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SECONDARY ALKYL SULPHATES AS WETTING AGENTS

Jacob N. Wickert, Charleston, W. Va., assignor, by
mesne assignments, to Union Carbide and Carbon
Corporation, a corporation of New York

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The invention relates to the manufacture of improved products having properties adapting them for use as wetting, penetrating, scouring, dye-levelling, and softening agents, especially in connection with treatment liquors employed in the textile, leather, and related industries.

Among the more important objects of the invention is the provision of treating agents of the above type which have unusually high penetrating power, and which are much more soluble in water than are sulphate esters of corresponding carbon content, but which have a primary alcohol group on a straight carbon chain; and the former are especially adapted for use in relatively high concentrations, either in dilute alkaline solutions as in wool scouring; in dilute acid solutions, as in wool carbonizing; or in simple aqueous solutions.

Water-soluble sulphuric acid esters formed by reacting sulphuric acid with fatty substances, fatty acids, esters, or with primary alcohols derived from such fatty substances, are now widely used as textile wetting, and penetrating agents. The sulphate esters produced from the fatty alcohols have the important advantage over those produced from the fatty substances, fatty acids and esters in that the tendency of the former to form insoluble alkaline earth soaps is very much less marked than that of the sulphate esters produced from the fatty substances and esters.

However, the utility of these sulphate esters of the primary, fatty alcohols having a straight-carbon chain structure is limited by such factors as the rather low solubility in water of the neutral alkali salts of these higher sulphate esters.

In accordance with the present invention, treating compositions having extremely high-wetting, penetrating, softening, and emulsifying powers are produced by adding thereto a product formed by sulphating a saturated secondary branched-chain high aliphatic monohydric alcohol having 8 or more carbon atoms in its molecular structure. These alkyl sulphates of secondary branched-chain higher alcohols not only are little if at all affected by the alkaline earth salts in moderately hard waters, since their alkaline earth salts are soluble in water, but, moreover, they are much more soluble in water than are substances of corresponding carbon content having a primary alcohol group on a straight-carbon chain. Consequently, these secondary alkyl sulphates can be employed conveniently in many operations where it is necessary to use such wetting agents in relatively high concentrations.

The said secondary alkyl sulphates are amorphous waxy solids, colorless or nearly so, com-

pletely soluble in organic solvents, such as the lower alcohols, esters, ketones, ether and hydrocarbons; and they are readily soluble in water, the solubility decreasing with increasing molecular weight. They are somewhat less soluble in dilute acid than in neutral or dilute alkaline solutions.

The high wetting power of these sulphates of secondary alcohols makes them highly active when present in treating liquors in very small amounts; and concentrations thereof as low as 0.02% have effected the desired wetting out of textile materials.

The secondary alkyl sulphates of the present invention may be prepared by sulphating, at low temperatures, preferably around 0° to 10° C., a saturated secondary branched-chain monohydric alcohol having at least 8 carbon atoms in its molecular structure. Such a secondary alcohol may be formed by hydrogenating an unsaturated ketone at temperatures up to around 150° C. and at pressures around 800 to 1000 pounds per square inch. The latter may be formed by the removal of elements of water from the product of the conjoint condensation of a primary or secondary aliphatic aldehyde having at least 4 carbon atoms in its molecule, with a ketone, such as acetone, methylethyl ketone, or a ketonic derivative of either, in the presence of an alkaline catalyst. By the term "secondary aldehyde" is meant an aldehyde in which the carbon atom connected to the aldehyde group is also directly connected with two and only two other carbon atoms.

The secondary branched-chain alcohols may be converted to the corresponding acid sulphate esters by any of the usual sulphating methods. According to one such method, the secondary alcohol is reacted with approximately an equivalent amount of equimolar proportions of 96% sulphuric acid and acetic anhydride, at low temperatures, preferably around 0° to 10° C.

The acid alkyl sulphate formed is neutralized, preferably with a caustic alkali, or ammonia, or with an organic amine such as one of the ethanolamines, yielding the corresponding salt of the secondary alkyl sulphate.

The following examples will serve to illustrate the invention:

Example 1

0.5 mol. of 7-ethyl-2-methylundecanol-4 was reacted with a mixture of 0.58 mol. acetic anhydride and 0.58 mol. concentrated (95%) sulphuric acid, at temperatures between 0° C. and 10° C. The reaction mixture was then neu-

tralized with caustic soda, thus forming the sodium sulphate ester of this tetradecyl secondary, branched-chain alcohol. This is removed from the inorganic compounds present by extraction with ether and evaporation of the extract.

The ethylmethylnundecanol used was produced by hydrogenating at 100° to 125° C. under pressures of 900 to 1000 pounds per square inch, the 14-carbon atom unsaturated ketone boiling at 256° C. under atmospheric pressures, formed by condensing ethylhexaldehyde with methylisobutyl ketone, at a temperature around 25° C., in the presence of a methanolic solution of caustic soda, and removing elements of water from the resultant ketol.

A 1% solution of this secondary tetradecyl sulphate wetted cotton yarn at 80° F. in one-fourth the time required by a well known alkylated naphthalene sulphonie acid salt now widely used as a wetting agent; and, in a 0.5% solution, the former wetted the cotton yarn in one-tenth the time required by the latter. At 212° F. the secondary tetradecyl sulphate required for wetting cotton but one-fortieth of the time required by the sulphonate.

Example 2

3,9 diethyltridecanol-6 was produced by jointly condensing 3,ethylheptanone-6 with ethylhexaldehyde in the presence of caustic soda, removing the elements of water from the resultant ketol, distilling off and recovering a fraction boiling at 146° C. under 3 mm. of mercury absolute pressure, and hydrogenating the latter under pressures of 800 to 1000 pounds per square inch, and at temperatures around 150° C. This secondary branched-chain heptadecyl alcohol was sulphated by reacting at about 10° C. a 50% solution thereof in $\beta\beta'$ -dichlorethyl ether with a 25% solution of chlorosulphonic acid in the said ether. The reaction product was cooled, diluted, and neutralized with caustic soda. This salt was extracted from the ether solution by washing with water, separating the liquid layers which formed, and evaporating to dryness the aqueous layer under reduced pressure at temperatures below 100° C. The residue was extracted with methanol to dissolve the alkyl sulphate, and the extract, upon evaporation to dryness under reduced pressure, yielded the neutral secondary heptadecyl sulphate.

A solution of this secondary heptadecyl sulphate containing 0.5% of the latter, at 80° F. effectively wetted cotton yarn in one-seventh the time required for the purpose by a solution of like strength of a well known alkylated naphthalene sulphonie acid salt now in commercial use as a wetting agent. At 212° F., a solution containing 0.25% of the former wetted the cotton yarn in about one-hundredth the time required by a solution of the latter of the same strength.

Wool yarn was wetted by a 0.5% aqueous solution of secondary heptadecyl sulphate in from about one-third to about one-fiftieth of the time required for the purpose by similar solutions of various well known wetting agents in commercial use in the textile industry, certain of which had been derived from primary alcohols prepared from fatty materials. The secondary sulphate is still more effective than the other wetting agents, when used in more dilute solutions, and is from around twenty to around two hundred times as rapid a wetting agent for wool in concentrations of 0.25% in water.

Example 3

3,ethylundecanol-6, formed by condensing ethylbutyraldehyde with methylamyl ketone, dehydrating the resultant ketol, and hydrogenating the thus-formed unsaturated tridecyl ketone, boiling at 258° C. at atmospheric pressure, was sulphated at around 0° to 10° C. with chlorosulphonic acid in solution in $\beta\beta'$ -dichlorethyl ether. The reaction product was neutralized with caustic soda, and the secondary tridecyl sulphate was recovered, following the procedure described in Example 2.

Wool immersed in a wool-carbonizing bath containing a 5% aqueous solution of sulphuric acid and 0.25% of the above-mentioned secondary tridecyl sulphate satisfactorily wetted wool in about one-fourth the time required by a solution of like strength of another type of well known wetting-out agent now in commercial use.

When using 0.062% of the tridecyl sulphate in 5% aqueous sulphuric acid solution, the desired wetting-out is effected in less than one-twenty-fifth the time required by a solution of like strength of the said other type of wetting agent.

Example 4

Cotton yarn, wound on packages, was dyed in a pressure-dyeing machine with a solution of a reduced dye color containing .18 pound of sodium secondary hexadecyl sulphate in 400 gallons of the dye solution. The said alkyl sulphate served to wet the yarn as effectively as did another and commercially known wetting agent used in six times the quantity of the former.

In Table I, below, is listed a number of the sodium and other alkyl sulphates of secondary alcohols suitable for use with the present invention. The table also specifies the secondary alcohol from which each alkyl sulphate is produced. However, a wide variety of other alkali metal salts and other salts of the secondary alkyl sulphates likewise may be employed.

Table I

Derivation of wetting agents

Alkyl sulphates	Apparent formula of the intermediate alcohol
Sodium octyl sulphate.....	2 ethylhexanol-1
Sodium nonyl sulphate.....	3 ethylheptanol-6
Sodium decyl sulphate.....	2 methylundecanol-4
Sodium undecyl sulphate.....	5 ethylundecanol-2
Sodium dodecyl sulphate.....	3 ethyl-8-methylundecanol-6
Sodium tridecyl sulphate.....	3 ethylundecanol-6
Sodium tetradecyl sulphate.....	7 ethyl-2-methylundecanol-4
Sodium pentadecyl sulphate.....	3,9 diethylundecanol-6
Sodium hexadecyl sulphate.....	9 ethyl-5-methyltridecanol-6
Sodium heptadecyl sulphate.....	3,9 diethyltridecanol-6
Sodium nonadecyl sulphate.....	5,11 diethylpentadecanol-8
Monoethanolamine tetradecyl sulphate.....	7, ethyl-2-methylundecanol-4
Triethanolamine heptadecyl sulphate.....	3,9 diethyltridecanol-6

Obviously, in place of the sodium salt of the alkyl sulphates, other salts thereof may be utilized in the process, such as those produced by neutralizing the alkyl hydrogen sulphate, from the sulphation step, with another alkali such as potassium, or with ammonia, or an organic amine such as triethanolamine, as indicated in Table I.

Secondary alkyl sulphates may be used which contain one or more methyl, ethyl, or other alkyl, aryl, or aralkyl groups so attached to the main carbon chain as to provide compounds having a branched-chain or chains in their structure. These secondary alkyl sulphates in a number of instances have at least one side-chain alkyl

group directly connected with the third carbon atom of the main chain spaced from that carbon atom to which the sulphate group is attached, as clearly indicated in Table I. As further shown in the said table, many of the higher secondary alkyl sulphates particularly adapted for use in neutral and dilute alkaline solutions have two branched-chain alkyl groups respectively connected directly to the carbon atom to which the sulphate group is attached.

The secondary alkyl sulphates having from 8 to 13 carbon atoms in their molecular structure generally are preferred for use in acid solutions, such as the usual aqueous wool-carbonizing baths. Under such conditions they are very active wetting-out agents. Alkali metal salts of the secondary undecyl and dodecyl sulphates are particularly well adapted for service as wetting-out agents in dilute acid solutions.

Those secondary alkyl, branched-chain sulphates above pentadecyl sulphate in molecular weight preferably are used in neutral solutions. The secondary tridecyl and tetradecyl sulphates serve effectively as wetting-out and penetrating agents for general use in water, in dilute alkaline solutions, and in acid solutions. Especially suitable in the preparation of textile treatment liquors are mixtures of the secondary tridecyl sulphates and the secondary tetradecyl sulphates. A treating liquor containing equal parts of sodium secondary tridecyl sulphate and sodium secondary tetradecyl sulphate has high wetting and penetrating powers for textiles.

The solubilities of the secondary alkyl sulphates decrease with increase of molecular weight; and those above the secondary pentadecyl sulphate are relatively insoluble in dilute acid, though they are very highly effective in neutral solution for wetting-out textiles, even when used in very small amounts, ranging as low as from .02% to 1%.

Textiles and fibrous materials which are heavily starch-sized may be penetrated and wetted in accordance with the present invention. The secondary hexadecyl, heptadecyl, and higher sulphates appear particularly efficient for the wetting of such materials.

By the expression "secondary alkyl sulphate", and similar terms used in the specification and claims, it is intended to designate an alkyl sulphate derived from a secondary saturated aliphatic alcohol containing 8 or more carbon atoms in its molecular structure.

The term "higher branched-chain secondary alcohol", and similar terms herein used, are intended to designate those alcohols having more than 8 carbon atoms in their molecular structures, and in which at least one of the carbon atoms of the molecule is directly connected with at least three other carbon atoms.

The sulphate esters herein described not only are serviceable in connection with alkaline, acid, and neutral treating baths for textiles, such as those used in the vat dyeing of animal and other fibers, and those used in the fulling of woollen fabrics, but they also are useful in treating liquids for the impregnation of powdered materials, and for the production of emulsions, homogeneous pastes and the like. Therefore, the expression "treating liquor" and similar expressions appearing in the claims are intended to designate alkaline, acid, and neutral solutions or baths of the type ordinarily employed in the textile, leather, and related industries for the scouring,

dyeing, softening, or other treatment of textiles, leather, etc.

The invention is susceptible of modification within the scope of the appended claims.

I claim:

1. A treating bath having high wetting and penetrating properties, comprising a liquid treating agent and a neutral sulphate ester of a saturated higher branched-chain secondary monohydric alcohol having at least 8 carbon atoms in its molecule and having at least one alkyl side chain directly connected with the third carbon atom of the main carbon chain spaced from the carbon atom to which the sulphate group is attached.

2. A treating bath having high penetrating and wetting powers for textiles, the said bath containing an aqueous treating agent and a sulphuric derivative of a saturated higher branched-chain secondary monohydric alcohol having at least 13 carbon atoms in its molecule and having at least one alkyl side chain directly connected with the third carbon atom of the main carbon chain spaced from the carbon atom to which the sulphate group is attached.

3. A treating liquor having high wetting and penetrating powers for textiles, said liquor containing an aqueous treating agent and a sulphate ester of a saturated higher branched-chain secondary monohydric alcohol having at least 8 carbon atoms in its molecule, the said alcohol being free from primary alcohol groups, and having two branched-chain alkyl groups respectively connected directly to the carbon atom to which the sulphate group is attached.

4. A penetrating and wetting composition which comprises a treating agent and a sulphate ester of a saturated secondary branched-chain monohydric aliphatic alcohol having two branched-chain alkyl groups respectively connected directly to the carbon atom to which the sulphate group is attached.

5. A penetrating and wetting composition, comprising an alkyl sulphate of a saturated secondary monohydric aliphatic alcohol having at least 13 carbon atoms in its molecular structure and having at least one alkyl side chain directly connected with the third carbon atom of the main carbon chain spaced from the carbon atom to which the sulphate group is attached.

6. A penetrating and wetting composition which comprises an aqueous liquid containing a sulphate ester of a saturated branched-chain secondary tridecyl alcohol having an alkyl side chain directly connected with the third carbon atom of the main carbon chain spaced from the carbon atom to which the sulphate group is attached.

7. A penetrating and wetting composition which comprises an aqueous liquid containing a treating agent and a sulphuric acid ester of a saturated branched-chain secondary tetradecyl alcohol.

8. A penetrating and wetting composition which comprises an aqueous liquid containing a sulphate ester of a saturated branched-chain secondary heptadecyl alcohol.

9. A penetrating and wetting composition which comprises an aqueous liquid containing a mixture of the respective neutral sulphuric acid esters of a saturated secondary branched-chain tridecyl alcohol and of a saturated secondary branched-chain tetradecyl alcohol.

JACOB N. WICKERT.