

ALIEN PROPERTY CUSTODIAN

PROCESS FOR FRACTIONATING MIXTURES OF FATTY ACIDS AND/OR ESTERS OF FATTY ACIDS

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in the Alien Property Custodian

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Substances active in lowering surface tension have long been employed in the refining and improvement of fatty acids and their esters for the purpose of eliminating undesirable accompanying substances, such as coloring substances, glue, albumin, soaps and the like. In this treatment of fatty acids and fats with substances acting in lowering surface tension, such as carbon, bleaching earths, silica gel and the like, large quantities of fatty substances have hitherto always been treated with small quantities of substances active in lowering surface tension.

It has been found that it is also possible to fractionate mixtures of fatty acids or esters of fatty acids by subjecting these mixtures to a selective adsorption process. According to the invention, the mixtures of fatty acids or their esters are treated for this purpose with large quantities of substances active in lowering surface tension which may amount to a multiple of the quantity of fatty substances. The fatty substances are preferably made to flow through a thick layer of substances active in lowering surface tension, because it has been found that if the substances active in lowering surface tension are suitably selected, the individual fatty acids and their esters, that is to say, esters containing alcohols of low molecular value, for example methyl alcohol, ethyl alcohol, propyl alcohol, glycol or glycerine, are of different adsorbability.

In this respect, saturated and unsaturated, hydroxylated and non-hydroxylated acids and the like of high and low molecular value and their esters differ from one another. Thus, the selective adsorption according to the invention may serve for fractionating mixtures of fatty acids, mixtures of esters thereof or mixtures containing both classes of substances. It is based upon the fine adjustment of the differences, even if sometimes very small, in the affinity with respect to the adsorbents employed. Mixtures containing derivatives of fatty acids such as oxy-acids, keto-acids, polymerised acids, estolides and the like, or mixtures of fatty acids or derivative thereof and esters of the fatty acids with alcohols of low molecular value, or mixtures of different esters of the fatty acids with alcohols of low molecular value, may also be treated and fractionated by the process according to the invention.

The practical application of this process to mixtures of fatty acids is important, for example, for separating acids of high and low molecular value as well as saturated and unsaturated acids. Polymerised compounds, oxidised acids and the like may also be selectively adsorbed. In practice, these possibilities are of importance in different directions, for example in the removal of saturated acids from olein, in the separation of drying acids from non-drying acids and

the like. In the separation of mixtures of fatty acids and fatty acid glycerides, deacidification plays a particular part. The separation of such mixtures by the process according to the invention is distinguished from the hitherto usual methods by its exceptional sparing nature. In deacidification by distillation, somewhat high temperatures are employed, so that the glycerides obtained no longer correspond to the native state. Furthermore, the accompanying substances are destroyed. This is also the case in deacidification by means of lyes. The separation by adsorption permits of recovering both the acid filtrate and coincidentally the acids in highly enriched form. They may then further be subjected to the known refining processes. With the high concentration thus obtained deacidification by distillation is also advisable.

The process will best be understood from the following example.

A mixture containing 5 parts each of stearic acid, oleic acid and linoleic acid constitutes a mass which is solid at room temperature. If this mixture is dissolved in 100 parts of benzene and the solution is subjected to a selective adsorption by passing it slowly through a high layer of granulated, water-free aluminium oxide, liquid fatty acids practically free from stearic acid remain behind after removal of the solvent. Analytic examination shows that the stearic acid is much more highly adsorbed than the unsaturated acids. It remains in the upper part of the adsorption column which, on the other hand, only contains small quantities of linoleic acid after elution with acetone. In the case of the unsaturated acids, the adsorption becomes weaker with increasing iodine number. The original mixture of the fatty acids had the iodine number 91, and the mixture recovered from the upper part of the column has only an iodine number of 60, while the mixture situated in the filtrate has the iodine number 135.

Consequently, a considerable fractionation has occurred by the simple treatment of a fatty acid mixture with a medium active in lowering surface tension. This fractionation may be carried further by repetition, if necessary employing other solvents and other adsorbents. However, this is frequently not necessary.

Further experiments showed that a stronger adsorbability of the fatty acids is present with increasing molecular weight. The analytical examination is in this case effected by the determination of the neutralisation number of the filtrate and of the elutions of different layers. Oxy-acids can also be well and selectively adsorbed.

Not only solutions, but also liquid mixtures, may be treated by the process according to the present invention. This will be shown by refer-

ence to an example of a natural glyceride mixture.

Varnish linseed oil having the iodine number 165 is made to flow very slowly through as high as possible a layer of alumina, this being assisted by the application of a vacuum. The oil flowing off shows a considerable increase in the iodine number to 192.

The selective adsorption can also be applied to mixtures of esters and free acids. If stearic acid is added to the linseed oil and the solution of the mixture is then subjected to the adsorption, the stearic acid is bound by the adsorbent. If an oil contains soaps, these are retained during its passage through adsorption columns.

The known adsorbents, such as alumina, bleaching earths, carbon, gypsum, calcium carbonate, magnesium oxide, fibrous clay and other inorganic or organic substances, may be employed for the process according to the invention. The adsorbents must be selected by preliminary tests according to the purpose of use. Similarly, it is also advisable to ascertain by preliminary tests whether and what solvents are to be employed.

The described fractionation of fatty acids of the most varied types—including the derivatives, such as oxy-acids, keto-acids and the like, their esters and mixtures of both is in the first place of value for purposes of analysis and preparation, particularly in view of the sparing treatment, which prevents modifications due to rearrangement and the like. In addition, however, the process is of considerable practical importance. This will merely be illustrated by a few examples.

The fractionation of fatty acids in the manner of the example given at the beginning may be employed in the production of olein, but particularly in the separation of more highly unsaturated fatty acids, in the soap industry. Such unsaturated fatty acids are known to impair the consistency of the soaps and the durability in storage. Similar advantages are also afforded by the fractionation of esters, while the desirability of employing more highly unsaturated fractions for the manufacture of varnish is to be noted. Finally, the fractionation of esters and fatty acids, for example for deacidification, is important, especially as a sparing treatment takes place in the present process.

For carrying out the present process, apparatus are employed in which the adsorption media necessary in large quantities are accommodated in towers, closed filter vessels having a bottom of porous or sintered material and the like, or in columns thereof or the like. The flow of the liquid is advantageously assisted by employing a vacuum on the one hand and pressure on the other hand. If danger of oxidation exists, the air must be excluded or replaced by inert gases. If a plurality of adsorption devices are connected in series, individual devices in continuous operation may be disconnected, withdrawn and rendered serviceable again. It is also possible, by subsequently passing through solvents, to effect more distinct separations or to dissolve the adsorbate, if necessary at increased temperature.

Examples

1. A mixture of stearic acid and myristic acid in the proportion of 1:1 is dissolved in 10 parts of benzene and slowly filtered, if necessary under suction, through about 6 times the quantity of aluminium oxide. The filtrate contains pure myristic acid, while the upper part of the column

contains pure stearic acid. The adsorbate contained in the remaining parts of the column is a mixture of both acids, the proportion of stearic acid decreasing towards the lower end.

2. A mixture of stearic acid and oleic acid treated in the same manner yields a filtrate representing pure oleic acid. Technical oleins lose the saturated acids upon filtration through aluminium oxide. The iodine number then increases more or less according to the quantity of linoleic acid present. Thus, an olein having an iodine number of 89 had an iodine number 93 after the filtration.

3. If a mixture of stearic acid, oleic acid and linoleic acid is employed, the filtrate is completely free from stearic acid. The original iodine number of 91 increases in the filtrate to 135.

4. Whale oil fatty acids having the iodine number 110.9, when dissolved in benzene give a filtrate in which the fatty acid mixture has the iodine number 136.7, and is therefore substantially richer in unsaturated acids than the starting material.

5. Olive oil to which 20% stearic acid is added is dissolved in benzene and filtered through aluminium oxide. The original mixture had the acid number 43.8, while the filtrate has the acid number 0.36. A complete deacidification has therefore practically occurred. If the adsorption column is divided into four parts the following is found: The uppermost part contains a fat of the acid number 129, the second part a fat of the acid number 1.75, the third part a fat of the acid number 1.63 and the lowermost part a fat of the acid number 0.80. The same result was attained with silica gel. The filtrate here had an acid number of 0.4.

As soon as the acid number begins to increase in the filtrate with this deacidification, a further column is connected and the first is regenerated by treatment with fresh solvents. A plurality of towers may thus be connected in series. Trichloroethylene is also suitable as a solvent. In this case, regeneration is preferably effected with a mixture of 95 parts of trichloroethylene and 5 parts of acetone. The columns may be connected one behind the other ten or more times after regeneration.

6. Whale oil of the acid number 6 was slowly filtered through silica gel of coarse grain. The acid number fell to 0.2, while at the same time the oil of the filtrate lost the train oil smell. Here, therefore, a desirable deodorisation occurred simultaneously. If the adsorbate is extracted with a solvent, for example acetone, an unpleasant smelling product of the acid number 60 is obtained.

7. A sulphur olive oil of the acid number 101.8 was dissolved in 10 parts of benzene and filtered through alumina. After adsorption through two columns, the fat of the filtrate has an acid number of 4, while that of the fat extracted from the first column amounted to 183.4.

Aluminium oxide, silica gel, fuller's earth, fibrous clay bentonite and the like may be employed as adsorbents. The miscellany or oil extraction may also be employed directly for the deacidification. In this case, other accompanying substances may if necessary also be adsorbed. The solvent and the adsorbents must be selected according to the particular case.

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