

ALIEN PROPERTY CUSTODIAN

PRODUCTION OF FATTY ALCOHOL SULFONATES

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This invention relates to the production of fatty alcohol sulfonates from mixtures of higher aliphatic hydrocarbons having about 8 or more carbon atoms in the molecule.

The principal object of the invention is to provide a new manner of utilizing substantially valueless higher aliphatic hydrocarbon mixtures of the kind that accrue in the synthetic preparation of benzine and to obtain valuable wetting, washing, cleaning, emulsifying and dispersing agents therefrom.

It is therefore a further object of the invention to provide a new process by which valuable fatty alcohol sulfonates may be prepared from by-product raw materials instead of the costly naturally occurring fatty acids and esters which have heretofore been used as raw materials in the manufacture of these sulfonates, and which usually must be imported.

We have found that the liquid-solid mixture of higher aliphatic hydrocarbons, consisting for the most part of compounds having from 8 to 18 carbon atoms in the molecule, which is obtained in the synthesis of benzine from carbon monoxide and hydrogen according to the process of Fr. Fischer (see Brennstoff-Chemie (1928), page 21; idem (1932), page 461 et seq) may be used as raw material for the production of fatty alcohol sulfonates. The physical properties of mixtures of this sort are such that they are not suitable for industrial uses. They are too viscous for use as lubricants, and their boiling point is too high for use as fuel in internal combustion engines. As a result they have heretofore been considered waste products. In accordance with our process, however, these mixtures are converted into fatty alcohol sulfonates and in this form they find uses in many technical fields, particularly the textile industry, as wetting, washing, cleaning, emulsifying and dispersing agents.

In general the process of our invention involves the production of a mixture of higher molecular hydrocarbons by reacting carbon monoxide and hydrogen in a manner which is the same or similar to the process of Fischer for the synthetic production of benzine, oxidizing a liquid-solid mixture of hydrocarbons having 8 or more carbon atoms obtained by this reaction to produce primarily acid oxidation products, reducing the said oxidation products to form a mixture of higher molecular alcohols and then sulfonating the mixture of higher molecular alcohols to obtain the desired fatty alcohol sulfonates. If desired the oxidation products obtained in the second of these operations may be esterified with

mono or polyvalent alcohols before the reduction reaction takes place. The sulfonation products obtained from the sulfonation reaction are usually neutralized before put to practical use.

Satisfactory conditions and procedure for preparing the mixture of higher molecular hydrocarbons are disclosed in the publication of Fischer referred to above. The oxidation of a mixture of this character is carried out in any of the several manners known to the art, and by the oxidation treatment the hydrocarbons are changed into reaction products consisting for the most part of acids and their derivatives such as esters and lactones, which products are herein referred to collectively as "oxidation products." If desired the mixture of hydrocarbons may be treated to separate the lower molecular hydrocarbons having 6 or less carbon atoms in the molecule before being subjected to the oxidation treatment.

Suitable oxidation treatments involve reacting the liquid-solid mixture with oxygen, an oxygen containing gas, such as air, or with compounds that liberate oxygen, such as ozone, nitric oxides, nitric acid or chromium acid. The treatment may be effected either in the presence or in the absence of oxidation catalysts such as the heavy metals and salts of heavy metals for example, manganese, nickel, cobalt, copper, lead and vanadium, or alkalis, alkaline earths or their salts. These catalytic metals may be employed in the form of their fatty acid derivatives or soaps as may be produced by neutralizing saturated or unsaturated fatty acids, naphthenic acids and resinic acids, which compounds form colloidal solutions with the hydrocarbon mixture undergoing treatment.

Before the reduction step of the process is carried out, it is desirable but not necessary to subject the oxidation products to a distillation, cooling, selective solvent or other treatment, whereby the alcohols or other unoxidized portions of the oxidation products are separated from the oxidized portions. Furthermore the oxidation products may be separated from each other if it is desired to treat any particular fraction in a more concentrated form.

The oxidation products may be reduced by processes already known to the art. The reduction of the acids may be accomplished most satisfactorily by treatment at elevated temperatures and pressures in the presence of hydrogen and a hydrogenation catalyst. Temperatures of from about 200 to 350° C. and pressures of from 50 to 300 atmospheres are suitable. Suitable hydro-

generation catalysts include nickel, copper, cobalt, chromium, mixed catalysts prepared from these metals, or noble metals. Instead of a hydrogenation treatment the oxidation products may be reduced according to other known methods, for example, in the treatment of ester components of such products it may be preferable to proceed according to the process of Bouveault and Blanc in which the reduction is effected by the action of an alkali metal, particularly sodium, in the presence of ethyl or other low molecular alcohols.

After a mixture of higher molecular alcohols has been obtained in accordance with one of the procedures above described, this mixture is sulfonated by treatment with known sulfonating agents, such as concentrated sulfuric acid, fuming sulfuric acid, or chlorosulfonic acid. The sulfonating reaction takes place more readily in the presence of solvents such as ether or dibutyl ether, benzene hydrocarbons, chlorhydrocarbons and the like, addition compounds of chlorosulfonic acid, sulfonated ether, ester or tertiary amine, such as pyridine. If necessary the sulfonation step can also be carried out in the presence of a water absorbing agent.

After sulfonation, the sulfonated product may be neutralized with alkaline agents, for example, alkaline lys, alkali carbonates and ammonical or organic bases.

Illustrative details of several modes of practicing the invention are set forth in the following examples.

Example I

A mixture of higher hydrocarbons obtained in the synthesis of benzine by the process of Fischer is oxidized by blowing it with air in the presence of a manganese soap at a temperature of 100 to 150° C. The oxidation product, after separation of most of the unsaponifiable material, is converted into a mixture of fatty alcohols by treating it with hydrogen at elevated temperatures and pressures.

One hundred and thirteen parts by weight of these fatty alcohols (boiling point, at 12 mm., 110 to 270° C. and hydroxyl number, 248) are treated with 20 parts by weight of pyridine. The resulting mixture is then added to a mixture of 100 parts by weight of pyridine and 67 parts by weight of chlorosulfonic acid, while stirring and cooling. The temperature is kept at 40° C. After neutralization with sodium hydroxide, removal of pyridine by distillation and drying, a fatty alcohol sulfonate mixture is obtained in the form of a colorless powder that dissolves entirely in water. Solutions of this powder have very good foaming and wetting properties.

Example II

One hundred and twenty-five parts by weight of a fatty alcohol mixture obtained in the same manner as described in Example I, having a hydroxyl number of 225, are dissolved in 125 parts by weight of ether and slowly treated by 67 parts by weight of chlorosulfonic acid while being stirred and cooled. During this treatment the temperature is not allowed to exceed 20° C. After neutralizing with sodium hydroxide the aqueous solution is spray dried. A white powder having all the properties of known fatty alcohol sulfonates is obtained.

Example III

According to this example, a fatty alcohol mixture is obtained, as in the preceding examples, by reducing an oxidation product of higher aliphatic hydrocarbons produced in the synthesis of benzine from carbon monoxide and hydrogen. The mixture has a boiling point of 90° C. at 14 mm., a boiling point of 288° C. at 3 mm., and its hydroxyl number is 260. 107 parts by weight of this mixture are sulfonated by the use of 67 parts by weight of chlorosulfonic acid in the same manner as described in Example II. The sulfonation product is neutralized and then spray dried, and a fatty alcohol sulfonate mixture is obtained which has the same properties as a fatty alcohol sulfonate mixture obtained from coconut oil.

The improved process for producing fatty alcohol sulfonates possesses certain outstanding advantages over processes heretofore employed. The reduction step of the process is extremely simple and proceeds very smoothly since it does not require special precautionary measures due to the fact that the oxidation products are free from catalytic poisons such as sulfur. The mixtures of fatty alcohol sulfonates produced by the process are very similar to the usual fatty alcohol sulfonates which have heretofore been prepared from imported natural fats and waxes. Since the raw materials for the improved process are obtainable in the form of substantially valueless by-products of domestic manufacture, the invention makes available an independent source of raw material at little expense. The products of the process may be used in the same manner as equivalent fatty alcohol sulfonates obtained from different raw materials, for example, as wetting, washing, cleaning, emulsifying and dispersing agents in the textile, leather, paper and other industries.

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