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3,840,574

PROCESS FOR THE PREPARATION OF HEAT-RESISTANT AND LIGHTFAST FATTY ACIDS

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No Drawing, Filed July 28, 1971, Ser. No. 166,993

Claims priority, application Germany, Aug. 3, 1970,

P 20 38 468.3

Int. Cl. C09f 5/10

U.S. Cl. 260—419

14 Claims

ABSTRACT OF THE DISCLOSURE

A process for producing heat-resistant and lightfast fatty acids having a chain-length of C_8 – C_{18} which comprises heating the fatty acids or mixtures thereof with certain polycarboxylic acids or their alkyl esters at temperatures of from about 180° C. to about 280° C. and then distilling off the fatty acids under a vacuum.

This invention relates to the production of heat-resistant and lightfast fatty acids and more particularly to a process for producing such fatty acids in the presence of certain polycarboxylic acid additives.

In applicant's copending application, Ser. No. 119,826 filed on March 1, 1971, a process is described for the production of heat-stable and lightfast fatty acids having a chain length of C_8 – C_{18} in which the crude fatty acids or the mixtures thereof are heated with 0.1–0.2% by weight of an aromatic carboxylic acid or the esters thereof, of the formula:



wherein x is an integer from 1 to 4, Ar is an aryl or alkylaryl radical or residue (which is mono- or polyvalent), R is hydrogen or an alkyl group containing 1 to 4 carbon atoms, optionally in the presence of 0.1–0.5% by weight of an alkyl ester of titanic or zirconic acid having 1 to 8 carbon atoms in the alkyl group, to temperatures of 180° C. to 260° C., preferably 200 to 250° C., under normal pressure, optionally under a weak vacuum, during a period of about 0.5 to about 8 hours, preferably about 1 to about 4 hours; and the fatty acid is thereafter distilled under vacuum.

It has now been found that it is likewise possible to obtain thermally stable and lightfast fatty acids of the chain length of C_8 – C_{18} in accordance with a mode of operation similar to that described in the heretofore mentioned copending application if the crude fatty acids or the mixtures thereof are heated, instead of with an aromatic carboxylic acid or the alkyl ester thereof, with the addition of about 0.05 to about 0.2% by weight of an aliphatic poly- or hydroxypolycarboxylic acid containing 2 to 10 carbon atoms or a cycloaliphatic polycarboxylic acid containing 5 to 10 carbon atoms or the alkyl esters of the aforementioned polycarboxylic acids with 1 to 4 carbon atoms in the alkyl groups, with or without the presence of about 0.05 to about 0.5% by weight of an alkyl ester of titanic or zirconic acid having 1 to 8 carbon atoms in the alkyl group, to temperatures of about 180 to about 280° C., preferably about 200° C. to about 250° C., under normal pressure, optionally under a weak vacuum (e.g. from 300 to 700 mm. Hg.) for a period of about 0.5 to about 8 hours, preferably about 1 to about 4 hours; and the fatty acid is subsequently distilled under vacuum.

The fatty acids can be heated, according to this invention in the presence of the polycarboxylic acids or the alkyl esters thereof by themselves. When conducting the step with the simultaneous presence of alkyl esters of

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titanic and/or zirconic acid, an optimum effect is attained with respect to the light and thermal stability, and the color of the distilled fatty acid.

The treatment period is dependent on the treatment temperature. This period is about 2 to about 3 hours in case of a temperature of about 250° C. to 260° C., about 3 to about 4 hours at about 230° C. to about 240° C., and about 5 to about 6 hours at about 220° C. to about 230° C.

The amount of the additives, i.e. acids or esters used to treat the fatty acids, is dependent on the type and quality of the crude fatty acids or the crude fatty acid mixtures. For C_8 – C_{12} fatty acids stemming from palm nut oil or coconut oil and being extremely light-sensitive and heat-sensitive, it is possible to add about 0.1 to about 0.2% of the aliphatic, cycloaliphatic, or hydroxypolycarboxylic acids, or the lower alkyl esters of the polycarboxylic acids, and about 0.1 to about 0.2% of the alkyl esters of titanic and/or zirconic acid; for C_{14} – C_{18} fatty acids, sufficient amounts are about 0.05 to about 0.1% of the polycarboxylic acids or the lower alkyl esters thereof, and about 0.05 to about 0.2% of alkyl esters of titanic or zirconic acid. It will be appreciated that larger amounts of the polycarboxylic acids or esters, e.g. up to about 0.5%, may be employed, but the excess amounts are unnecessary for the purposes of the invention.

In the mode of operation of this invention, the polycarboxylic acids and the titanic or zirconic acid are left bound in the distillation residue, together with the impurities contained in the fatty acid.

In a discontinuous distillation procedure, the sump temperature and the concentration of the treatment agents increase. Sump temperatures which are too high and distillation times which are too long can lead to a splitting off of the bound impurities, thus impairing the quality of the distillate. For this reason, it is necessary, particularly when treating long-chain fatty acids, to effect the distillation under a vacuum of at least 1–2 torr [mm. Hg.].

The process of this invention has the advantage that the amount of unsaponifiable compounds in the distillate is no larger than in the distillate of the untreated fatty acid.

Another special advantage of the process resides in that the distillation residue of the thus-treated fatty acid does not contain any newly formed condensation products, which occur in the conventional treatment methods operating with boric acid or the esters thereof. The boron compounds, which have the effect of Lewis catalysts, promote the formation of unsaponifiable, undistillable condensation products. After the termination of the distillation, high-boiling derivatives of the aliphatic and cycloaliphatic polycarboxylic acids and undistillable titanic acid and/or zirconic acid compounds are found in the distillation residue.

Examples for the polycarboxylic acids to be employed according to this invention are oxalic acid, maleic acid, fumaric, itaconic, succinic acid, adipic acid, malic acid, tartaric acid, citric acid, and cyclopropane-, cyclobutane-, and cyclohexanedicarboxylic acid. Thus, it will be appreciated that saturated and unsaturated aliphatic polycarboxylic acids are suitable. The alkyl esters of these acids include partial and full esters such as monomethyl maleate, monobutyl itaconate and dimethyl maleate.

The source of the crude fatty acids can be natural fats and oils, as well as synthetic fatty acids. A large portion of these fatty acids is formed as a technical product during various stages of the refinery of nutrient oils and fats, for example during the deacidification by neutralization with an alkali, or during the direct distillation of nutrient oils and fats with a higher content of free acids under vacuum, decolorization, and deodorization.

The color stability characteristics of the fatty acids, treated according to this invention and those of the untreated fatty acids were determined by the heating of samples in a small glass tube having a diameter of 14 millimeters and a filling level of 115 millimeters to 200° C. during a period of 6 hours. This heating test was con-

The fatty acid blend is understood to mean the distillation cut of the untreated fatty acids containing predominantly (at least 80%) of fatty acids of the chain length set forth in the table. Moreover, it will also be understood that the amount of additive employed is based on the weight of the fatty acids to be treated.

TABLE

Ex.	Fatty acid blend	Fatty acid type	Additive	Treatment		Fore-run per-cent by weight	Per-cent by weight	Main run		ICN after 6 hrs. at 200° C.	Residue	
				Time (hrs.)	Temp. (° C.)			Acid number	Color HU		Per-cent by weight	Un-saponifi-able
1a	C ₈ -C ₁₀	Coconut				3.1	91.8	360	125	>50	5.1	1.6
2	C ₈ -C ₁₀	do.	0.2% adipic acid	3.5	240	3.5	91.3	361	20	9	5.2	1.7
3	C ₈ -C ₁₀	do.	0.2% succinic acid	3	240	2.8	92.4	360	20	7-8	4.8	1.8
4	C ₈ -C ₁₀	do.	0.2% tartaric acid	3	240	2.4	93.0	361	10	7-8	4.6	1.7
5	C ₈ -C ₁₀	do.	0.2% succinic acid, 0.2% butyl titanate.	3	240	3.1	92.0	360	10	6-7	4.9	1.8
6a	C ₈ -C ₁₀	Palm nut				3.3	91.4	355	100	>50	5.3	1.4
7	C ₈ -C ₁₀	do.	0.2% citric acid	3	240	2.6	91.6	356	20	7	5.8	1.6
8	C ₈ -C ₁₀	do.	0.2% 1,4-Cyclohexane-dicarboxylic acid, 0.2% butylzirconate.	3	240	3.2	91.7	355	10	6-7	5.1	1.5
9a	C ₁₂ -C ₁₄	Coconut				3.6	91.6	260	200	40	4.8	1.8
10	C ₁₂ -C ₁₄	do.	0.2% methylmaleate, 0.1% butyltitanate.	2	260	3.8	90.6	259	20-30	10-15	5.6	2.0
11a	C ₁₆ -C ₁₈	Tallow hardened.				3.8	90.4	205	125	30-40	5.8	2.2
12	C ₁₆ -C ₁₈	do.	0.2% tartaric acid, 0.05% butylzirconate.	2	280	3.9	90.2	205	30	10-15	5.9	2.6

NOTE.—HU=hazen unit; ICN=iodine color number.

ducted in a thermostated drying oven which was not opened during the entire period of the experiment. The test tubes were in each case covered by a cap. The color intensity was measured in iodine color number units, wherein the iodine color number indicates how many milligrams of free iodine are contained in 100 milliliters of an aqueous iodine-potassium iodide solution at the same depth of color when measuring at a layer thickness of 25 millimeters.

It will be understood that the process of the present invention can be conducted discontinuously as well as continuously.

In the examples of the following table, a comparison was made in each case for the individual fatty acid types, by setting forth the characteristic data of the single-distilled, untreated fatty acids as compared to the data of the distilled fatty acids treated according to this invention.

EXAMPLES

In the examples set forth in the table, the anhydrous fatty acid mixtures were heated under agitation to about 220° C. with the addition of the polycarboxylic acid or the polycarboxylic acid ester. At this temperature, in each respective case, the alkyl ester of titanate or zirconate, respectively, was added thereto. The treatment time was 2 to 3.5 hours. During this period, a temperature of 240° C. to 280° C. was maintained. Thereupon, the temperature of the sump was lowered, by cooling, to 90° C., and the thus-treated fatty acids were distilled under a vacuum of 1-2 torr over a small distillation column; within 2 hours, withdrawing a small first run, i.e. a fatty-acid forerunning (3-4%) and a main run or fraction (90-93%). The first run from most of the treated technical fatty acids exhibits a strongly unpleasant odor and is not utilized. In the residue, amounting to 4-6% by weight of the unsaponifiable component was determined. With respect to the main run of the untreated and of the treated fatty acids, the hazen color unit of freshly distilled samples was determined. Furthermore, the iodine color number of samples maintained for 6 hours at 200° C. was observed. The iodine color number and the hazen unit were measured in the "Lovibond 1000" comparator and the accessories thereof by Tintometer.

For comparison purposes, the untreated fatty acid mixture was distilled under the same conditions (Examples 1a, 6a, 9a and 12a). The results are indicated in the table.

From the above data it is apparent that the color and iodine values for the treated fatty acids are substantially improved.

While the novel principles of the invention have been described, it will be understood that various omissions, modifications and changes in these principles may be made by one skilled in the art without departing from the spirit and scope of the invention.

What is claimed is:

1. A process for the preparation of heat-resistant and lightfast fatty acids from crude fatty acids having a chain length of C₈-C₁₈ which comprises heating the crude fatty acids or the mixtures thereof with a polycarboxylic acid selected from the group consisting of an aliphatic poly- or hydroxypolycarboxylic acid containing 2 to 10 carbon atoms, and a cycloaliphatic polycarboxylic acid containing 5 to 10 carbon atoms or a lower alkyl ester of said polycarboxylic acid to temperatures of about 180° C. to about 280° C., for a period sufficient to improve the heat-resistant and lightfastness of the fatty acids and subsequently distilling off the fatty acids under a vacuum.

2. The process of claim 1 in which the fatty acids are heated with from about 0.05 to about 0.2% by weight of the polycarboxylic acid or the alkyl ester thereof based on the weight of the fatty acid.

3. The process of claim 1 in which the fatty acids are heated with the simultaneous presence of an alkyl ester of titanate or zirconate containing from 1 to 8 carbon atoms or mixture thereof in the alkyl group.

4. The process of claim 3 in which the alkyl ester of titanate or zirconate is present in an amount varying from 0.05 to 0.2% by weight, based on the weight of the fatty acids.

5. The process of claim 1 in which the fatty acids are heated with the polycarboxylic acid or the alkyl ester thereof for a period of from about 0.5 to about 8 hours.

6. The process of claim 1 in which the polycarboxylic acids are saturated or unsaturated acids.

7. The process of claim 1 in which the fatty acids are heated with the polycarboxylic acid or the alkyl ester thereof under normal pressure.

8. The process of claim 1 in which the heating and distilling are effected in a continuous manner.

9. The process of claim 1 in which the heating and distilling are effected in a batch-wise manner.

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10. The process of claim 1 which the lower alkyl esters contain from 1 to 4 carbon atoms in the alkyl group.

11. A process for the preparation of heat-resistant and lightfast fatty acids from crude fatty acids having a chain length of C_8-C_{18} which comprises heating the crude fatty acids or the mixtures thereof, with an additive selected from the group consisting of an aliphatic polycarboxylic acid or hydroxycarboxylic acid containing 2 to 10 carbon atoms, a cycloaliphatic polycarboxylic acid containing 5 to 10 carbon atoms, and an alkyl ester of said acids containing from 1 to 4 carbon atoms in the alkyl group to a temperature of from about 180°C . to about 280°C . under normal pressure for a period of from about 0.5 to about 8 hours and subsequently distilling off the fatty acids under a vacuum.

12. The process of claim 11 in which the heating is conducted to about 200°C . to 250°C . for a period of from about 1 to 4 hours.

13. The process of claim 11 in which the amount of additive added is from about 0.05 to about 0.1% by weight when the fatty acids have a chain length of $C_{14}-C_{18}$ and from about 0.1 to about 0.2% by weight when the fatty acids have a chain length of C_8-C_{12} , the percent by weight being based on the weight of the fatty acids.

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14. The process of claim 13, in which the fatty acids are heated with the simultaneous presence of an alkyl ester of titanate or zirconate containing from 1 to 8 carbon atoms or mixtures thereof in the alkyl group, the amount of said alkyl ester of titanate or zirconate being from about 0.05 to about 0.2% by weight when the fatty acids have a chain length of $C_{14}-C_{18}$ and from about 0.1-0.2% by weight when the fatty acids have a chain length of C_8-C_{12} .

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