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COMPLETE SPECIFICATION

Improvements in or relating to the Manufacture of Soap-forming Carboxylic Acids

We, DEUTSCHE HYDRIERWERKE AKTIENGESELLSCHAFT, a Joint Stock Company organised under German law, of Postfach 32, Dessau-Rosslau, Germany, and Kantstrasse 163, Berlin-Charlottenburg, Germany, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention relates to improvements in or relating to the manufacture of soap-forming carboxylic acids.

Several methods of manufacturing soap-forming carboxylic acids by oxidation of hydrocarbons have already been proposed, especially such as employ the paraffin hydrocarbons as starting materials. However, the fatty acid products obtained by these known processes are scarcely satisfactory since they are contaminated to a very high degree by unsaponifiable as well as unaltered starting material and also by unsaponifiable partial oxidation products, from which they can only be separated with considerable difficulty. In addition these fatty acids, owing to the said admixtures, have an unpleasant smell.

It has now been found that in a comparatively simple way a most satisfactory yield of very good soap-forming carboxylic acids or their salts may be obtained by a method wherein technical mixtures of glycols or products containing oxide groups produced by oxidation of naturally occurring or artificially produced technical mixtures of aliphatic, aliphatic-alicyclic or aliphatic-aromatic hydrocarbons containing besides one or more unsaturated linkages in an aliphatic hydrocarbon chain, at least one continuous aliphatic hydrocarbon chain of at least 6 carbon atoms linked together by single linkages, are treated with fused alkali metal or alkaline earth metal bases, the salts formed then being acidified to yield the free acids if desired.

The technical mixtures of oxidation products employed as starting materials in the above process may be obtained for example by oxidation of the olefinic hydrocarbons, such as are present in the fractions of the hydrocarbon mixtures rich in olefines which occur naturally or are obtained chemically. Among the naturally occurring hydrocarbon mixtures of this kind certain tar oils obtainable by distillation of lignite and boiling at temperatures between 200 and 350° C. and containing a large portion of unsaturated hydrocarbons may be mentioned by way of example. Furthermore, cracking gas oil fractions boiling at temperatures between 200 and 325° C. and possessing 70 to 75% of olefines, whilst their molecular size corresponds to carbon chains of 12 to 18 carbon atoms are also suitable. Finally, hydrocarbon mixtures, in so far as they are of an olefinic character which are obtainable synthetically for example, by the hydrogenation of carbon monoxide, also come into consideration. The olefinic hydrocarbons preferably possessing an unsaturated linkage at or near the end of the carbon chain, are, in general, to be preferred for this process. The hydrocarbons may, however, also contain some other unsaturated linkages or they may be substituted or interrupted by cyclo-aliphatic or aromatic hydrocarbon residues.

For the oxidation of the unsaturated hydrocarbons at the unsaturated linkage to the corresponding glycols or oxides, the usual oxidising agents, such as potassium permanganate, hydrogen peroxide, alkali persulphate, alkali hypochlorite, chlorine, oxygen, air and the like, may be employed. The oxidation is preferably effected in the presence of suitable solvents or diluents such as glacial acetic acid, acetic acid anhydride, dioxane, acetone and the like or mineral oils, whereby the unsaturated hydrocarbons may, in certain cases, be employed directly in admixture with the saturated hydrocarbons such as are present in the hydrocarbon mixtures employed as starting materials. The unsaturated hydrocarbons may, however, also be converted by means of suitable dispersing or emulsifying agents such as

[Price 1/-]

soaps, fatty alcohol sulphonates, substances having a soap-like action and the like, into aqueous emulsions which may then be treated with oxidising agents in a similar manner. The oxidising process is preferably promoted by suitable increases of temperature which in each individual case depend on the oxidising agents employed. In certain cases it may, moreover, be advantageous to work with closed vessels under pressure.

The time taken in any particular case for completion of the oxidation treatment will depend upon the conditions employed. The duration of the oxidation may be controlled by observing the decrease in the iodine number of the material under treatment. A further control, which is particularly efficacious for preventing the oxidation proceeding too far, is provided by the appearance of alkali solubility in the material and of carboxylic acid groups which may be determined by titration with alkali.

The technical mixtures obtained by the oxidation are now subjected in a manner known per se to melting with alkali metal or alkaline-earth metal bases either in anhydrous condition or in highly concentrated form, that is with addition of very small quantities of water, whereupon the formation of the salts of the corresponding carboxylic acids takes place with the development of hydrogen. In the case of this process temperatures of above 200° C. and preferably temperatures varying from 250 to 300° C. are employed. As soon as the development of hydrogen and the oxidation are complete the carboxylic salts obtained may be worked-up in the usual manner.

In the form of their alkali salts the products obtained from the above mentioned process are soaps of an excellent washing power which may most advantageously be used for all those purposes for which hitherto the soaps of natural fatty acids or fats with alkalis, alkaline earths, earth- or heavy metals were used.

In order that the invention may be well understood the following examples are given by way of illustration only. In these examples the duration of the oxidation treatment will be determined as described above.

EXAMPLE 1.

A mixture of benzine synthetically obtained by the hydrogenation of carbon monoxide and containing about 50% of mono-olefines, comprising mainly olefines containing besides an unsaturated linkage at least one continuous aliphatic hydrocarbon chain of at least 6 carbon atoms linked together by single linkages, is formed into an aqueous emulsion by means of a small amount of soap. To this emulsion a slight excess of 30—40% hydrogen peroxide is gradually added whilst the temperature is preferably kept at about 90° C. When the oxidation is finished the excess of hydrogen peroxide is destroyed by the addition of small quantities of alkali and the mass is evaporated to dryness. The oxidation product thus obtained is then melted with caustic alkali at a temperature of 250 to 280° C. The melt, after cooling, is decomposed with diluted mineral acid and gives a valuable fatty acid mixture which may be purified by distillation.

EXAMPLE 2.

A cracking gas oil fraction with a boiling point varying from 200 to 325° C. and containing 70 to 75% of olefines, comprising mainly olefines containing besides one or more unsaturated linkages at least one continuous aliphatic hydrocarbon chain of at least 6 carbon atoms linked together by single linkages, is dissolved in glacial acetic acid and carefully oxidised with hydrogen peroxide at the water-bath temperature. As soon as the reaction, which may be followed up by observing the diminishing of the iodine number of the initial oil, is completed the solvent and any unaltered initial material is distilled off and the remaining oxidation product, in the form of the acetic acid ester, is subjected if desired after a previous splitting-off of the ester group, to melting with caustic alkali. After acidifying and distilling a valuable fatty acid mixture is obtained.

EXAMPLE 3.

300 parts by weight of olefines (boiling point 140—180° at a pressure of 5 mm., iodine number 90—95, hydroxyl number 20—25, obtained by splitting-off water from a technical mixture of cetylalcohol and stearylalcohol) are heated with 1250 parts by weight of glacial acetic acid at a temperature of 90° C. and gradually mixed with 230 parts by weight of 40% hydrogen peroxide whilst stirring. At first the liquid is turbid and becomes clear and transparent after completion of the formation of glycol. The acetic acid is then distilled off and the residue is saponified with caustic potash. The output of glycol amounts to 280—290 parts by weight after washing and drying. The glycol boils between 320 and 345° (at a pressure of 2—3 mm) and has the hydroxyl number of 320—345 and is of a waxy consistency. By melting 1 mole of the glycol at a temperature of 230—270° with 1—2 moles of caustic

soda a fatty acid is obtained having the titer 26—27 and the acid number 221.

EXAMPLE 4.

300 parts by weight of cracking benzine (iodine number 55, boiling range 120—205°, containing 40% of olefines comprising mainly olefines containing besides one or more unsaturated linkages at least one continuous aliphatic hydrocarbon chain of at least 6 carbon atoms linked together by single linkages,) are mixed with 900 parts by weight of acetic acid (98%) and heated to a temperature of 90° C. At this temperature 180 parts by weight of hydrogen peroxide (40%) are added whilst stirring in the course of ½—1 hour and the reaction mass is cooled externally to prevent the temperature of the reaction rising above 110° C. The addition of oxygen is completed after about 2 hours stirring and the benzine (about 190 parts by weight) which has not reacted is separated from the acetic acid solution of the glycol formed. The acetic acid is removed by distillation in vacuo and the glycol formed is obtained as residue in the form of the acetic acid ester. After saponification with alkali the ester yields 110—120 parts by weight of glycol, distilling over between 110—130° C. (at a pressure of 3—4 mm) without leaving behind any considerable residue. The distillate has the hydroxyl number 530. For converting the glycol into the corresponding carboxylic acid 220 parts by weight of glycol, 85 parts by weight of caustic soda (97%) and 30 parts by weight of water are heated in a stirring autoclave gradually up to 230° C. and subsequently to 250—260° C. As soon as a pressure of 10 at. is formed, it is gradually relieved to 6—8 at. Water as well as the hydrogen formed escape and the cessation of this escape indicates the completion of the oxidation. The soap formed foams well and upon acidification produces a fatty acid with the acid number 305 and a solidifying point of +8°, which corresponds to caproic acid, a coconut oil fatty acid. The content of unsaponifiable portions amounts to 3—5%.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A method of manufacturing soap forming carboxylic acids or salts thereof, wherein technical mixtures of glycols or products containing oxide groups produced by oxidation of naturally occurring or artificially produced technical mixtures of aliphatic, aliphatic-alicyclic or aliphatic-aromatic hydrocarbons containing besides one or more unsaturated linkages in an aliphatic hydrocarbon chain, at least one continuous aliphatic hydrocarbon chain of at least 6 carbon atoms linked together by single linkages, are treated with fused alkali metal or alkaline earth metal bases, the salts formed then being acidified to yield the free acids if desired.

2. A method as claimed in Claim 1, wherein technical mixtures produced by oxidation of tar oil distillation products of lignite, boiling at 200—350° C. cracking gas oil fractions boiling at 200 to 325° C. or hydrocarbon mixtures of olefinic character obtainable by the hydrogenation of carbon monoxide are employed.

3. A method as claimed in either of Claims 1 or 2 wherein technical mixtures produced by the oxidation of aqueous emulsions of the unsaturated hydrocarbons are employed.

4. A method as claimed in any of the preceding claims in which the said technical mixtures are subjected to melting with highly concentrated alkali metal or alkaline-earth metal bases at temperatures from 200 to 300° C.

5. A method of manufacturing soap-forming carboxylic acids or salts thereof substantially as described.

6. Soap-forming carboxylic acids and salts thereof when made by a method particularly described and ascertained herein or by its obvious chemical equivalent.

Dated the 22nd day of February, 1937.

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