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PRODUCTION OF HYDROXY-SULFONIC ACIDS

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The present invention relates to the production of assistants for the textile and related industries.

It has already been proposed to convert the higher members of the aliphatic alcohol series, as for example the alcohols corresponding to the acids of vegetable or animal fats or oils, into water-soluble products by treatment with sulfonating agents, the resulting products being employed as washing, cleansing, and emulsifying agents. In this manner the sulfuric esters of the alcohols are obtained which may be saponified by boiling with mineral acids or sometimes even by concentrating their aqueous solutions, or, when employing energetic conditions in the sulfonation, the true sulfonic acids are formed, but these can only be obtained in a pure form with difficulty. The alkaline earth metal salts of these sulfuric esters are generally speaking only soluble in water when heated and even the alkali metal salts of the higher representatives of these compounds only dissolve slowly in water.

It has also been proposed to convert unsaturated cyclic hydrocarbons or aliphatic hydrocarbons containing either a short chain of up to four carbon atoms or a long chain in which the double linkage is situated about in the centre of the chain as occur in mineral oils, into compounds containing sulfonic groups by treatment with sulfonating agents in the presence of inorganic or organic acids, acid chlorides or acid anhydrides for example as described by one of the present applicants, together with another, in the U. S. Patent No. 2,037,229. Sulfonic acids have also been prepared from unsaturated compounds by treatment with chlorsulfonic acid esters, chlorsulfonic acid or other strong sulfonating agents in the presence of solvents or diluents capable of forming onium salts for example as described by one of the present applicants in the U. S. Patent No. 1,931,491. As pointed out above it is also known to treat mixtures of petroleum hydrocarbons containing olefines with energetically sulfonating agents.

We have now found that wetting, cleansing and emulsifying agents of great purity, which even when boiled with acids are practically not saponified but remain in the form of clear solutions or emulsions in water and which even at low temperatures are to a great extent stable to the substances forming the hardness of water, are obtained in a very smooth manner by subjecting hydrocarbons of the aliphatic olefine series having one double linkage at the end of the chain containing at least 8 carbon atoms, and if desired further double linkages, such as may be obtained for example by acting with allyl bromide on Grignard's magnesium compounds of α-bromo hydrocarbons or from the corresponding monohydric alcohols by splitting off water, to a sulfonation with strong liquid sulfonating agents. According to the conditions chosen, sulfonic acids or, if desired, mixtures of these with sulfuric esters or products which are both sulfonic acids and sulfuric esters are obtained. By the term "strong" sulfonating agents are meant, liquid sulfonating compounds stronger than sulfuric acid, such as chlorsulfonic acid, or solutions of sulfuric acid anhydride in sulfuric acid, chlorsulfonic acid or organic inert solvents, such as carbon tetrachloride, nitrobenzene and the like, or SO_2 or liquid mild sulfonating compounds, such as sulfuric acid in mixture with agents removing water, such as acid anhydrides or chlorides; as for example acetic anhydride, acetyl chloride, butyric anhydride, phosphorus pentoxide, phosphorus trichloride, boric anhydride and the like; these agents may also be employed conjointly with the energetic sulfonating agents; highly concentrated fuming sulfuric acids, which may solidify at certain temperatures may be also employed and are included in the above definition. The employment of anhydrous liquid diluents, such as trichlorethylene, ethyl acetate, diethyl ether, carbon tetrachloride, nitrobenzene and the like or SO_2 allow of obtaining particularly pure products also in the case of employing other sulfonating agent than sulfuric acid anhydride. If such diluents be employed gaseous sulfur trioxide may be used, the liquid sulfonating agent being thus formed during the process. Sulfur trioxide cannot be employed, however, in the absence of a diluent, since the olefines would be decomposed thereby. Catalysts, such as diatomaceous earth, animal charcoal and other agents hitherto employed in the sulfonation of aromatic compounds, as for example boric acid or mercury sulfate, may also be employed. If sulfonating agents be employed which contain at least 50 per cent of sulfuric acid and no water removing agents or if the sulfonating agents be employed in insufficient quantities, products may be obtained which are mixtures of sulfonic acids and sulfuric esters or which consist of products containing both sulfonic and sulfuric ester groups, these last-mentioned products may be also obtained on working with sulfur trioxide in the presence of a diluent. The quantity of sulfonating agent employed is generally at least 1 atomic proportion of sulfur per each molecular proportion of olefine in order to avoid a separa-

tion of unsulfonated material which may be required if lower quantities be employed. The temperatures of the reaction depend on the initial materials and are generally below 100° C. preferably between about 5° and 50° C. In some cases, however, higher or lower temperatures may be employed. In any case the sulfonation is proceeded with until a sample remains soluble or miscible in water after boiling with an aqueous 10 per cent hydrochloric acid. Products which are especially suitable for the purposes of the present invention are obtained by employing olefines as can be obtained by splitting off water from primary alcohols having from about 10 to 20 carbon atoms in the molecule, or from mixtures of different alcohols of the said molecular size as are obtainable for example by the catalytic reduction of olive oil. A method of preparation of alcohols by catalytic hydrogenation of esters is described for example in the French Patent No. 689,713. The splitting off of water may be carried out catalytically or by distilling in vacuo the esters of the said alcohols with acids of oils or fats, as for example the waxes, or with specially good yields by distilling the phosphoric acid esters of the alcohols, especially those corresponding to the acids of vegetal, i. e. animal or vegetable fats of solid or liquid nature. The esterification of the alcohols with phosphoric acid and the formation of the olefines may be carried out simultaneously.

The products according to the present invention correspond to the general formula

$$\overset{\alpha}{H_2C}X—\overset{\beta}{H}CY—R$$

in which one of the radicles X and Y is $—SO_3H$ and R is an aliphatic radicle containing at least 6 carbon atoms. As indicated above X or Y may be $—SO_3H$ and Y (or X respectively) may then be a hydroxyl or ester group, such as $—OSO_3H$, Cl (if chlorsulfonic acid be employed), CH_3COO (if acetic acid or anhydride be employed), all these ester groups being exchangeable for hydroxyl groups or double linkages (by saponification by heating with water or aqueous acids or alkalies). The exact position of the sulfonic group in the X or Y positions has not been ascertained. The radicle denoted by R may contain sulfonic and/or sulfuric ester groups or the other groupings denoted above by X and Y.

The wetting, cleansing and emulsifying agents obtained according to the present invention have excellent properties. They, as well as their salts, are readily soluble in water and yield a very stable foam with a soft touch; they have at the same time a high wetting and washing power and are extremely stable to acids and do not give water insoluble salts with alkaline earths. Their salts are neutral and do not split off alkali by hydrolysis. By reason of these excellent properties they may be employed quite generally for all branches of daily and industrial use in which a powerful wetting, washing and dispersing power is desired. They are especially suitable, for the industries concerned with the preparation and working up of fibrous materials, such as in the production of artificial silk, and in the leather and textile industries, as softening, wetting, scouring and levelling agents and for preparing dispersions of solid or liquid, difficultly water soluble agents required in the said industries. In all cases the said products may be employed as such, as free acids or salts or together with one or more of a great variety of additional materials. As the said additional materials may be mentioned other washing, cleansing, emulsifying and wetting agents, such as soaps, Turkey red oils, alkylated naphthalene sulfonic acids, or other aliphatic or aromatic sulfonic acids or sulfuric esters, mineral oil sulfonic acids and products having similar properties, such as saponin and the like. Furthermore, all the additional materials which increase the washing and emulsifying power, such as neutral, acid or basic salts of inorganic or organic nature, such as Glauber's salt or sodium phosphate or acetate, bleaching agents such as perborates, or the sodium salt of para-toluene sulfonic acid chloramide, organic acids or bases, protective colloids, such as glue, gelatine, water-soluble varieties of gum, vegetable mucilages and the like are suitable. By employing the products according to the present invention even water-insoluble organic solvents of the most varied nature may be converted into stable emulsions in water, and solid substances, such as pigments or other water-insoluble colouring materials or dyestuffs or waxes, may be finely dispersed in water with their aid. The products according to the present invention retain their valuable properties even in acid and alkaline baths and the materials treated with the said products have an agreeable softness of touch, and inconveniences, such as frequently arise when employing soaps as additional or washing agents with hard water, do not occur.

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

900 parts of phosphoric acid having a specific gravity of 1.8 are added at 100° C. to 500 parts of octadecyl alcohol and the water formed is then distilled off in vacuo. The temperature is then raised to 200° C., the octadecylene formed in very good yields is distilled off and dried with a little anhydrous sodium sulfate. The phosphoric acid may be employed again after dilution with a little water, followed by the removal of small amounts of organic constituents which separate out, and subsequent concentration.

461 parts of the octadecylene thus obtained are worked with a mixture of 175 parts of acetic anhydride and 175 parts of sulfuric acid monohydrate at from 20° to 25° C., while stirring vigorously, and the whole is then stirred for about 12 hours at from 30° to 35° C. As soon as a sample withdrawn remains dissolved in water to give a clear solution even after boiling such sample with dilute hydrochloric acid, the whole is poured on to ice, neutralized with caustic soda, evaporated to dryness and dried in vacuo. The resulting product dissolves in water giving a clear solution and has an excellent wetting and washing power, even in very dilute solutions, especially in hot solutions. On the addition of hard water to aqueous solutions of the product, no insoluble salts separate in the cold even after standing for long periods of time. When boiled with dilute hydrochloric acid the product does not lose its solubility in water but retains its good properties. It probably consists mainly of a hydroxyoctadecyl sulfonic acid.

Example 2

500 parts of a mixture of alcohols obtained by the catalytic hydrogenation of coconut fat are allowed to flow at 200° C. and at from 14 to 16

millimetres (mercury gauge) while stirring below the surface of 900 parts of phosphoric acid having a specific gravity of 1.8, whereby a mixture of olefines and water is obtained which at first has a pasty consistency. The mixture is separated by heating gently and the olefines obtained are dried.

100 parts of the olefines are added at room temperature to a mixture prepared at from 20° to 30° C. of 100 parts of ethyl ether and 116 parts of chlorsulfonic acid. The whole is stirred until a sample withdrawn remains soluble in water even when such sample has been boiled with dilute hydrochloric acid; it is then poured on to ice, neutralized with 200 parts of 10 N caustic soda, and after distilling off the ether the whole is concentrated and dried. A product which dissolves in water giving a clear solution and having properties equally as good as those of the product described in Example 1 is obtained.

A solution of 2 grams of the resulting product in 1000 grams of water wets wool or cotton in quite a short period of time even when the solution has been acidified or rendered alkaline. Wool in the suint is washed without difficulty in a short time at from 40° to 45° C. by a solution of the same strength even when the bath has been rendered acid.

Example 3

500 parts of oleum containing 23 per cent its weight of SO_3 are added at from 10° to 15° C. to 650 parts of octadecylene while stirring vigorously and the temperature of the reaction mixture is raised to from 25° to 30° C. The whole is then stirred at this temperature for from about 4 to 5 hours until the product dissolves in water to give a clear solution, and is then poured on to ice, neutralized with caustic soda, treated with 100 parts of sodium phosphate to prevent the hydrolysis of the part of the product present in the form of a sulfuric acid ester when the solution is concentrated, concentrated on the water-bath and dried in vacuo. A product of soap-like appearance and having excellent washing and emulsifying powers is obtained which even after being boiled for half an hour with a 10 per cent aqueous hydrochloric acid remains as a strongly foaming emulsion, without separation of flakes or oily layers.

When oleum having a content of more than 70 per cent of SO_3 is employed particularly efficient cooling is necessary in order to avoid the formation of water-insoluble bodies, or a diluent, such as carbon tetrachloride, must be employed and in this latter case SO_3 may be introduced in a finely divided liquid or gaseous state.

Example 4

63 parts of octodecadiene, obtainable by splitting off water from octodecandiol which can be obtained by a catalytic reduction, with the aid of hydrogen, of castor oil, are mixed with 50 parts of acetic anhydride, whereupon 50 parts of sulfuric monohydrate are added at from 25° to 30° C. and the whole is stirred at from 30° to 35° C. for 14 hours. The reaction product is then poured on to ice, rendered neutral with the aid of caustic soda and inspissated. The product possesses a very good wetting and levelling power. Owing to the quantity of sulfonating agent employed the product consists practically completely of the sodium salt of an α, β-hydroxysulfonic acid containing a further hydroxyl and sulfonic group and some sodium sulfate and sodium acetate.

What we claim is:—

1. The process for the production of assistants for the textile and related industries which comprises acting on an olefine containing at least 8 carbon atoms and one double linkage at the end of the chain, with a strong liquid sulfonating agent.

2. The process for the production of assistants for the textile and related industries which comprises acting on an olefine, containing at least 8 carbon atoms and one double linkage at the end of the chain, with a quantity of a strong liquid sulfonating agent corresponding to at least 1 atomic proportion of sulfur per each molecular proportion of olefine.

3. The process for the production of assistants for the textile and related industries which comprises acting on an olefine, containing at least 8 carbon atoms and one double linkage at the end of the chain, with a sulfonating compound stronger than concentrated sulfuric acid in the presence of an anhydrous liquid diluent.

4. The process for the production of assistants for the textile and related industries which comprises acting on an olefine, containing at least 8 carbon atoms and one double linkage at the end of the chain, with a liquid sulfonating agent comprising essentially a sulfonating compound and an agent capable of removing water.

5. The process for the production of assistants for the textile and related industries which comprises acting on an olefine, containing at least 8 carbon atoms and one double linkage at the end of the chain, with a strong liquid sulfonating agent at a temperature of the range of from 5° to 50° C.

6. The process for the production of assistants for the textile and related industries which comprises acting on an olefine, containing at least 8 carbon atoms and one double linkage at the end of the chain, with a mixture of concentrated sulfuric acid and acetic anhydride at a temperature of the range of from 5° to 50° C.

7. The process for the production of assistants for the textile and related industries which comprises acting on an olefine, containing from 10 to 20 carbon atoms and one double linkage at the end of the chain, with a strong liquid sulfonating agent at a temperature of the range of from 5° to 50° C.

8. The process for the production of assistants for the textile and related industries which comprises acting on an olefine, containing from 10 to 20 carbon atoms and more than one double linkage one of which is situated at the end of the chain, with a strong liquid sulfonating agent at a temperature of the range of from 5° to 50° C.

9. The process for the production of assistants for the textile and related industries which comprises acting on an olefine, containing 18 carbon atoms and more than one double linkage one of which is situated at the end of the chain, with a strong liquid sulfonating agent at a temperature of the range of from 5° to 50° C.

10. The process for the production of assistants for the textile and related industries which comprises acting on a mixture of olefines which contain a double linkage, situated at the end of the chain of each, and which result from the vacuum-distillation of phosphoric esters of the alcohols corresponding to the acids of fats of vegetal origin, with a strong liquid sulfonating agent at a temperature of the range of from 5° to 50° C.

11. Sulfonic acids corresponding to the formula formula

$$\overset{\alpha}{H_2C}X—\overset{\beta}{H}CY—R$$

in which one of the radicles X and Y is $—SO_3H$ and the other is a substituent selected from the group consisting of the hydroxyl radicle and an ester grouping and R denotes a saturated aliphatic radicle containing at least 6 carbon atoms.

12. Sulfonic acids corresponding to the formula

$$\overset{\alpha}{H_2C}X—\overset{\beta}{H}CY—R$$

in which one of the radicles X and Y is $—SO_3H$ and the other is a substituent selected from the group consisting of the hydroxyl radicle and an ester grouping and R denotes a saturated aliphatic radicle containing at least 6 carbon atoms and at least one group selected from the group consisting of sulfonic and sulfuric ester groups.

13. Sulfonic acids corresponding to the formula

$$\overset{\alpha}{H_2C}X—\overset{\beta}{H}CY—R$$

in which one of the radicles X and Y is $—SO_3H$ and the other is OH, and R denotes a saturated aliphatic radicle containing at least 6 carbon atoms.

14. Sulfonic acids corresponding to the formula

$$\overset{\alpha}{H_2C}X—\overset{\beta}{H}CY—R$$

in which one of the radicles X and Y is $—SO_3H$ and the other is a substituent selected from the group consisting of the hydroxyl radicle and an ester grouping and R denotes a saturated aliphatic radicle containing from 8 to 18 carbon atoms.

15. Sulfonic acids corresponding to the formula

$$\overset{\alpha}{H_2C}X—\overset{\beta}{H}CY—R$$

in which one of the radicles X and Y is $—SO_3H$ and the other is a substituent selected from the group consisting of the hydroxyl radicle and an ester grouping and R denotes a saturated aliphatic radicle containing from 8 to 18 carbon atoms and at least one group selected from the group consisting of sulfonic and sulfuric ester groups.

16. Sulfonic acids corresponding to the formula

$$\overset{\alpha}{H_2C}X—\overset{\beta}{H}CY—R$$

in which one of the radicles X and Y is $—SO_3H$ and the other is a substituent selected from the group consisting of the hydroxyl radicle and an ester grouping and R denotes a saturated aliphatic radicle containing 16 carbon atoms.

17. Sulfonic acids corresponding to the formula

$$\overset{\alpha}{H_2C}X—\overset{\beta}{H}CY—R$$

in which one of the radicles X and Y is $—SO_3H$ and the other is OH and R denotes a saturated aliphatic radicle containing 16 carbon atoms.

18. Sulfonic acids corresponding to the formula

$$\overset{\alpha}{H_2C}X—\overset{\beta}{H}CY—R$$

in which one of the radicles X and Y is $—SO_3H$ and the other is OH and R denotes a saturated aliphatic radicle containing 16 carbon atoms containing the group

$$—CH(OH)—\underset{|}{C}H—SO_3H$$

19. In a process for preparing surface active substances, the step which comprises reacting an aliphatic unsaturated hydrocarbon, containing at least 8 carbon atoms and having a double bond at the end of the chain, with a strong sulfonating agent in the presence of a sulfonating catalyst.

20. In a process of preparing surface active substances, the step which comprises reacting an olefine containing at least 8 carbon atoms and having a double bond at the end of the chain, with a strong sulfonating agent in the presence of mercury sulfate.

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