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METHOD FOR THE PRODUCTION OF SULPHONIC ACIDS

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This invention relates to sulphonic acids useful as wetting-out, emulsifying, dispersing, peptizing and cleansing agents and methods of producing the same.

It has been found, that excellent wetting-out-, emulsifying-, dispersing-, peptization- and cleansing agents are obtained by converting mineral acid esters or estersalts, for instance the halogen hydracid ester or sulphuric acid ester salts of higher molecular mono- or polyvalent aliphatic or hydrocyclic alcohols with at least one primary alcohol group, such as may be obtained from natural waxes by splitting off or reduction (hydrogenation) or from natural fats, fatty acids or their other esters as well as from hydrocyclic carboxylic acids, for instance naphthenic acids or their esters by reduction, at first with alkali polysulphides at an increased temperature with or without pressure, preferably in the presence of an inert diluent into the corresponding organic polysulphides and by treating these latter with oxidizing agents until they become water- and alkali-soluble.

It has been tried already to produce cetyl sulphonc acid by oxidation of cetylmercaptane with potassium permanganate. This process however in comparison with the present inventon is a very expensive and indirect one as in spite of greater expenses for chemicals, apparatus and time rather unsatisfactory yields only could be obtained. That is why this process hitherto has not been carried out practically. Furthermore is it already known that the cetylsulphonic acid has some soaplike properties, the prior art however does not contain the new knowledge, that the sulphonc acids of the aliphatic or hydrocyclic rank with a sulphonc acid group attached to the end carbon atom of the chain, are far superior as regards the capillary activity to the corresponding soap forming carboxylic acids and also to other sulphonic acids. The production therefore of aliphatic or hydrocyclic sulphonic acids having the sulpho-group at the end of the chain, by a process which can be carried out technically and commercially without difficulty as herein described constitutes industrial progress.

The products obtained in accordance with the present invention contain the sulphonic acid group at the end of the chain only whereby as regards the capillary activity they far surpass all other substances used according to hitherto proposed methods for the production of wetting-out, emulsifying and dispersing agents.

This fact was unknown hitherto and had therefore not been taken into consideration in the known processes of producing sulphonic acids for the purposes of wetting-out, emulsifying and similar purposes. In contrast with other processes, which are based for instance on the conversion of mineral acid esters of alcohols with neutral salts of sulphurous acid yielding also compounds with the sulpho-group at the end of the chain, the present invention shows the following advantages: The alkali polysulphides are distinguished from the alkali sulphides by a considerably increased reaction-energy; therefore it is possible to operate the conversions under milder conditions regarding pressure and temperature, as is evident from the following examples. Furthermore by this method also side-reactions, as for instance saponification of the esters or estersalts are avoided and the addition of expensive reaction-accelerators, as for instance alkali iodides, which have to be regenerated, can be dispensed with.

The oxidation of the disulphides obtained as intermediate products to the sulphonic acids can be carried out by various means. As suitable agents we have found for instance free halogens, hypohalogenous acids and their salts, halogenates (sodium-chlorate) in the presence of traces of osmiumtetroxide, free chloric acid, iodic acid, nitric acid of various concentration, hydrogen peroxide and its inorganic or organic derivatives (as for instance persulphuric acid peracetic acid) chromic acid and chromates respectively in acid solution, permanganates, preferably in acid solution. All these oxidizing agents may be applied in aqueous solution with or without the addition of known catalyst. In case oxidizing agents are used which react with evolution of gas, foaming compounds may be yielded if the oxidation is carried on in aqueous solution. For this reason it is recommended that there should be added to the medium in which the oxidation is carried on such substances as destroy either wholly or partially the colloidal nature of the resulting sulphonic acids and which are able to convert these sulphonic acids more or less into a molecularly dispersed state. Such substances, which of course must to be inert to the oxidizing agent used in the special case, are for instance methyl alcohol, acetone, acetic acid.

Example I

Cetyl alcohol which has been obtained in the usual manner such as by extraction from saponified spermaceti is converted by one of the known methods for instance by means of gaseous hydrochloric acid into cetylchloride in the presence of

traces of zinc chloride as catalyst. 261 parts of this are cooked under reflux at ordinary pressure together with a concentrated aqueous solution of 43 parts of sodium-sulphide (Na_2S) and 18 parts of sulphur after 300–350 parts of alcohol are added until after about 2–3 hours the conversion is completed. The alcohol then is distilled off, the residue diluted with water and the dicetyldisulphide, which is already at slight warth oleaginous is decanted from the watery layer. After cooling it solidifies to a white waxy mass.

The disulphide is suspended in warm, dilute sulphuric acid, so that it is just molten, and then gradually while stirring vigorously a 5% solution of sodium permanganate is added until the violet color persists. The resulting sodium salt of cetylsulphonic acid is extracted by means of butylalcohol and upon evaporating the latter it is yielded in a solid form. Or the oxidation mixture is evaporated to dryness and the sodium salt of cetyl sulphonic acid is extracted with alcohol.

Example II

A mixture of higher aliphatic primary alcohols, such as is obtained by catalytic high pressure hydrogenation of coconut oil or mixture of coconut oil fatty acids or by reduction with sodium and alcohol, is converted to the corresponding alkyl sulphuric acids in the usual manner with chlorsulphonic acid at low temperatures. These are introduced into the calculated quantity of 40% caustic soda lye while stirring and with or without cooling and to the resulting paste are added a quantity of alcohol, approximately equal to the water present and a concentrated solution of potassium trisulphide about in excess of 10% over the theoretically necessary amount. The mixture is then heated in a stirring autoclave to 150° C. until all the sulphuric acid of the ester-salts is split off in the form of sodium-sulphate, the alcohol is distilled off and the oily trisulphide mixture is separated from the watery layer.

Twice the amount of 20% nitric acid as theoretical necessary for the quantitative oxidation of the trisulphide mixture is heated up to 85° C. and to this is added at intervals, while stirring, the trisulphide mixture, waiting each time until the brisk reaction, which proceeds with foaming, subsides before adding another portion of the trisulphide mixture After the whole mass is introduced, it is necessary to start at 85 to 95° C. until a sample of the reaction mixture gives a clear solution in water and dilute alkali lye. It is then neutralized with caustic soda lye and extracted with butylalcohol. The butylalcoholic layer is decated and upon evaporation yields a mixture of the sodium salts of higher alkylsulphonic acids. From the watery layer sodium nitrate may be obtained.

Example III

A mixture of naphthenic alcohols boiling at about 90°–125° C. under 15 mm. Hg pressure as obtained for instance by reduction of naphthenic acids with sodium and butylalcohol according to the method of Blanc and Bouveault, is heated up to 150° C. 1% dry zinc chloride is added and a vigorous stream of dry hydrochloric gas is passed through until no more water distills off. The raw naphthenylchloride which remains as residue is refined with some sulphuric acid, neutralized by washing, dried and distilled in vacuum.

116.4 parts of the resulting chloride boiling point at 13 mm. 75–200° C. with 15,22% chlorine contents are added to a boiling solution of 35.8 parts of sodium sulphide (techn. conc. with 60–62% Na_2S) and 11 parts of sulphur in 150 parts 90% alcohol. This mixture is kept boiling under reflux for some hours. Then the alcohol is distilled off, the sodium chloride brought into solution in warm water, the oily disulphide separated and gradually during active stirring introduced into a mixture, which is kept continuously at 55°–60°, of 100 parts of glacial acetic acid, 100 parts of water and 125 parts of 60–62% nitric acid, to which 1 part of ammonium metavanadate is added. Then the reaction mixture is heated up for some time to 75–80° C. until no action more can be observed, and the watery acetic acid distilled off under vacuum, the residue dissolved in water and neutralized with caustic soda lye. The solution is evaporated to dryness, perferably in vacuum, and the dry residue is extracted with benzene, benzine or other fat solvents, in order to remove water insoluble by products. The sodium salts of the naphthenylsulphonic acids remain as dry yellowish-white powder, which is easily soluble in cold as well as in warm water and which possesses in these solutions an extraordinarily high wetting-out and penetrating power and also high lathering capacity. Also calcium and magnesium salts in higher concentrations cause no precipitation. The product is furthermore, as real sulphonic acid, wholly stable towards acids and alkalies and therefore constitutes a rather valuable soap body particularly suitable for use in the textile, leather-, paper- and all other industries, in which it is essential to produce the especially important, technically valuable capillaractive properties of these compounds together with a general chemical stability.

Example IV

498 parts of dodecylbromide (as obtainable from lauric alcohol according to known processes) are heated up with 121 parts of sodium disulphide solved in 500 parts of alcohol 80–90% under reflux condenser until the conversion is completed. Then the alcohol is distilled off, and in order to dissolve the sodium bromide the residue is mixed with water, the didodecylsulphide congealing to crystals in cold is separated from the salt lye and stirred with four times the quantity of acetic acid 50%, to which some concentrated hydrochloric acid is added. The whole is heated up in a waterbath and during active stirring about 180 parts of sodium chlorate are introduced in small portions until after some further stirring a complete water and alkali-solubility of the reaction mixture is arrived at. Now the reaction mixture is salted out with Glauber's salt (sodium sulphate) and the sodium salt of dodecylsulphonic acid precipitated in crystals is vacuum drained and refined by recrystallizing with water. An excellent wetting-out and emulsifying product is yielded.

I claim:

1. The process of producing high molecular sulphonic acids or sulphonates which comprises converting alcohols of the group consisting of mono- and poly-hydroxy aliphatic alcohols obtained from natural fats and waxes and having 8 or more carbon atoms in the molecule a naphthenic acid into mineral acid esters, converting the mineral acid esters into organic polysulphides by treatment with alkali polysulphides and converting the polysulphides into products of the group consisting of sulphonic acids and sulphonates by oxidation.

2. The process of producing high molecular sulphonic acids or sulphonates which comprises converting high molecular alcohols of the group consisting of the mono- and poly-hydroxy aliphatic alcohols obtained from natural fats and waxes, and naphthenic alcohols, into mineral acid esters, converting the mineral acid esters into organic polysulphides by treatment with alkali polysulphides at elevated temperatures and converting the polysulphides into products of the group consisting of sulphonic acids and sulphonates by oxidation.

3. The product resulting from the process defined in claim 2.

4. The process of producing high molecular sulphonic acids or sulphonates which comprises converting aliphatic alcohol obtained from natural fats and waxes into mineral acid esters, converting the mineral acid esters into organic polysulphides by treatment with alkali polysulphides at elevated temperatures and converting the polysulphides into products of the group consisting of sulphonic acids and sulphonates by treatment with an oxidizing agent of the group consisting of free halogens, hypohalogenous acids and their salts and halogenates.

5. The product resulting from the process defined in claim 4.

6. The process of producing high molecular sulphonic acids or sulphonates which comprises converting aliphatic alcohol obtained from natural fats and waxes into mineral acid esters, converting the mineral acid esters into organic polysulphides by treatment with alkali polysulphides at elevated temperatures and converting the polysulphides into products of the group consisting of sulphonic acids and sulphonates by treatment with an oxidizing agent of the group consisting of free halogens, hypohalogenous acids and their salts and halogenates in the presence of material selected from the group consisting of osmium tetroxide, free chloric acid, iodic acid, nitric acid, hydrogen peroxide and its organic and inorganic derivatives, chromic acid and chromates in acid solution, and permanganates.

7. The process of producing high molecular sulphonic acids or sulphonates which comprises converting aliphatic alcohol obtained from natural fats and waxes into mineral acid esters by treatment with an acid of the group consisting of hydrochloric acid, sulphuric acid, nitric acid, converting the mineral acid esters into organic polysulphides and converting the polysulphides into products of the group consisting of sulphonic acids and sulphonates.

8. The product resulting from the process defined in claim 7.

9. In the process of producing high molecular sulphonic acids or sulphonates from high molecular alcohols of the group consisting of the mono- and poly-hydroxy aliphatic alcohols obtained from natural fats and waxes, and naphthenic alcohols, the step which consists of converting mineral acid esters of such high molecular alcohols into organic polysulphides by treatment with alkali polysulphides.

10. In the process of producing high molecular sulphonic acids or sulphonates from high molecular alcohols of the group consisting of the mono- and poly-hydroxy aliphatic alcohols obtained from natural fats and waxes, and naphthenic alcohols, the step which consists of converting mineral acid esters of such high molecular alcohols into organic polysulphides by treatment with alkali polysulphides of the group consisting of sodium polysulphide and potassium polysulphide.

11. In the process of producing high molecular sulphonic acids or sulphonates, the step which consists of converting an alkyl chloride having 8 or more carbon atoms in the molecule into a di-alkyl disulphide by boiling with sodium sulphide and sulphur at an elevated temperature with refluxing.

12. In the process of producing high molecular sulphonic acids or sulphonates, the step which consists of converting an alkyl polysulphide into a product of the group consisting of sulphonic acids and sulphonates by suspension in warm sulphuric acid of alkyl polysulphide having 8 or more carbon atoms in the alkyl group and reaction with an oxidizing agent.

13. In the process of producing high molecular sulphonic acids or sulphonates, the step which consists of converting a di-alkyl disulphide into a product of the group consisting of sulphonic acids and sulphonates by treatment of a di-alkyl disulphide having 8 or more carbon atoms in the alkyl group with an oxidizing agent of the group consisting of free halogens, hypohalogenous acids and their salts and halogenates.

14. In the process of producing high molecular sulphonic acids or sulphonates, the step which consists of converting an alkyl polysulphide into a product of the group consisting of sulphonic acids and sulphonates by treatment of an alkyl polysulphide having 8 or more carbon atoms in the alkyl group with an oxidizing agent of the group consisting of free halogens, hypohalogenous acids and their salts and halogenates in the presence of materials of the group consisting of osmium tetroxide, free chloric acid, iodic acid, nitric acid, hydrogen peroxide and its organic and inorganic derivatives, chromic acid and chromates in acid solution and permanganates.

15. In the process of producing high molecular sulphonic acids or sulphonates, the step which consists of converting an alkyl polysulphide into sodium sulphonate by treatment of an alkyl polysulphide having 8 or more carbon atoms in the alkyl group with sodium permanganate in the presence of warm sulphuric acid as a diluent.

16. In the process of producing high molecular sulphonic acids or sulphonates, the step which consists of converting an alkyl polysulphide into a product of the group consisting of sulphonic acids and sulphonates by treatment of an alkyl polysulphide having 8 or more carbon atoms in the alkyl group with an oxidizing agent in the presence of an agent of the group consisting of methyl alcohol, acetone and acetic acid.

17. In the process of producing high molecular sulphonic acids or sulphonates from high molecular alcohols the step which consists of reacting an alkali sulphate of a high molecular monohydroxy aliphatic alcohol with polysulphide of the group consisting of sodium polysulphide and potassium polysulphide.

18. The process of producing high molecular sulphonic acids or sulphonates which comprises converting alcohols of the group consisting of mono- and poly-hydroxy aliphatic alcohols obtained from natural fats and waxes and having 8 or more carbon atoms in the molecule into chlorides by treatment with hydrochloric acid, converting the chloride into organic disulphides by treatment with sodium sulphide and sulphur and converting the disulphides into products of

the group consisting of sulphonic acid and sulphonates by oxidation while suspended in warm dilute sulphuric acid.

19. The process of producing high molecular sulphonic acids or sulphonates which comprises converting alcohols of the group consisting of mono- and poly-hydroxy aliphatic alcohols obtained from natural fats and waxes and having 8 or more carbon atoms in the molecule into sulphuric acid ester salts, converting the ester salts into alkyl polysulphides by treatment with potassium polysulphide and converting the polysulphides into sulphonic acid by treatment with nitric acid.

20. The process of producing high molecular sulphonic acids or sulphonates which comprises converting naphthenic alcohol into naphthenic chloride converting the naphthenic chloride into naphthenic sulphide by boiling with sodium sulphide and sulphur with refluxing and converting the naphthenic sulphide into sulphonic acid by oxidizing with nitric acid.

21. The process of producing molecular sulphonic acids or sulphonates which comprises converting dodecyl bromide into disulphide by treatment with sodium disulphide with refluxing and converting the dodecyl disulphide into sodium sulphonate by treatment with sodium chlorate.

22. The process of producing high molecular sulphonic acids and sulphonates which comprises converting aliphatic monhydroxy alcohols having approximately 12 to 16 into mineral acid esters, converting the mineral acid esters into organic polysulphides by treatment with alkali polysulphides at elevated temperatures and converting the polysulphides into products of the group consisting of sulphonic acids and sulphonates by oxidation.

23. The product resulting from the process defined in claim 22.

24. The process of producing high molecular sulphonic acids and sulphonates which comprises converting aliphatic monhydroxy alcohols having approximately 12 to 16 into mineral acid esters, converting the mineral acid esters into organic polysulphides by treatment with alkali polysulphides at elevated temperatures and converting the polysulphides into products of the group consisting of sulphonic acids and sulphonates by treatment with an oxidizing agent of the group consisting of free halogens, hypohalogenous acids and their salts, and halogenates in the presence of an oxidation catalyst.

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