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SULPHO-CARBOXYLIC ESTERS SUITABLE
AS ASSISTANTS FOR THE TEXTILE AND
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The present invention relates to the produc-
tion of assistants for the textile and related in-
dustries, particularly of wetting, cleansing and
emulsifying agents.

We have found that assistants for the textile
and related industries, particularly wetting,
cleansing and emulsifying agents, having ex-
cellent properties are obtained by esterifying
saturated or non-saturated aliphatic, i. e. open
chain or cycloaliphatic, mono- or polyhydric al-
cohols containing more than 8 carbon atoms in
their molecule with the carboxylic groups of
aliphatic sulpho-carboxylic acids ($C-SO_2OH$)
containing up to 8 carbon atoms in their mole-
cule. Instead of the sulpho-carboxylic acids,
aliphatic, sulphonatable carboxylic acids con-
taining up to 8 carbon atoms in their molecule
and comprising no sulphonic group may also be
used, the esters obtained being then sulphonated.

The term "alcohols" is to be understood in a
broad sense and is meant to include alcohols
which contain further substituents as for ex-
ample halogen and/or carboxylic radicles.

As suitable alcohols may be mentioned octo-
decyl alcohol, dodecyl alcohol, oleic alcohol, octo-
decane diol (obtainable by reduction of castor
oil with the aid of hydrogen), alcohol mixtures
which may be obtained by reduction with the
aid of hydrogen of fats and oils of vegetal, i. e.
animal and vegetable origin, alcohols which are
formed by the oxidation of paraffins, such as
paraffin wax or paraffin oil, and alcohols cor-
responding to resinic, naphthenic and montanic
acids and obtainable therefrom by reduction with
the aid of hydrogen. Instead of the said simple
alcohols, derivatives thereof may also be ester-
ified to yield similar products, suitable derivatives
being for example dichlor-octodecyl alcohol and
ricinoleic acid. The alcohols obtainable by in-
troducing alkyl or cycloalkyl groups into one
hydroxyl group of polyhydric alcohols containing
up to 8 carbon atoms in their molecule may also
be employed provided the total amount of carbon
atoms in the final molecule is greater than 8;
as examples of such alcohols may be mentioned
propylene-glycol mono-octodecyl ether and bu-
tylene-glycol mono-hexyl ether.

As suitable sulpho-carboxylic acids, sulpho-
acetic acid, α -sulpho-propionic and sulpho-iso-
butyric or -valeric acids may be mentioned. Suit-
able carboxylic acids containing no sulphonic
groups are those which contain up to 8 carbon
atoms in their molecule and one or more groups
which render sulphonation to true sulphonic
acids possible without destructive attack on the
ester, such as double linkages or halogen atoms,

for example crotonic acid, dimethyl acrylic acid
mono-chlor acetic acid, or α -brom propionic acid.
Carboxylic acids containing up to 8 carbon atoms
in their molecule may also be employed into
which the said sulphonatable groups can be in-
troduced after esterification, for example by
halogenation of the radicle of a saturated ali-
phatic acid.

The esterification is usually carried out by
acting with the alcohols on the acids, or acid
chlorides, under the usual conditions, as for ex-
ample by treating the alcohols with the acids in
the presence of an acid reacting catalyst such as
hydrochloric or sulphuric acid, or by heating the
alcohols with the acids, or their chlorides, at
elevated temperatures such as from about 50°
to about 100° C., or above the boiling point of
water for removing the latter, or halogen hydride
respectively; when working with acid chlorides
the alcohols may be employed in the form of
alcoholates. When mineral acid esters of the
alcohols such as octodecyl mono-iodide are used,
it is preferable to employ salts of the organic
acids for the esterification. When employing
sulpho-carboxylic acids it is particularly advan-
tageous to heat the alcohols with the acids in the
free state to say 100° C. preferably in vacuo or
the mono-sodium salt of the acid with the al-
cohols to a temperature of say 120° C. prefer-
ably above 150° C. Thus for example the ali-
phatic alcohols containing more than 8 carbon
atoms in their molecule which are obtainable by
reduction with the aid of hydrogen of fatty acids
may be esterified by heating with the mono-
sodium salt of sulpho-acetic acid at 200° C. or an
alkyl ester, such as the methyl ester, of the
mono-sodium salt of sulpho-acetic acid may be
re-esterified with the alcohol desired.

The esters which do not contain sulphonic
groups must, as has already been mentioned, sub-
sequently be sulphonated. This sulphonation is
generally carried out in the usual manner, by a
treatment with sulphonating agents stronger than
concentrated sulphuric acid until true sulphonic
acids are obtained which can be ascertained by
the fact that a sample does not split off the sul-
phonic groups when boiled with dilute mineral
acids, as for example a 10 per cent aqueous hy-
drochloric acid. The esters may be sulphonated
for example by means of oleum, sulphur trioxide
or chloro-sulphonic acid if desired in the pres-
ence of inert organic diluents, such as carbon
tetrachloride, trichlorethylene, and/or catalysts
such as the superficially active charcoal or
bleaching earth, and/or agents capable of re-
moving water, as for example acetic or propionic

anhydrides and the like. Esters obtained from carboxylic acids containing a halogen atom may be converted into esters of sulpho-carboxylic acids by a treatment with salts of sulphurous acid such as alkali, alkaline earth metal or heavy metal salts, the reaction being preferably carried out with alkali metal sulphites or ammonium sulphite. It is particularly advantageous to carry out this treatment by heating at about 80° C. the mixture of the ester with an aqueous solution of an alkali metal sulphite together with a small amount of an organic solvent soluble in water, such as ethyl alcohol, or of an emulsifying agent for which purpose use may be made of the products obtained by the process itself. The esters, the acid radicles of which contain halogen atoms, may also be converted into true sulphonic acids by a treatment with alkali metal hydrosulphide and subsequent oxidation.

Esters which already contain a sulphonic group may, if so desired, be subjected to one of the sulphonation methods described, so that the final product contains two or more sulphonic groups, such products being also obtainable from esters of poly-halogen carboxylic acids with the aid of sulphites.

Products of the nature hereinbefore defined are also obtained by employing for the esterification polyhydric alcohols containing 8 or less carbon atoms in which molecule in which case alkyl or cycloalkyl groups must be introduced into at least one free hydroxyl group of the ester, for example with the aid of alkylene oxides containing the required number of carbon atoms, so that the resulting alcoholic radicle contains more than 8 carbon atoms.

The products according to the present invention correspond to the general formula $R-COO-R_1$ in which R denotes an aliphatic radicle containing up to 7 carbon atoms and at least one sulphonic radicle and R_1 denotes a radicle of an aliphatic mono- or polyhydric alcohol containing more than 8 carbon atoms. R_1 will usually contain from 10 to 18 carbon atoms, the products from alcohols containing from 12 to 18 carbon atoms being particularly valuable.

The products obtained according to the present invention are excellent washing, cleansing and emulsifying agents for many purposes in daily and commercial use. They may be employed alone or together with various additions such as salts as for example sodium chloride, sodium sulphate or sodium perborate, diluted acids, such as dilute hydrochloric or acetic acid, glue, organic solvents such as carbon tetrachloride, cyclohexanol, oil of turpentine and/or mineral, vegetable or animal oils.

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

162 parts of the mono-sodium salt of sulpho-acetic acid are heated with 270 parts of octodecyl alcohol for 8 hours at 200° C. while stirring, the water set free during the esterification being removed from the reaction vessel by means of a current of nitrogen. A water-soluble product having excellent washing and foaming power is obtained, and octodecyl alcohol which has not reacted and other water-insoluble matter being removed by extraction with ethyl ether.

Example 2

325 parts of the mono-sodium salt of sulpho-acetic acid are heated with 500 parts of oleic alcohol ($C_{18}H_{35}OH$) for 15 hours at 180° C. while stirring, the water set free during the esterification being removed from the reaction vessel by means of a current of nitrogen. After removing the oleic alcohol which has not reacted and small quantities of other water-insoluble matter as described in Example 1, an excellent, water-soluble washing agent is obtained, which consists of practically pure oleyl sulpho-acetate.

Example 3

1 part of the mono-sodium salt of sulpho-acetic acid is heated at 180° C. during 18 hours while stirring, with 1 part of a mixture of alcohols such as is obtained by the catalytic reduction of coconut oil, the water being removed as in the preceding examples. The reaction product is worked up in the usual manner; it is an excellent wetting and detergent agent. Instead of the mono-sodium salt, free sulpho-acetic acid may be employed, the reaction being then carried out at about 100° C. and preferably at about 20 millimeters mercury gauge.

Example 4

140 parts of the ester prepared by treating the mixture of alcohols resulting from the catalytic reduction of coconut oil with chloroacetic acid are boiled for some time with an aqueous solution of 70 parts of anhydrous sodium sulphite containing about 30 per cent of ethyl alcohol, until a sample of the reaction product forms a clear solution with water. The reaction mixture itself, containing some sodium chloride, as well as the product obtained by evaporation of the liquid is an excellent detergent and wetting agent.

Example 5

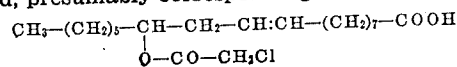
50 parts of the mixture of esters, obtained by the esterification of crotonic acid with the mixture of alcohols of high molecular weight prepared by a catalytic reduction of coco fat, are mixed at 20° C. with a mixture of 25 parts each of sulphuric acid monohydrate and of acetic anhydride. After stirring for several hours the reaction product is poured onto ice and rendered neutral with the aid of aqueous caustic soda solution. Non-sulphonated constituents are removed whereupon the water-soluble sulphonation product is recovered by salting out. The sodium salt of the sulphonic acid of the initial ester possesses a high wetting power.

Example 6

36 parts of an ester obtained by esterifying one molecular proportion of chloro-acetic acid with one molecular proportion of octodecane-7,18-diol, obtainable by the catalytic reduction of castor oil, are stirred for 5 hours at 83° C. with a solution of 15 parts of sodium sulphite in 150 parts of a 30 per cent aqueous solution of ethyl alcohol. An efficient washing and scouring agent is obtained, the efficient constituent of which may be obtained in the solid form by evaporating the aqueous alcoholic solution.

Example 7

38 parts of the chloro-acetic ester of ricinoleic acid, presumably corresponding to the formula



and obtainable for example by heating equimolecular proportions of chloro-acetic acid and of ricinoleic acid to 160° C., are refluxed for 2 hours with a solution of 15 parts of sodium sulphite, and 5 parts of sodium carbonate in 150 parts of an aqueous 30 per cent solution of ethyl alcohol. After évaporation of the alcohol a product having a good washing and foaming power is obtained.

What we claim is:

1. Sulpho-carboxylic esters, suitable for use as assistants in the textile and related industries, corresponding to the general formula $R-COO-R_1$ in which R denotes an aliphatic radicle, containing up to 7 carbon atoms and at least one sulphonic radicle, and R_1 denotes a radicle of an aliphatic alcohol obtainable by reduction of the unsaturated fatty acids of vegetable oils and fats.

2. Oleyl sulpho-acetate.

3. Esters of lower fatty acids and higher unsaturated aliphatic alcohols, said esters containing a sulphonic group on the alkyl portion of the acyl group of the ester molecule.

4. The chloroacetic acid ester of an unsaturated non-cyclic alcohol containing a chain of 18 carbon atoms in its structure.

5. The process which comprises reacting with chloroacetic acid upon an unsaturated non-cyclic alcohol containing a chain of 18 carbon atoms in its structure, whereby to produce the chloroacetic acid ester of said alcohol.

6. Sulpho-acetates of aliphatic alcohols obtainable by reduction of unsaturated fatty acids of oils and fats of vegetable origin.

7. Esters suitable for use as assistants in the textile and related industries corresponding to the general formula $R-COO-R_1$ in which R denotes an aliphatic radicle containing up to 7 carbon atoms and a substance selected from the group consisting of Cl and SO_3H and R_1 denotes a radicle of an aliphatic alcohol obtainable by reduction of the unsaturated fatty acids of vegetable oils and fats.

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