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3,520,816

SOAP BAR COMPOSITIONS

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7 Claims

ABSTRACT OF THE DISCLOSURE

Soap bar products high in beta-phase crystallinity are produced from unworked soap compositions comprising (a) 10% to 90% tallow soap and (b) soap of mixed C₁₂—C₁₅ carboxylic acids wherein at least a portion of the mixture is of odd carbon number and at least a portion of acid of any single carbon number is of straight-chain structure and at least a portion is of branched-chain structure.

This invention relates to certain novel soap compositions. More particularly, it relates to certain solid soap compositions adaptable for utilization in the manufacture of soap bars.

As typically defined, soap is considered to be an alkali metal salt of one or more long-chain fatty acids, particularly sodium or potassium salts of straight-chain hydrocarbon carboxylic acids of even carbon number. At present, most high-volume commercial soaps comprise sodium salts of coconut acids and tallow acids and are frequently termed coco-tallow soaps.

The term "coconut acid" is applied to a mixture of acids such as are obtained by saponification of coconut oil. The composition of coconut acid is variable, but principally consists of lauric and myristic acids with lesser amounts of C₆, C₈, C₁₀, C₁₆ and C₁₈ normal carboxylic acids also being present. Tallow acids, on the other hand, are acids of generally higher carbon number. The term "tallow acid" typically is applied to a mixture of C₁₆ and C₁₈ straight-chain carboxylic acids, e.g., palmitic, stearic and oleic acids, with relatively minor amounts of C₁₂ and C₁₄ acids also being present. As employed historically, the terms coconut acid and tallow acid served to identify the natural product origin of the acid mixtures. It should be understood, however, that the terms as employed herein are not intended to limit the acids to those of natural origin but are intended to be equally applicable to synthetic mixtures of acids of similar composition. As a practical matter, all commercial soaps except for certain specialty formulations contain amounts of both coconut acid soaps and tallow acid soaps in varying proportion. A typical soap bar is prepared from a mixture of about 20% of coconut acid soap and about 80% of tallow acid soap, which mixture serves to impart desirable properties of lathering quickness, hardness, smooth feel to the touch, mildness to the skin, and the like to resulting soap bar formulations.

It is well known that subtle differences in the composition of a soap bar may account for considerable differences in the quality of the soap as well as in the acceptance of the soap bar by the purchasing public. Gross differences in the chemical composition of the soap will obviously result in substantially different properties, but aside from chemical considerations, physical differences in soap compositions are also important factors in determining the quality and acceptance of the soap product. One such physical characteristic relates to the crystalline form in which the soap is found. Although as a general matter,

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commercial soaps are not entirely crystalline, some degree of crystallinity is observed in all cases.

It is known that soap may exist in at least four crystalline forms. Ferguson et al., Ind. and Eng. Chem., 35, 1005 (1943) discuss the existence of soap phases denoted as the alpha, beta, delta and omega forms and extensively describe the X-ray identification of the various forms in sodium soaps. The predominant crystalline form found in most commercial framed or milled soaps is the omega form which is probably the most stable form of most soaps. Although the alpha and delta phases of most soaps are not considered to have substantial commercial significance, there is considerable interest in preparing soap formulations relatively high in beta phase crystallinity as compared to omega phase crystallinity as such soaps are characterized by increased lathering ability and on occasion by some degree of translucency. Freshly prepared soap, frequently termed "kettle" soap is substantially entirely of the omega phase. The conversion of the omega phase of kettle or framed coco-tallow soap is accomplished by successive milling or plodding operations, but such a conversion is normally accomplished only with difficulty and the ratio of beta phase to omega phase never becomes as high as would be desirable, despite repeated working.

It is an object of the present invention to provide certain novel soap compositions. More particularly, it is an object to provide certain kettle soap compositions which are readily converted to worked soap formulations of a high ratio of beta phase to omega phase. An additional object is to provide certain novel milled soap bar formulations of a high beta phase content.

It has now been found that these objects are accomplished by the provision of soap compositions comprising:

(a) A proportion of soap of tallow acids;

(b) A proportion of soap of a mixture of carboxylic acids in the C₁₂—C₁₅ range, which mixture contains carboxylic acids of odd carbon number and acids of both straight-chain and branched-chain structure; and optionally

(c) A proportion of soaps of coconut acids.

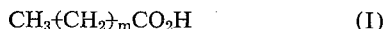
Therefore, unlike conventional soap preparations, the soap compositions of the invention are characterized by the presence of alkali metal salts of acids having an odd number of carbon atoms and by acids having branched chain structures. The soap compositions offer the advantage of a high rate of conversion of omega phase to beta phase upon milling or other working operations and serve as precursors of prepared soap manufactures exhibiting a high ratio of beta phase to omega phase therein.

The soap compositions, as previously stated, do have a certain proportion of tallow acid soaps and optionally may have a proportion of coconut acid soaps. The novel feature of the soap compositions of the invention resides in the presence therein of soap of a mixture of saturated carboxylic acids in the C₁₂ to C₁₅ range, at least a portion of which soap is soap of an acid of an odd carbon number and at least a portion of which soap is soap of an acid of a branched-chain structure. For convenience, this soap component is herein referred to as "mixed C₁₂—C₁₅ acid" soap.

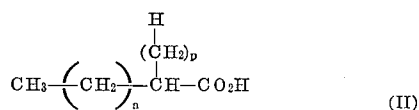
The mixed C₁₂—C₁₅ acid soap component does not necessarily contain acids of each carbon number within the C₁₂—C₁₅ range, provided, of course, that at least some proportion of acid of odd carbon number is present. Mixtures of acids having 12, 13, 14 and/or 15 carbon atoms wherein the percentage of acid of each carbon number varies from 0% to 50% based on the total mixed C₁₂—C₁₅ acids are satisfactory. Thus, mixtures of C₁₂ and C₁₃ acids, of C₁₂ and C₁₅ acids, of C₁₃ and C₁₅ acids and the like are suitably employed. Preferred, however, are

mixtures of at least 3 acids of different carbon number within the C₁₂ to C₁₅ range, e.g., mixtures of C₁₂, C₁₃ and C₁₅ acids, of C₁₂, C₁₃ and C₁₄ acids or of C₁₃, C₁₄ and C₁₅ acids. Best results are obtained when the mixed C₁₂-C₁₅ acid component is a mixture of C₁₂, C₁₃, C₁₄ and C₁₅ acids with from about 10% to about 40%, based on the total mixture of acids, of acid of each carbon number being present.

Within the quantity of acid of each carbon number within the C₁₂ to C₁₅ carbon atom range, there is at least a portion of the acids of that carbon number which have a straight-chain structure. These acids, herein termed "normal" acids, are repeated by the formula



wherein m is a whole number from 10 to 13 inclusive. Additionally, at least a portion of the acids of any given carbon number are of a branched-chain structure wherein the single carbon side-chain branching is on the carbon atoms alpha relative to the carboxy moiety. Such α -branched acids, herein termed "iso" acids, are represented by the formula



wherein p is a whole number from 1 to 5 inclusive and n is a whole number from 4-11 inclusive selected so that $n=m-(p+1)$ wherein m and p have the previously stated significance. The above Formula II provides for acids having an alpha branch which is methyl, ethyl, propyl, butyl or amyl and in most cases at least a minor amount of acid having each type of branch is encountered. A substantial proportion, typically about 50%, of the iso acids are α -methyl carboxylic acids with lesser amounts of the other branched-chain isomers being admixed therewith.

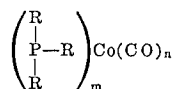
The ratio of normal to iso acids within the mixed C₁₂-C₁₅ acid component is variable. In certain compositions the percentage of normal acids is as high as about 98% with only about 2% of the acids being of the iso structure. In other compositions, the percentage of normal acids is as low as about 15% with the percentage of iso acids being about 85%. In preferred modifications, the percentage of normal acids is from about 20% to about 80% with the percentage of iso acids correspondingly varying from about 80% to about 20%.

One convenient source of the branched chain iso acids is oxidation of the corresponding aldehydes and primary alcohols. The aldehydes and/or alcohols may advantageously be obtained from straight-chain olefins having 11 to 14 carbon atoms by reaction with carbon monoxide and hydrogen. The reaction can be carried out to produce aldehydes in accordance with the well known Oxo process, or can be conducted as a hydroformylation reaction in which the aldehydes initially formed are simultaneously hydrogenated and converted to saturated primary alcohols of 12 to 15 carbon atoms. In these methods straight-chain aldehydes and alcohols are generally formed along with the branched-chain products. The branched-chain or the straight-chain products can be more or less completely separated, as for example, by distillation, before or after conversion of the aldehydes and/or primary alcohols to the carboxylic acids and are subsequently blended or remixed in any desired proportion.

Suitable methods of producing Oxo aldehydes which are used as starting materials for oxidation to useful mixtures of branched-chain and straight-chain carboxylic acids whose soaps are suitable in mixed C₁₂-C₁₅ acid component are described, for example, in U.S. Pats. 2,564,456 and 2,587,858. As a rule it is more advantageous to use a hydroformylation method to make a mixture of straight and branched-chain alcohols which can be oxidized to the

mixture of carboxylic acids suitable for conversion to the desired soaps. U.S. Pats. 2,504,682 and 2,581,988 describe processes of this type which are suitable and U.S. 2,525,354 claims a method of alcohol purification particularly advantageous with these products.

The hydroformylation is suitably carried out in the presence of a hydrogenation catalyst, advantageously using a temperature of about 200° to 400° C. under superatmospheric pressure preferably at least 200 atmospheres with a mole ratio of olefin to carbon monoxide to hydrogen in the range from about 1:2:2 to about 1:5:20. British Pat. 638,574 describes suitable methods of operation using cobalt, cooper, nickel, or ruthenium and their carbonyls as catalysts. More advantageous results as regards proportions of straight-chain and alkyl substituted alcohols can be obtained, however, by use of the complex metal carbonyl-tertiaryorgano catalysts containing phosphorus, arsenic, or antimony whose use in hydroformylation is described in Belgian Pat. 606,408. Especially, preferred are the cobalt-carbonyl trialkyl phosphine catalysts represented by the simplest formula



where R is alkyl of 1 to 20 carbon atoms preferably 2 to 6 carbon atoms and m and n are integers each equal to at least 1 and whose sum is 4. Two of the R's can be joined to provide a heterocyclic phosphine and the catalyst can be in the dimer form. These give exceptionally good results in the process of the present invention, particularly since production of the desired alkyl-substituted primary alcohols can be promoted by controlling the ratio of phosphine to cobalt in the complex carbonyl catalyst. Ratios in the range of about 2.5 to 0.5 atoms of phosphorus per atom of cobalt are useful with ratios between about 2 and about 0.8 being generally more advantageous.

The initially produced aldehyde or alcohol mixture is oxidized to the corresponding carboxylic acids of 12 to 15 carbon atoms by known methods. U.S. Pat. 2,010,358, for example, describes a method of oxidizing isoaldehydes which is especially suitable for use in making the branched-chain acids. Alcohols are oxidized to aldehydes by the methods of U.S. 2,042,220 and U.S. 2,883,426 for instance, and the aldehydes are then oxidized to the branched-chain carboxylic acids. Alternatively, the branched-chain alcohols from the hydroformylation reaction are oxidized directly to the corresponding branched-chain carboxylic acids.

The required branched-chain carboxylic acid salts are also produced from olefins of 11 to 14 carbon atoms per molecule by carboxylation with carbon monoxide and water using, for example, nickel carbonyl and a tertiary phosphine to catalyze the reaction. A suitable method of carrying out this reaction is described in U.S. 2,658,075, for instance. By conducting the carboxylation in the presence of an alcohol, esters of the desired carboxylic acids can be obtained instead of the free acids. This method of operation is advantageously carried out as described in U.S. 3,168,553, for example.

In expressing the overall composition of the soaps of the invention, it is convenient to initially classify the materials present as soaps of tallow acids and other soaps herein termed soaps of non-tallow acids. Broadly speaking, the compositions suitably contain from about 10% to about 90% of tallow acid soaps and from 90% to about 10% of non-tallow acid soaps. However, at least in part because of the relatively low cost of tallow acids, in the preferred modification of the invention, soaps of tallow acids comprise a major component with from about 70% to about 90% of the total soap being tallow acid soap.

The non-tallow acid soap portion comprises the mixed C₁₂-C₁₅ acid soap component and any coconut acid soap

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that may be present. The mixed C_{12} - C_{15} acid component comprises at least 25% and preferably at least 50% of the non-tallow acid soap present with any remainder of this portion being coconut acid soap. To obtain the most desirable properties, however, it is preferred that the non-tallow acid soap component be entirely of the mixed C_{12} - C_{15} acid type with no coconut acid soap being present. In this modification, of course, the soap composition will consist essentially of tallow acid soap and mixed C_{12} - C_{15} acid soap.

The soap compositions are prepared in conventional manner by neutralization of the carboxylic acids, as by reacting the acids with alkali metal hydroxides, ammonium hydroxide or organic amines. In one modification, the tallow acid, the mixed C_{12} - C_{15} acid and any coconut acid are mixed in the desired proportions and the resulting mixture is neutralized. It is also useful to separately prepare the individual soap components and subsequently mix the soap components. In yet another modification, esters of the acid types are mixed and saponified with alkali metal hydroxide. In any modification, the resulting soap mixture is obtained as a composition containing a certain amount of water, typically up to about 30%, and is frequently referred to as kettle soap or neat soap. These terms as employed herein refer to unworked soap compositions.

The kettle soap compositions are advantageously employed in producing soap in the form of flake, bead, bar or cake. However, the compositions offer special advantage in soap bars and cakes wherein it is important to have a high content of beta phase soap.

The new soap bars are advantageously prepared by a milling and plodding process rather than by the framing method because bars having the most desirable beta phase content are prepared in this way. In the milling process, kettle soap prepared from the mixture of tallow acids and mixed C_{12} - C_{15} acids with or without coconut acids is cooled and dried to chip or granular form. The soap particles are then mechanically mixed with any or all of various conventional additives such as perfume, coloring materials or whitening agents that may be desired, and then milled to produce chips of homogeneous composition. The milled particles are compacted under pressure in a plodder from which the soap is extruded as a continuous bar having a cross section approximating that of the finished cake. It is desirable to control the free moisture content of the soap chips, preferably within the range of about 5 to about 20% in order to facilitate the plodding. The continuous bar is then cut into individual cakes which usually are pressed to give a smooth and polished appearance to the finished cake, and when desired, to impress upon the cake a trade name, trademark or the like.

Toilet soap chips can be made from the new soap mixtures in the same way by omitting the plodding, while the new soap in granular form can be produced by spray drying in the conventional manner, for example.

As previously stated, it is a principal advantage of the compositions of the invention that the rate of conversion of omega phase to beta phase during working operations is substantially higher than for analogous coco-tallow bars, and the ultimate ratio of beta phase to omega phase is also substantially higher. One method of determining the presence and relative proportion of beta phase soap is by subjecting the soap to X-ray analysis. As found by Ferguson et al., supra, the beta phase is characterized by the 2.75 A. band in the X-ray diffraction pattern whereas the omega phase is characterized by a band at 2.95 A. The ratio of intensity at 2.75 A. to that at 2.95 A. is thus indicative of the ratio of beta phase to omega phase. The data of Table I which follows illustrate the conversion of omega phase to beta phase at the end of each of five milling passes for a conventional soap composition comprising 80% of sodium soap of tallow acid and 20% of sodium soap of coconut acid. The dif-

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fractometer technique employs a precise mechanical instrument comprising an X-ray source, a principle protractor and a suitable detector, plus the necessary gearing, supports, power, slits and appropriate controls. A slice from each face of a soap bar is presented to the X-rays and scanned through varying angles while a trace of the line intensities of diffracted X-rays is recorded on a strip chart recorder. The intensities of peaks observed are measured and comparisons made on the basis of these observed intensities. The film densitometer technique employed is similar, except that a powdered sample is employed and reflections from the sample are recorded on a photographic film. The densitometer, a measuring device, is an instrument which provides for the transmission of a constant, focused light beam through the film negative being examined. A condenser system produces a patch of light on the cathode of a photomultiplier tube whose output is a measure of the light transmitted by the film. This results in a series of peaks drawn on a strip chart that are accurate reproductions of line intensities and which can be measured and compared accordingly.

TABLE I

Milling pass	Ratio of intensities, 2.75 A./2.95 A.	
	Diffractometer scan	Film densitometer scan
1.....	<0.1	0.23
2.....	0.15	0.26
3.....	0.28	0.42
4.....	0.38	0.63
5.....	0.75	0.69

The data of Table II which follows illustrate a similar comparison of beta phase to omega phase of a soap composition within the scope of the invention. In this case, the soap composition comprised 80% of sodium soap of tallow acids and 20% of sodium soap of mixed C_{12} - C_{15} acid wherein the percentage of each of the C_{12} , C_{13} , C_{14} and C_{15} acids was 25% and the percentage of normal acids in the mixed C_{12} - C_{15} acid was 75%.

TABLE II

Milling pass	Ratio of intensities, 2.75 A./2.95 A.	
	Diffractometer scan	Film densitometer scan
1.....	0.25	0.30
2.....	0.41	0.49
3.....	1.45	0.88
4.....	>10	1.24
5.....	>10	1.33

A second composition within the scope of the invention was examined. This composition was identical to that examined in Table II except that the mixed C_{12} - C_{15} acid component consisted of 20% normal acids and therefore 80% iso acids. This analysis is given in Table III.

TABLE III

Milling pass	Ratio of intensities, 2.75 A./2.95 A.	
	Diffractometer scan	Film densitometer scan
1.....		1.0
2.....	2.70	1.1
3.....	3.5	1.3
4.....	8.0	1.5
5.....	9.0	2.0

A series of finished soap bars was prepared containing varying proportions of tallow acid soap, coconut acid soap and mixed C_{12} - C_{15} acid soap. Within the mixed C_{12} - C_{15} acid component the proportions of normal acids and iso acids were also varied. Each bar was prepared in the same way and was subjected to 5 milling passes. The

bars were analyzed by X-ray analysis to determine the ratio of beta phase to omega phase. The results are given in Table IV wherein the headings indicate the amount of soap derived from each type of acid and the percentage of normal acids in the mixed acid component.

TABLE IV

Percent tallow	Percent coconut	Percent mixed C ₁₂ -C ₁₅ (percent normal)	Ratio of intensities 2.75A./2.95A.	
			Diffraction-eter scan	Film densitometer scan
80.....	15	5 (75)	>3	1.0
80.....	10	10 (75)	>3	1.30
80.....	0	20 (98)	>10	1.30
80.....	0	20 (75)	>10	1.9
80.....	0	20 (50)	>10	1.5
80.....	0	20 (35)	>5	1.3
85.....	0	15 (75)	>10	1.35

It is apparent from the above data that the soap compositions offer the advantage of a high rate of conversion of omega phase to beta phase and that this advantage is available throughout a broad range. It has been found, however, that within the scope of the contemplated soap compositions there are certain combinations that offer particular advantages.

One such particular advantage is that of translucency and certain combinations of tallow acid soaps and mixed C₁₂-C₁₅ acid soaps exhibit unusual translucency not found in other compositions. Commercial translucent soap bars contain substantial quantities of additives, particularly glycerol and alcohol which account to a great extent for the observed property of translucency. Not only are these additives expensive, but they also decrease the average detergent character of the soap bar product. It is considered to be highly desirable to obtain some degree of translucency in the soap per se and thereby diminish the requirement for additives. Although it is not desired to be bound by any particular theory, translucency appears to be associated with relatively high proportions of straight chain acids of odd carbon number in soap compositions consisting essentially of tallow acid soap and mixed C₁₂-C₁₅ acid soap, as the addition of coconut acid soap or an increase in the iso acid content of the soap formulation serves to decrease the light transmission of a formulated soap bar. The property of translucency does not appear, however, to be directly dependent on the beta/omega phase ratio.

In a series of comparative experiments, a Fischer Electrophotometer was modified by installing a 20% transmission gelatin filter in the reference beam so that the scale reading would represent percentage of light transmission times 5. The scale employed was calibrated in units from 10 to 100 where a reading of 10 was considered to be opaque. The results of measuring the light transmission of a series of soap bar formulations is shown in Table V wherein each soap formulation consisted of 80% tallow acid soap and 20% mixed C₁₂-C₁₅ acid soap of equal proportions of C₁₂, C₁₃, C₁₄ and C₁₅ soap. The heading "% Normal" refers to the percentage of the mixed C₁₂-C₁₅ acid having a normal structure

TABLE V

Percent normal:	Scale reading
98	15.8
75	39.0
50	19.0
20	16.8

It is observed that optimum properties of translucency are encountered when the percentage of normal acids in the mixed C₁₂-C₁₅ acid soap component is above 50%. The compositions having from about 60% to about 85% of normal acids in the mixed C₁₂-C₁₅ acid component of mixed C₁₂-C₁₅ acid-tallow acid soap formulations are preferred. In terms of the overall soap present, it is de-

sired that at least 5% and preferably at least 7.5% of the total soap be of a normal structure and of an odd carbon number.

A second particular property attributable to certain soap bar formulations of the invention is the property of reduced cracking of the surface of the soap bar upon drying. This property is an important factor in determining customer acceptance of a soap bar product since a bar which cracks upon drying tends to trap soil within the crevices thereof and become generally unsightly. This property also does not appear to be dependent on the beta/omega phase ratio but it seems likely that the proportion of acids of iso structure in the mixed C₁₂-C₁₅ acid proportion has some bearing upon the resistance to cracking of the resulting soap bar.

A series of soap bars was prepared from 80% of tallow acid soap and 20% of mixed C₁₂-C₁₅ acid of equal proportions of C₁₂, C₁₃, C₁₄ and C₁₅ acids and a varying proportion of acids having the iso structure. Each bar had approximately the same moisture content. The bars were evaluated by immersing each in water to one-half its depth for one-half hour and then allowing each to dry overnight at ambient conditions. After this period of standing, the ends of the bars were examined and visually evaluated as to the degree of cracking observed. The results of the series is shown in Table VI wherein the heading "Percent Iso" refers to the percentage of iso acids in the mixed C₁₂-C₁₅ component and the heading "Rating" expresses the extent of cracking observed based on a scale of 1-10 where 1 represents very severe cracking and 10 signifies no observable cracking.

TABLE VI

Percent Iso:	Rating (cracking)
2	3 (severe).
25	8 (slight).
50	9 (very slight).
80	10 (none).

On the same basis, a bar of 20% coconut acid soap and 80% tallow acid soap had a rating of 6.

To obtain the desirable property of resistance to cracking, therefore, the soap bar formulation suitably contains no more than about 20% of the mixed C₁₂-C₁₅ acid soap of the normal structure, i.e., at least about 80% of the mixed C₁₂-C₁₅ acid is of the iso structure. As applied to the total soap composition, at least 8%, preferably at least 15%, of the total soap should have the α -branched iso structure.

Similar advantageous specific properties are demonstrable for other compositions within the scope of the invention. It should be understood that the above data are provided to more fully illustrate the soap compositions and formulations of the invention and are not to be regarded as limitations.

We claim as our invention:

1. A soap bar product having a high ratio of beta phase crystallinity consisting essentially of a soap composition of

(A) from 10% to 90% of alkali metal salt of tallow acid, and

(B) from 90% to 10% of acid soap wherein (a) at least 50% of said acid soap is alkali metal salt of mixed unsubstituted aliphatic saturated carboxylic acids of the C₁₂-C₁₅ range, at least 10% of the acids of said mixture being of odd carbon number and from 15% to 98% of acids of each carbon number being of straight-chain structure and from 2% to 85% of acids of each carbon number being of alpha branched-chain structure, and wherein (b) any remainder of said acid soap is alkali metal salt of coconut acids.

2. The product of claim 1 wherein from 70% to 90% of said soap is alkali metal salt of tallow acid.

3. The product of claim 2 wherein the mixed carboxylic acids consist essentially of from 0% to 50% of each of C₁₂, C₁₃, C₁₄ and C₁₅ carboxylic acid.

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4. The product of claim 3 consisting essentially of said alkali metal salt of tallow acid and said alkali metal salt of mixed carboxylic acids of the C₁₂ to C₁₅ range.

5. The product of claim 4 wherein the mixed carboxylic acids consist essentially of from 10% to 40% of each of C₁₂, C₁₃, C₁₄ and C₁₅ carboxylic acids.

6. The product of claim 4 wherein the percentage of acids of the mixed carboxylic acids of the C₁₂ to C₁₅ range which are straight-chain acids is from 60% to 80%.

7. The product of claim 4 wherein the percentage of acids of the mixed carboxylic acids of the C₁₂ to C₁₅ range which are straight-chain acids is from 15% to 20%.

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