

UNITED STATES PATENT OFFICE.

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MIXED ESTERS OF LOWER AND HIGHER FATTY ACIDS AND PROCESS OF MAKING SAME.

No Drawing.

Application filed April 11, 1922. Serial No. 551,734.

To all whom it may concern:

Be it known that I, GEORGE L. SCHWARTZ, a citizen of the United States, and a resident of Wilmington, in the county of New Castle and State of Delaware, have invented certain new and useful Mixed Esters of Lower and Higher Fatty Acids and Processes of Making Same, of which the following is a specification.

This invention relates to mixed esters of the lower and higher fatty acids, and particularly to the mixed glycerides of coconut oil acids and acetic acid, and comprises, as new products, mixed esters of this kind having certain characteristics as hereinafter defined, and a process of making said products.

These new mixed esters are to be used primarily as softeners of pyroxylin, especially in connection with the manufacture of artificial leather. The vegetable oils have long been used as softeners of pyroxylin, and in particular castor oil and blown rapeseed oil have been used. Both of these oils are glycerides of unsaturated fatty acids. Their iodine numbers are high, and probably as a result of this unsaturated condition they are subject to certain physical or chemical changes. For example, castor oil readily becomes rancid when exposed in a pyroxylin film, and it gradually undergoes oxidation which causes a hardening of the film. Practically the only low melting vegetable oil that does not have a high iodine number is coconut oil. This oil is available in large quantities and would be an excellent softener of pyroxylin if its melting point were somewhat lower. It is much less subject to rancidity development and to gradual oxidation than oils now used, because the percentage of unsaturated glycerides which it contains is very low. One object, therefore, of my invention is to reduce the melting point of coconut oil so as to make it a better softener of pyroxylin.

Another object of my invention is to impart some solvent power for pyroxylin to coconut oil. I have found that it is often desirable to use as a softener a substance which has mild solvent power for pyroxylin.

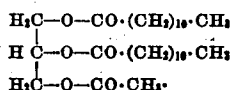
All of the known vegetable oils are practically without solvent action on pyroxylin, and it has heretofore been thought necessary, if solvent power was required, to add a solvent softener to the vegetable oil.

I have discovered that if an acyl group of a lower fatty acid be introduced into one or more of the glycerides of coconut oil, or of various other vegetable oils, the solvent power of the resulting glyceride for pyroxylin is appreciably increased, while at the same time the freezing point of the glyceride is lowered. This lowering of the freezing point is sometimes quite marked. Commercial coconut oil, for example, has a freezing point of from 14 to 22° C., whereas, after the introduction of an acetyl group to form a mixed ester, the melting point is usually between -5 and -13° C., the exact value depending upon the extent to which the acetyl group has displaced higher fatty acid radicals in the glycerides present. In general a mixed glyceride made in accordance with my invention should have a freezing point below 10° C., especially where the mixed glyceride is to be used as a softener of pyroxylin, although in some cases the increase in solvent power attending the introduction of a lower fatty acid radical may be so great as to render the glyceride suitable as a softener even though the freezing point thereof be substantially above 10° C.

The expression "lower fatty acid" is used herein to mean either formic, acetic, or propionic, acid; and the expression "higher fatty acid" has reference to acids of the aliphatic series containing more than nine carbon atoms. The alcohol radical of the mixed ester may be the radical of any one of various polyhydric alcohols, and especially of the lower polyhydric alcohols having between one and four hydroxyl groups, the principal members of this class being glycerol and ethylene, propylene, and butylene, glycols.

Where the new product has been obtained by the action of acetic acid on coconut oil, of which the chief constituent is the glyceride of lauric acid, the new product will

consist of a mixture of mixed esters of which the major part will be acetyl-laurins, with acetyl-palmitin and acetyl-myristin present in small proportions. The mono-acetyl-laurin formed has probably the following graphical formula:



Inasmuch as the mixture of acetyl derivatives of coconut oil glycerides is considered the most important of the products coming within the scope of my invention, the various methods of producing the new derivatives will be described with particular reference to coconut oil and acetic acid as starting materials. The several methods which I may use are briefly outlined as follows:

1. Glycerine, glacial acetic acid and coconut oil acids are heated at a relatively low temperature until the mixture of mono-, di- and triacetins is formed in equilibrium with the acetic acid. Then the excess acetic acid is distilled off, the temperature is raised to 180–200° C. and heating is continued until all but about 1% of the coconut oil acids are neutralized (esterified), using a stream of nitrogen to sweep out water as formed.

2. To the ingredients in (1) a small amount of sulfuric acid is added as a catalyst and the same procedure is followed except that the highest temperature of heating is 170° and the product after practical neutralization is washed with water to remove sulfuric acid.

3. The same ingredients and method are used as in (2) except that the sulfuric acid is neutralized with sodium acetate after the heating period at a low temperature.

4. Coconut oil and glacial acetic acid are heated under pressure until the requisite amount of coconut oil acids are displaced, free acetic acid is then distilled off and the free coconut oil acids are neutralized with diacetin, diacetin and glycerine, or a crude mixture of mono-, di- and triacetins by heating at 180–200° C. with a stream of nitrogen to remove water as formed.

5. Coconut oil, glacial acetic acid and a small amount of sulfuric acid are heated at a relatively low temperature until a sufficient amount of coconut oil acids has been replaced by acetic acid. Glycerine is then added and heating at a relatively low temperature is continued until a crude acetin mixture is formed. Then the excess acetic acid is distilled off and the temperature is raised and held at 150–170° C. using a stream of nitrogen to sweep out water as formed until neutralization is practically complete.

6. Coconut oil, glacial acetic acid, glycer-

ine and a small amount of sulfuric acid are treated as in (5) except that no further addition of glycerine is made.

7. Coconut oil and triacetin are heated at 180–200° C.

8. Coconut oil, triacetin and a small amount of sulfuric acid are heated together at 150–170° C. until equilibrium is established, whereupon the sulfuric acid is washed out with water.

Method (2) is at present believed to be most satisfactory, taking into consideration time, materials cost and quality of product, so for this reason I shall give an example of method (2) in detail.

The following ingredients are mixed in a flask that is provided with a reflux condenser and are heated for 1¾ hrs. in an oil bath at a temperature where the acetic acid boiled vigorously: Glycerine (containing 5% water) 967 parts (by weight), glacial acetic acid (99.5% acid) 2250 parts (by weight), coconut oil acids (mean mol. wt. 208) 1560 parts (by weight), sulfuric acid 0.7 parts (by weight).

The condenser is then changed to a distilling position and as the acetic acid concentration decreases the temperature of the mixture rises and is held at 160–175° C. throughout the remaining heating period. A stream of nitrogen is passed through the mixture throughout this latter heating stage to sweep out water as formed. After neutralization is practically complete the crude product is washed with an aqueous sodium chloride solution to remove sulfuric acid. The washed product is then heated for two hours on a steam bath with 2% of its weight of decolorizing carbon and is filtered. The finished product obtained by carrying out this process on a small scale was a light brown, transparent, oily liquid with a slight odor resembling coconut oil and freezing at –10 to –11° C. It contained 1.03% free coconut oil acids. The yield was 87.2% of the theoretical. The finished product is miscible in all proportions in mineral oil; it colloids pyroxylin at normal temperatures; and it does not become rancid.

A mixture of mixed glycerides prepared by any of the above methods is practically non-volatile and cannot be distilled at pressures as low as 14 mm. without partial decomposition. This product consists of a mixture of all the possible glycerides of acetic acid and coconut oil acids, ranging from some triacetin through the mixed glycerides to and including some coconut oil. The freezing point varies according to the ratio of acetyl to coconut oil acid groups and usually falls within the range of –5 to –13° C.

I have referred above to sulfuric acid as the catalyst but there is no doubt that various other mineral acids will have the same

action, though varying in degree. The temperature range for esterification has been given as above 150° C. but it is probable that esterification of the coconut oil acids can be carried on as low as 100° C. with a catalyst. Temperatures higher than 170° C. cause much discoloration. Lower temperatures require longer time for esterification but give lighter colored products.

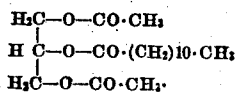
Wherever glycerine is cited it can be substituted by chemical equivalents of crude acetin mixtures which are obtained by heating glycerine and glacial acetic acid with or without a catalyst at the boiling point of acetic acid in the mixture until equilibrium has been reached between the acetins and acetic acid.

The coconut oil acids that I have used were obtained by hydrolysis of commercial coconut oil, with subsequent distillation under reduced pressure.

Although in the above description of methods of making the new acetyl derivatives, I have referred to the use of glacial acetic acid, it will be understood that acetic acid of a concentration lower than what is signified by the word "glacial" may be used.

Coconut oil, as has been indicated above, is the oil with which I prefer to start, but other materials may with advantage be converted into acetyl-glycerides in the manner above described, as, for example, commercial stearic acid, which contains a large proportion of palmitic acid, or palm kernel oil, or the acids of this oil.

The new products, when obtained from oils such as coconut oil, may be defined generically as mixtures of acetyl derivatives of glycerides of two or more higher fatty acids each having from 10 to 16 carbon atoms. The glyceride mixture prepared in accordance with the above examples will contain a substantial proportion of diacetyl-glycerides of the higher fatty acids, as, for example, diacetyl-laurin, diacetyl-myristin, and diacetyl-palmitin. The molecular structure of the alpha-gamma-diacetyl-laurin, which is typical, is probably as follows:



In addition to the alpha-mono-acetyl-laurin whose structure has been shown in the first of the above graphical formulas, the new product contains the beta-mono-acetyl derivative of the various glycerides; and in addition to the alpha-gamma-diacetyl derivative, the alpha-beta-diacetyl derivative is believed to be formed, although in minor proportions.

An approximate idea of the relative proportions of the mixed esters of the various glycerides obtained by my process, may be

gained from the following showing the relative proportions of combined fatty acids which are present in coconut oil: Caproic ($\text{C}_6\text{H}_{12}\text{O}_2$) 0.25%, caprylic ($\text{C}_8\text{H}_{16}\text{O}_2$) 0.25%, capric ($\text{C}_{10}\text{H}_{20}\text{O}_2$) 19.5%, lauric ($\text{C}_{12}\text{H}_{24}\text{O}_2$) 40.0%, myristic ($\text{C}_{14}\text{H}_{28}\text{O}_2$) 24.0%, palmitic ($\text{C}_{16}\text{H}_{32}\text{O}_2$) 10.6%, oleic ($\text{C}_{18}\text{H}_{34}\text{O}_2$) 5.4%.

A decidedly greater lowering of the freezing point and increase in solvent power of the higher fatty acid glycerides is attained by introducing two, instead of merely one, acetyl group into the glyceride molecules. My invention includes broadly the diacetyl-mono-acyl-glycerides, where "acyl" is used to mean the acid radical of a higher fatty acid, as well as corresponding glycerides containing two formyl or two propionyl groups.

I claim:

1. The process of producing a composition containing mixed glycerides of lower and higher fatty acids which comprises heating the glyceride of a higher fatty acid together with concentrated acetic acid in the presence of an esterification catalyst until the desired proportion of higher fatty acid radicals have been replaced by acetic acid radicals in said glycerides, adding glycerine, heating the resulting mass at a temperature substantially below 150° C. until a crude acetin mixture is formed, distilling off any excess acetic acid, and then heating the resulting mixture at a temperature above 150° C. but below that at which thermal decomposition of the glycerides occurs, while passing an inert gas through the mixture to remove water as it is formed, until esterification of the higher fatty acid by the acetin is practically complete.

2. The process of producing a composition containing mixed glycerides of lower and higher fatty acids which comprises heating together coconut oil and concentrated acetic acid in the presence of an esterification catalyst until the desired proportion of coconut oil acid radicals have been replaced by acetic acid radicals in the glycerides of said oil, adding glycerine, heating the resulting mass at a temperature substantially below 150° C. until a crude acetin mixture is formed, distilling off any excess acetic acid, and then heating the resulting mixture at a temperature of from about 150 to 170° C., while passing an inert gas through the mixture to remove water as it is formed, until esterification of coconut oil acids by the acetin is practically complete.

3. A composition of matter comprising a mixed ester of a lower and a saturated higher fatty acid, the alcohol radical of said ester being that of a polyhydric alcohol having between 1 and 4 hydroxyl groups, said composition having a freezing point below 10° C.

4. A composition of matter comprising mixed esters of a lower fatty acid and at least two higher fatty acids each having from 12 to 16 carbon atoms, the alcohol radical of said esters being that of a polyhydric alcohol having between 1 and 4 hydroxyl groups, said composition having a freezing point below 10° C.
5. A composition of matter comprising a mixed glyceride whose molecules contain two lower-fatty-acid radicals and one saturated higher fatty acid radical.
6. A composition of matter comprising a mixed glyceride whose molecules contain two lower-fatty-acid radicals and one higher fatty acid radical having from 10 to 16 carbon atoms.
7. A composition of matter comprising a mixed glyceride whose molecules contain two acetyl radicals and one saturated higher fatty acid radical.
8. A composition of matter comprising a mixed glyceride whose molecules contain two acetyl radicals and one higher fatty acid radical having from 10 to 16 carbon atoms.
9. A composition of matter comprising diacetyl-laurin.
10. A composition of matter comprising a mixed glyceride whose molecules contain two acetyl radicals and one higher fatty acid radical, and a mixed glyceride whose molecules contain two acetyl radicals and one radical of another higher fatty acid, the freezing point of said composition being below 10° C.
11. A composition of matter comprising a mixed glyceride whose molecules contain two acetyl radicals and one higher fatty acid radical, and a mixed glyceride whose molecules contain two acetyl radicals and one radical of another higher fatty acid, each of said higher fatty acid radicals having from 10 to 16 carbon atoms, the freezing point of said composition being below 10° C.
12. A composition of matter comprising an acetyl-glyceride of a higher fatty acid, said glyceride containing at least one acetyl group and a diacetyl-glyceride of a higher fatty acid.
13. A composition of matter comprising an acetyl-glyceride of a higher fatty acid having from 10 to 16 carbon atoms, said glyceride containing at least one acetyl group, and a diacetyl-glyceride of a higher fatty acid having from 10 to 16 carbon atoms.
14. A composition of matter comprising a mixed ester of a lower fatty acid and lauric acid, the alcohol radical of said ester being that of a polyhydric alcohol, having between 1 and 4 hydroxyl groups.
15. A composition of matter comprising a mixed ester of a lower fatty acid and lauric acid, the alcohol radical of said ester being that of a polyhydric alcohol, having between 1 and 4 hydroxyl groups, said composition having a freezing point below 10° C.
16. A composition of matter comprising a mixed ester of a lower fatty acid, lauric acid, and at least one other higher fatty acid, the alcohol radical of said ester being that of a polyhydric alcohol having between 1 and 4 hydroxyl groups.
17. A composition of matter as set forth in claim 16 in which the composition has a freezing point below 10° C.
- In testimony whereof I affix my signature.
- GEORGE L. SCHWARTZ.