatty acids having an iodine value of substantially 3 to 10, and a titre below 15° C., said acids being the products of the process of claim 1.

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