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AIR DRYING MIXED ESTERS AND PROCESS FOR PREPARING THE SAME

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16 Claims. (Cl. 260—97.5)

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The invention relates to a new process of preparing air drying mixed esters showing improved technical properties as regards drying rate, resistance to physical and chemical stresses and so on, as compared with the hitherto known mixed esters.

It has been known to prepare mixed esters of organic acids by esterifying a polyhydric alcohol with several acid residues differing from one another. This operating method is applied in the present process for the purpose of improving the technical properties of unsaturated higher molecular fatty acids or of substances containing such acids in a free state or as esters particularly as regards their coating properties. Such substances comprise for instance natural drying oils such as linseed oil and also the free higher molecular unsaturated fatty acids themselves and furthermore products containing in addition other esterifiable or non-esterifiable constituents such as tall oil.

The natural drying oils consisting essentially of higher molecular unsaturated fatty acids with isolated double bonds or their esters, such as linseed oil are known to dry only comparatively slowly as compared with wood oil or oiticica oil and are distinctly inferior to these last mentioned oils as regards their resistance to water and other chemical stresses, at least in the unpigmented state. Such natural fatty drying oils, however, may be rendered more similar to wood oil, for example by boiling them down to the so-called stand oil. However, such treatment does not improve the drying rate, but rather impairs it.

It is true that the joint esterification of linseed oil fatty acids and wood oil fatty acids with polyhydric alcohols leads to mixed ester products showing improved technical properties as compared with the pure linseed oil product. But in this case it is necessary to use the expensive wood oil which is only obtainable in restricted quantities.

It has now been found that the technical properties of the higher molecular unsaturated fatty acids or of substances containing said acids in a free state or as esters can be essentially improved especially for coating purposes by reacting them in the heat with a polyhydric alcohol and low molecular monocarboxylic acids which contain conjugated double bonds, whereby mixed esters are obtained. By low molecular monocarboxylic acids I mean acids containing not more than about 10 carbon atoms per molecule. Suitable unsaturated monocarboxylic acids are

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for example the hexadiene (2,4)-carboxylic acid-(1) or sorbic acid ($CH_3.CH:CH.CH:CH.COOH$) and octatriene (2.4.6)-carboxylic acid (1) ($CH_3.CH:CH.CH:CH.CH:CHOOH$).

Especially valuable products can be obtained by employing, besides the before mentioned low molecular carboxylic acids, such higher molecular unsaturated fatty acids or substances containing same which acids contain at least 2 isolated double bonds per molecule such as contained in many drying oils.

By way of example, a mixture of linseed oil fatty acid with 25% by weight of sorbic acid and the quantity of glycerine necessary to completely esterify both acids, is slowly heated to 240–250° C., until the acid value is correspondingly reduced. The final product has the consistency of a thin stand oil and if diluted for instance with some varnish benzine and siccativated it dries quickly and leaves coatings with excellent surfaces. Compared with a product prepared solely of linseed oil fatty acid such films show furthermore an increased resistance to water, atmospheric humidity and so on.

Furthermore it has been found that it is also possible to proceed in such a way as to prepare first of all a mixture of mono- or diglycerides, etc., by heating linseed oil with the respective amount of glycerine and to esterify subsequently the still existing free hydroxy groups of the polyhydric alcohol with the unsaturated monocarboxylic acid.

As regards the polyhydric alcohol it is not necessary to use only glycerine, but other polyhydric alcohols are also suitable for this purpose. In any case products are obtained differing advantageously from the starting material by improved drying rate, increased body and higher resistance to water and other chemical and physical stresses.

The esterification can be carried out in absence of atmospheric oxygen in order to avoid oxidising during the reaction.

Example 1

80 parts of linseed oil fatty acid, 20 parts of sorbic acid, 15 parts of glycerine of 28° Bé. are heated in a carbonic acid atmosphere successively two hours to 180° C., two hours to 200° C., three hours to 240° C. and finally further 1–2 hours to about 270–280° C. The acid value is then reduced to below 10. The final product has the consistency of a thin stand oil and is cleansed of any insoluble impurities by filtration.

Example 2

80 parts of technical tall oil distillate containing about 70% fatty acids and 30% resinous acids are slowly heated with 20 parts of sorbic acid and 14.8 parts of glycerine of 28° Bé. in a carbonic acid current to 240–250° C. and this temperature is maintained for 4–5 hours. Thereupon further two parts of glycerine are added and the reaction is completed by quickly heating to 280° C. The esterification product has the consistency of a viscous stand oil; it may be diluted for example with aromatic hydrocarbons and on addition of suitable drying materials it will furnish rapidly drying films of excellent surface and of unexpected high resistance, for example to water (humidity).

Example 3

90 parts of the tall oil distillate as used in Example 2 are slowly heated together with 10 parts of octatriene carboxylic acid (made of sorbic aldehyde and malonic acid) and 13 parts of glycerine of 28° Bé. in a current of nitrogen to 250° C. Notwithstanding the comparatively small amount of octatriene carboxylic acid used the final product after dilution and addition of drying materials shows a drying rate distinctly improved as compared with that of pure tall oil tri-glyceride.

The mixed esters prepared according to the invention are not only valuable products for coating purposes, but may also be employed for example in the manufacture of linoleum and furthermore for foils and laminations and such like.

The technical and economical advantage of the present invention consists in the fact that the low molecular monocarboxylic acids with conjugated double bonds are a relatively easily accessible synthetic material to be used as esterification components. In this way the use of expensive substances which can only be obtained in restricted quantities, such as wood oil, can be avoided. On the other hand, the products made in accordance with the present invention, are at least equivalent to the products made of said materials and sometimes even superior.

I wish it to be understood that I do not desire to be limited to the exact details shown and described for obvious modifications will occur to a person skilled in the art.

What I claim is:

1. A process which comprises heating a mixture of 80 parts of linseed oil fatty acid, 20 parts of sorbic acid and 15 parts of glycerine in a carbonic acid current successively 2 hours to 180° C., 2 hours to 200° C., 3 hours to 240° C., and 1–2 hours to 270–280° C.

2. A process which comprises heating slowly a mixture of 80 parts of tall oil-distillate, 20 parts of sorbic acid and 14.8 parts of glycerine in a carbonic acid current to 240–250° C., holding the mixture for 4–5 hours on this temperature, adding 2 parts of glycerine and finally heating for a short time to 280° C.

3. A process which comprises heating slowly a mixture of 90 parts of tall oil distillate, 10 parts of octatriene (2,4,6)-carboxylic acid (1) and 13 parts of glycerine in a nitrogen current to 250° C.

4. Process of preparing a mixed ester which comprises reacting as essential ingredients a polyhydric alcohol with a monocarboxylic acid containing conjugated carbon-to-carbon double bonds and of a low molecular weight characterized by not more than about ten carbon atoms in the molecule and with a higher molecular unsaturated compound from the group consisting of drying oil monocarboxylic acids with at least two isolated double bonds in the molecule and of polyhydric alcohol esters of the acids, said mixed ester having an oily to viscous consistency and drying in air to form coatings.

5. Process according to claim 4 in which the compound is linseed oil fatty acid.

6. Process according to claim 4 in which the compound is tall oil.

7. Process according to claim 4 in which the low molecular weight acid is sorbic acid.

8. Process according to claim 4 in which the low molecular weight acid is octatriene carboxylic acid.

9. Process according to claim 4 in which the polyhydric alcohol is glycerol.

10. Process according to claim 4 in which the low molecular weight acid comprises 25 per cent by weight of the compound.

11. A mixed ester of a polyhydric alcohol with a monocarboxylic acid containing conjugated carbon-to-carbon double bonds and of a low molecular weight characterized by not more than about ten carbon atoms in the molecule and with a higher molecular unsaturated compound from the group consisting of drying oil monocarboxylic acids with at least two isolated bonds in the molecule and of polyhydric alcohol esters of the acids, said mixed ester having an oily to viscous consistency and drying in air to form coatings.

12. Product according to claim 11 in which the compound is linseed oil fatty acid.

13. Product according to claim 11 in which the compound is tall oil.

14. Product according to claim 11 in which the low molecular weight acid is sorbic acid.

15. Product according to claim 11 in which the low molecular weight acid is octatriene carboxylic acid.

16. Product according to claim 11 in which the polyhydric alcohol is glycerol.

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The following references are of record in the file of this patent:

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Certificate of Correction

Patent No. 2,420,694. May 20, 1947.

RUDOLF BARTHEL

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Column 2, line 4, for that portion of the formula reading "CHOOH" read *CH.COOH*; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 1st day of July, A. D. 1947.

[SEAL]

LESLIE FRAZER,
First Assistant Commissioner of Patents.