Patented Apr. 21, 1936 2,037,974

UNITED STATES PATENT OFFICE

2,037,974

SULPHONIC ACIDS OF HIGHER ALIPHATIC KETONES

Fritz Guenther and Hermann Holsten, Ludwigshafen-on-the-Rhine, Germany, assignors to I. G. Farbenindustrie Aktiengesellschaft, Frankfort-on-the-Main, Germany

No Drawing. Application April 14, 1930, Serial No. 444,342. In Germany April 16, 1929

9 Claims. (Cl. 260—134)

The present invention relates to the production of wetting, cleansing and dispersing agents.

We have found that valuable wetting, cleansing and dispersing agents and the like can be prepared by converting open chain or cyclic aliphatic ketones obtainable from fatty acids containing at least 8 carbon atoms, which term is meant to include the derivatives or substitution products of the said ketones, such as stearone or oleone, halogen substitution products of such ketones, ketones containing amino or hydroxyl groups, or oximes, hydrazines or bisulphite compounds of ketones, or mixtures containing these, for example the products arising in the preparation of ketones, or derivatives thereof into sulphonic acids or water-soluble salts of these. Initial materials particularly suitable for sulphonation are for example the ketones obtainable from the acids of vegetal, i. e., vegetable or animal, fats or oils or from similar mixtures of acids obtainable in the oxidation of paraffin or similar high molecular hydrocarbons or waxes.

The sulphonation may be carried out with sulphuric acid or also with stronger sulphonating agents such as sulphur trioxide or chlorsulphonic acid or mixtures of these sulphonating agents. The sulphonation may be carried out in the presence of organic inert diluents such as carbon tetrachloride, trichlor ethylene, nitrobenzene, acetic acid and the like and/or in the presence of agents capable of chemically binding water, such as anhydrides or chlorides of organic or inorganic acids, such as acetic anhydride, acetyl chloride or chlorides of phosphoric acids. The quantity of sulphonating agent usually corresponds to at least one molecular proportion of sulphonating agent to each molecular proportion of the ketone employed.

The temperature of a sulphonation by means of sulphuric acid mono-hydrate must exceed 40° centrigrade, a temperature of about 100° centigrade being preferably chosen, since otherwise sulphuric esters are formed, which are saponifiable by boiling with aqueous 10 per cent hydrochloric acid solution, or no reaction takes place. When stronger sulphonating agents such as sulphur trioxide or chlorsulphonic acid or mixtures of mild sulphonating agents with these or with agents removing water are employed for the sulphonation of compounds containing one or more hydroxyl groups the quantity of these strong sulphonating agents or of the agents removing water must exceed one molecular proportion per each hydroxyl group present.

The said products are characterized by their stability against the substances which form hardness in water and by an equally good wetting power in alkaline, acid and neutral liquors. Thus for example they may be employed as a wetting agent in the textile, leather or artificial silk industries, for example by adding it to the dye bath, carbonizing bath, tanning bath or artificial silk spinning bath and may be added to the baths employed for the said purposes or to the preparations required for the said purposes before their dilution with water. The sulphonic acids and their salts are moveover highly suitable as washing and scouring agents in the place of soap and may find useful application as dispersing agents in the production of stable aqueous emulsions or suspensions from water-insoluble liquids or solids. The sulphonic acids and their salts may be employed as such or in conjunction with other wetting or emulsifying agents such as soaps, products of the type of Turkey red oils, sulphuric esters of high molecular aliphatic alcohols, sulphonic acids of aliphatic or aromatic and particularly of polynuclear aromatic compounds or their salts, hydroxyalkyl amines, quaternary ammonium bases or their salts, or with protective colloids such as glue, gelatine or vegetable mucilages or gums. Salts as for example soda, sodium bicarbonate, waterglass, common salt, neutral or acid sodium sulphate may be added or organic solvents, such as monocresyl ethylene glycol ether, cyclohexanol or cyclohexanone, trichlor ethylene or bleaching agents such as perborates, percarbonates, para-toluene sulphonic chloramide sodium. The said agents are employed in quantities depending on the desired purpose and several of them may be added conjointly. Thus for example the quantity of these additions may be the same as that of the sulphonic acids or considerably higher depending on the purposes of emulsifying, wetting, washing, cleaning or dispersing solid water-insoluble materials in water. In baths for the treatment of textiles the quantity of the sulphonic acids or their salts may be as low as a few per cent, say up to about 10 per cent, or even a few per thousand of the whole liquors. In some cases the products will already contain some salts from their production but these salts do not impair the properties of the products.

The following examples will further illustrate the nature of this invention, but the invention is not restricted to these examples. The parts are by weight.

Example 1

Oleic acid is converted into oleone by heating it with iron shavings at 340° C. 100 parts of the ketone obtained are treated with 100 parts of fuming sulphuric acid containing 23 per cent of sulphur trioxide until the product is soluble in water. The reaction mass is then poured onto ice, neutralized with aqueous caustic soda or ammonia, and the product is then recovered by salting out. The product obtained possesses a very good wetting power.

Example 2

250 parts of oleone are dissolved in 500 parts of carbon tetrachloride and 200 parts are chlorsulphonic acid are added at 20° to 25° C. drop by drop while stirring. After stirring for several hours the reaction mass is poured onto ice and after adding common salt the carbon tetrachloride is distilled off. The aqueous salt solution is then drawn off and the reaction product is neutralized and dried. The product obtained possesses a good wetting power in neutral as well as in acid or alkaline solutions and baths.

Example 3

100 parts of palmitone are stirred together with 500 parts of carbon tetrachloride and 60 parts of gaseous sulphuric anhydride are introduced into the mixture. The carbon tetrachloride is then distilled off and the residue is dissolved in water and separated, if necessary, from unattacked palmitone by filtration, whereupon the solution is rendered neutral and evaporated to dryness. The sodium salt of the sulphonic acid is rather difficultly soluble in cold water, but furnishes with warm water intensely foaming solutions having a good washing effect.

Example 4

"Tall oil" having an acid value of 150 and a saponification value of 160, as is obtained as a fatty and resinous by-product from the waste liquors in making pulp from wood by means of the sulphate process, is heated together with 10 per cent its weight of iron powder in an autoclave for 5 hours at 300° C. for the production of a mixture of ketones. The reaction product is freed from iron, for example by filtration, which is rendered more easy by previously diluting the reaction product with ethyl ether or benzene, and possesses an acid value of 30 and a saponification value of 53.

150 parts of the mixture of ketones obtained in the aforesaid manner are diluted with 90 parts of ethyl ether and after adding 125 parts of chlorsulphonic acid the mixture is stirred for several hours at room temperature. The reaction mixture is then poured onto ice and rendered neutral with aqueous caustic soda, whereupon the upper layer is drawn off, freed from ethyl ether and diluted with water as desired. When the reaction product has been diluted with water up to 600 parts, 100 parts of the solution are capable of dissolving 25 parts of tetrahydronaphthalene to a clear and thoroughly transparent solution; on further diluting the solution with water stable emulsions are obtained which effect can be also obtained with other substances insoluble in water.

What we claim is:—

1. Sulphonic acids of aliphatic ketones obtainable from fatty acids containing at least 8 carbon atoms, and suitable for use as wetting, cleansing and dispersing agents.

2. Mixtures comprising essentially sulphonic acids of aliphatic ketones obtainable from fatty acids containing at least 8 carbon atoms, and suitable for use as wetting, cleansing and dispersing agents.

3. Sulphonic acids of aliphatic ketones obtainable from the acids of vegetable oils, and suitable for use as wetting, cleansing and dispersing agents.

4. Sulphonic acids of aliphatic ketones obtainable from the acids of vegetable and animal fats and oils, and suitable for use as wetting, cleansing, and dispersing agents.

5. A sulphonic acid of oleone, suitable for use as a wetting, cleansing and dispersing agent.

6. A sulphonic acid of palmitone, suitable for use as a cleansing, wetting and dispersing agent.

7. As new products high molecular weight sulphonic acids of aliphatic ketones having the following formula



in which R and R′ are saturated or unsaturated sulphonated aliphatic hydrocarbon radicals containing more than 12 carbon atoms.

8. The process which comprises sulphonating aliphatic ketones having the formula



in which R and R′ are saturated or unsaturated aliphatic hydrocarbon radicals having at least 8 carbon atoms, said sulphonation being carried out by treating the ketone with a strong sulphonating agent.

9. A process for producing oil preparations for use in the textile and leather industries which consists in sulphonating aliphatic ketones containing more than 20 carbon atoms by a vigorously reacting sulphonating agent forming a true sulphonic acid.

FRITZ GUENTHER.
HERMANN HOLSTEN.