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CARBOXYLATES OF ALIPHATIC ALCOHOLS
WITH NON-AROMATIC SULPHONIC CAR-
BOXYLIC ACIDS

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

It is already known that esters of carboxylic acids are obtained when the said acids are boiled for long periods of time under a reflux condenser with a quantity of alcohols exceeding that required for esterification. It is preferable to add inorganic acids, other acid-reacting catalysts or agents removing water such as gaseous hydrochloric acid, or concentrated sulphuric or phosphoric acids, potassium pyrosulphate, or aromatic sulphonic acids. It has already been proposed to carry out esterifications in the presence of solvents, as for example benzene whereby the solvent together with the water formed by the conversion are distilled off slowly during the reaction, the equilibrium of the esterification thus being displaced so as to favour the formation of esters.

Sulphonic acids of carboxylic acids, especially those of the non-aromatic series, frequently can only be esterified in an unsatisfactory manner. In particular, additions of acid catalysts or agents removing water are injurious because they often cause decompositions during the reaction which may impair the value of the reaction products for industrial employment. Especially the alpha-sulphonic carboxylic acids cannot be converted in the desired manner by the usual methods, or can only be converted with difficulty and inconvenience.

We have now found that the esterification of non-aromatic sulphonic-carboxylic acids containing at least 8 carbon atoms, especially of alpha-sulphonic-carboxylic acids, is carried out in a manner which is extremely simple industrially by acting with aliphatic alcohols, i. e. aliphatic open chain or cycloaliphatic alcohols or aliphatic alcohols in which a hydrogen atom connected to a carbon atom is substituted by an aromatic nucleus, such as open chain aliphatic mono-hydric alcohols, as for example methyl, ethyl, propyl, butyl, iso-butyl, amyl, hexyl, octyl or dodecyl alcohols, or glycols, or mono-ethers of the latter, cyclohexanol or its homologues or benzyl alcohol, on an acid sulphonic carboxylic acid substance, i. e. on the said sulphonic-carboxylic acids in the free state or acid salts thereof. In this way products are obtained which are entirely free from troublesome by-products and decomposition products, the working up of which offers no difficulty at all. Generally speaking the acid salts of all sulphonic-carboxylic acids containing at least 8 carbon atoms as for example

the sulphonic acids of carboxylic acids, oils, fats or waxes of vegetal i. e. vegetable and animal, origin, such as palmitic sulphonic acids or stearic sulphonic acids or lauric sulphonic acid, naphthenic sulphonic acid and the like or the free acids are suitable for the formation of the esters (carboxylates). Acid salts of substituted sulphonic acids containing carboxyl groups, as for example those containing halogen or hydroxy groups, such as bromo-stearic sulphonic acids or hydroxy stearic sulphonic acid, obtainable by the sulphonation of oleic acid and like acids, or the acids in the free state, may also be employed. Generally we prefer aliphatic open chain or cycloaliphatic alpha sulphonic carboxylic acids or their acid salts since they furnish particularly valuable products.

The esterification proceeds smoothly by heating the components to elevated temperatures preferably above 50°, up to 250° C., generally between 100° and 180° C. if acid salts be employed, and between 50° and 100° C. if free sulphonic carboxylic acids be used. When employing alcoholic components of low boiling point, such as methyl or ethyl alcohols, the reaction can be accelerated by working in pressure-tight vessels at temperatures above the normal boiling point of the alcohols. In order to produce as complete an esterification of the acid components as possible it is generally speaking preferable to employ a quantity of alcoholic component exceeding that required for esterification.

The esters obtainable in the said manner when employing alpha-sulphonic-carboxylic acid substances are, contrasted with the acid salts employed as initial materials, generally very readily soluble in water and organic solvents such as lower alcohols (from methyl to amyl alcohols), ethers or ketones, anhydrous acetic acid, benzene or benzene, if the alcohols and sulphonic-carboxylic acids employed in the esterification do not contain more than eight carbon atoms, whereas those prepared from alcohols containing more than eight carbon atoms are less readily soluble in water but still readily soluble in organic solvents. The aqueous solutions of all such reaction products have a high wetting, cleansing and dispersing power and do not give water-insoluble salts with the quantities of the substances forming the hardness in water usually occurring in hard water. They may therefore be employed with great advantage for example for all purposes in the treatment of fibrous materials such as wool, cotton, silk or artificial silk, as for example in wetting, carbonizing, washing or scouring or

in the treatment of the said materials with emulsions or suspensions as for example in oiling, impregnating or finishing, and in dyeing. The esters of alpha-sulpho-carboxylic acids have the capacity of imparting a soft touch and great flexibility to fibrous materials in a high degree.

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

100 parts of the monosodium salt of palmitic sulphonic acid are heated to about 180° C. in a pressure-tight vessel with 300 parts of methyl alcohol while stirring. After the reaction is completed the remainders of methyl alcohol are distilled off. The crude methyl ester obtained may be pulverized after cooling and may be directly employed without further purification as wetting agent or for softening textile materials. If desired the reaction may also be carried out at about 150° C. with a smaller quantity of methyl alcohol and without stirring.

The ethyl, isopropyl, butyl, isobutyl, amyl and like esters of palmitic sulphonic acid may be prepared in the same manner.

Example 2

100 parts of the mono-sodium salt of stearic sulphonic acid are boiled under a reflux condenser with 100 parts of ethylene glycol until esterification has taken place. The reaction mixture is worked up as described in Example 1. The esterification may be carried out in the same manner with other alcohols of high boiling point, such as octyl alcohol, benzyl alcohol, glycerine, cyclohexanol, alcohols of wool fat and the like. Lauric sulphonic acid may be employed instead of stearic sulphonic acid.

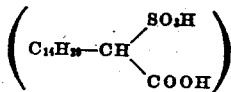
Example 3

100 parts of the mono-sodium salt of hydroxystearic sulphonic acid are heated to 160° C. with 200 parts of methyl alcohol in a pressure-tight vessel until esterification has taken place.

The resulting carboxylic acid ester dissolves readily in water and dilute sulphuric acid and has, even in acid baths, an excellent wetting power, so that it may be employed with special advantage as an addition to carbonizing baths.

Example 4

100 parts of crude palmitic sulphonic acid,



are dissolved in 250 parts of methanol, whereupon the mixture is refluxed for about 5 hours. The hot solution is then filtered, rendered neutral with the aid of aqueous caustic soda solution and

the remainders of methanol are distilled off whereupon the residue is dried in vacuo.

The ester obtained (methyl palmitate sulphonic acid) can be further purified by re-dissolution in ethyl ether, ethyl alcohol or benzene and is easily soluble in cold water. The aqueous solution of the ester possesses a high wetting, foaming and dispersing power and the ester is not precipitated from the solution by the compounds forming the hardness of water.

Example 5

100 parts of the mono-sodium salt of di-bromostearic sulphonic acid are heated in a pressure-tight vessel while stirring for 10 hours at 140° C. with 300 parts of methanol. The reaction product is then worked up as described in Example 1.

Example 6

2 grams of butyl palmitate sulphonic acid are dissolved in 1 litre of an aqueous sulphuric acid solution of 4° Bé. strength. Woolen piece goods are soaked with the liquid solution, squeezed off and carbonized by heating for 1 hour at from 80° to 90° C. The goods are then rinsed in the usual manner and washed with alkali. A uniform carbonization is attained, the goods being completely freed from vegetable material. In the place of the butyl palmitate sulphonic acid the same quantity of amyl palmitate sulphonic acid may be employed as well as a sulphuric acid solution of 2° Bé. strength. The same or even better results are obtained with a carbonizing liquor containing per litre of an aqueous sulphuric acid solution of 4° Bé. strength one gram of isobutyl palmitate sulphonic acid.

What we claim is:—

1. Carboxylates of aliphatic alcohols with aliphatic alpha-sulphonic carboxylic acids containing at least 8 carbon atoms.
2. Carboxylates of aliphatic alcohols containing from 1 to 12 carbon atoms with aliphatic alpha-sulphonic carboxylic acids containing at least 8 carbon atoms.
3. Carboxylates of methyl alcohol with non-aromatic α -sulphonic carboxylic acids containing at least 8 carbon atoms.
4. Carboxylates of dyhydric aliphatic alcohols with non-aromatic sulphonic carboxylic acids containing at least 8 carbon atoms.
5. Carboxylates of ethylene glycol with non-aromatic sulphonic carboxylic acids containing at least 8 carbon atoms.
6. A methyl carboxylate of a palmitic sulphonic acid.
7. An ethylene glycol mono-carboxylate of a palmitic sulphonic acid.
8. A methyl carboxylate of a hydroxystearic sulphonic acid.

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