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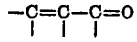
ALKOXY-SUBSTITUTED ALIPHATIC CARBOXYLIC ACID COMPOUNDS

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2 Claims. (Cl. 260—535)

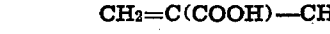
The present invention relates to alkoxy-substituted aliphatic carboxylic acids and salts thereof which are washing, wetting, emulsifying and similar textile-treating agents. Specifically, the invention relates to acids and water-soluble salts of acids which may be referred to as reaction products of alcohols with maleic anhydride and similar unsaturated aliphatic carboxylic acids or anhydrides containing the alpha-beta-enal grouping



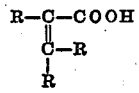
The present application is a continuation-in-part of my prior copending application, Serial Number 181,597, filed December 24, 1937, which has issued as Patent Number 2,283,214. The invention, as it pertains specifically to the present application, is based upon my discovery that alkoxy-substituted acids and alkali-metal salts of such acids obtained by the addition or condensation of aliphatic alcohols containing from five to sixteen carbon atoms, inclusive, in the molecule, such as dodecyl (lauryl) alcohol, with various unsaturated aliphatic carboxylic acids possessing the alpha-beta-enal grouping, are characterized by pronounced surface activity. These compounds are comparable in their surface activity to similar well-known washing, wetting and emulsifying agents such as the sulfated alcohols and the sulfonated alkyl aromatic hydrocarbons commonly used for this purpose, but many of them do not foam or lather as readily when added to water in the manner that is typical of other wetting agents. This failure to foam is a definite advantage for certain purposes, and does not detract from their desirability as wetting agents or detergents.

The alkoxy-substituted aliphatic carboxylic acids to which the present invention pertains are those derived from aliphatic alcohols containing from five to sixteen carbon atoms, inclusive, in the molecule. Such alcohols are the various amyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl (lauryl), tridecyl, tetradecyl, pentadecyl and hexadecyl (palmityl) alcohols, many of which are obtained by hydrogenation of the corresponding fatty acids or fatty acid esters and are available in commercial quantities.

The foregoing alcohols are condensed with unsaturated aliphatic carboxylic acids containing the alpha-beta-enal grouping, preferably in the form of esters. Unsaturated aliphatic carboxylic acids of this type are fumaric or maleic acid, HOOC—CH=CH—COOH, itaconic acid,

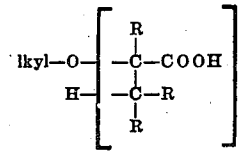


citraconic acid, $CH_3—C(COOH)=CH—COOH$, acrylic acid, $CH_2=CH—COOH$, and crotonic acid, $CH_3CH=CH—COOH$. These acids possess the following structural formula:



in which R is selected from the group consisting of hydrogen, alkyl and carboxyl radicals. Maleic acid is the most common and most readily available acid of this series and hence compounds derived from that acid are particularly considered throughout this specification. Aromatic acids, such as phthalic acid, in which the reactive portion of the alpha-beta-enal grouping is partly incorporated in the phenyl nucleus, are not operative.

The general formula of the alkoxy-substituted acids which are specified in the present application may be represented as:



in which R is a hydrogen, alkyl or carboxyl radical and alkyl is an alkyl group having not less than five nor more than sixteen carbon atoms. However it is not definitely ascertained to which of the two pivotal carbon atoms in the above formula the alkoxy (alkyl—O—) group and the hydrogen atom from the alcohol are attached, or whether a mixture of both possible types of compounds is formed, hence the brackets are used to indicate this uncertainty. Stated more generally, the compounds specified in the present application are those derived from the condensation of an alcohol as above specified with an unsaturated carboxylic acid as above specified, and include both the alkoxy-substituted acids thus formed and the water-soluble, particularly alkali-metal, salts of such acids.

In effecting the addition or condensation, an ester or other suitable compound, in which the carboxyl groups of the unsaturated acid are blocked, is preferably used. The condensation product is then hydrolyzed to yield the desired alkoxy-substituted acid or saponified to yield a

salt of the acid. When maleic acid or a suitable ester or other derivative of maleic acid is used in the condensation, the resulting compound is an alkoxy-succinic acid derivative; acrylic acid yields propionic acid derivatives; and itaconic acid and citraconic acid yield alkoxy-pyrotartaric (methylsuccinic) acid derivatives.

Various methods are available for preparing the alkoxy-substituted acids of the invention. In my preferred method, I prefer to start with an alcohol or metal alcoholate and an ester of the unsaturated acid containing the alpha-beta-enal grouping. When an alcohol is used the condensation may be effected in the presence of sodium. Alternatively, I may convert the alcohol to a metal alcoholate by adding sodium hydroxide to the alcohol and removing the water of reaction, and thereafter use the sodium alcoholate, as more specifically described in Towne Patent No. 2,120,-688.

Instead of using the ester of the unsaturated acid, for example, diethyl maleate, a salt of the half-ester, such as monoethyl maleate, or a salt of the acid, such as disodium maleate, may be used. The resulting ester, half-ester salt, or salt of the alkoxy-substituted acid is thereafter converted to the acid, by acid hydrolysis, or to a salt by saponification. In preparing lauroxy-succinic acid, as described in Example 1 which follows, lauryl alcohol and diethyl maleate are condensed in the presence of metallic sodium under anhydrous conditions. The resulting diethyl ester of lauroxy-succinic acid is saponified and the salt formed after saponification is used as such or is converted to the acid.

Instead of starting with diethyl maleate I may start with the half ester, monoethyl maleate, by forming the sodium salt of the half ester and reacting this salt with lauryl alcohol under anhydrous conditions with metallic sodium. Saponification of the resulting salt and recovery as before, yield lauroxy-succinic acid.

To prevent trans-esterification I prefer to use an ester of the unsaturated acid containing the alpha-beta-enal grouping and the same alcohol which is to be later used for the substitution of the alkoxy group. Thus, as shown in Example 2, to make decoxy-succinic acid, the decyl ester of maleic acid is preferred instead of the ethyl or some other alkyl ester; in making octoxy-succinic acid I prefer to start with the di-octyl ester of maleic acid.

The following examples illustrate preferred methods of making alkoxy-substituted acids of the invention:

Example 1.—Lauroxy-succinic acid

Three hundred forty-four (344) grams of diethyl maleate (approximately 2 mols) and 410 grams of lauryl alcohol (approximately 2.2 mols) were placed in a flask provided with a reflux condenser. Approximately 5 grams (0.2 gram atoms) of sodium metal (in small pieces or in rolled form) were then continuously added. Reaction started immediately and the mixture became warm. The mixture was allowed to stand until the initial reaction subsided and it was thereupon heated on a steam bath for several hours. To the mixture was then added alcoholic sodium hydroxide in quantity sufficient to saponify the ester and the mixture was subjected to refluxing. After saponification was complete the mixture was cooled, ethyl alcohol was distilled from the mixture and unreacted lauryl alcohol was extracted from the alkaline solution with a non-aqueous solvent. The reaction mixture was then made acid with hydrochloric acid and the precipitated lauroxy-succinic acid was removed by extraction with chloroform. The residual solution contained maleic acid resulting from unreacted diethyl maleate. The lauroxy-succinic acid was converted to its sodium salt and recovered as such.

The free lauroxy-succinic acid is a solid of waxy appearance and its sodium salt is a mass resembling soap in appearance and feel.

Example 2.—Decoxy-succinic acid

A small amount of sodium metal (2.3 grams, approximately 0.1 mol) was dissolved in 474 grams (approximately 3 mols) of n-decyl alcohol and this solution was then added to 396 grams (approximately 1 mol) of di-n-decyl maleate. The reaction mixture was allowed to stand in a stoppered flask for about 100 hours, after which the mixture was hydrolyzed by shaking with about 500 cc. of water. About 400 cc. of dioxane was then added to the mixture and it was saponified with about 100 grams (approximately 2.5 mols) of sodium hydroxide by refluxing therewith for about 17 hours. The mixture was cooled and the resulting layers were separated. The aqueous layer was washed about 4 or 5 times with benzene to remove any decyl alcohol and dioxane remaining in the aqueous solution. The aqueous solution was acidified with hydrochloric acid and the resulting oil was washed with saturated salt solution.

The oil, consisting predominantly of decoxy-succinic acid, was dissolved in methanol and converted to the calcium salt by adding a slight excess of an aqueous solution of calcium chloride. A heavy precipitate of the calcium salt of decoxy-succinic acid separated. The precipitate was filtered with the aid of suction and washed with a small amount of methanol. The salt was then added to an excess of 75% to 85% aqueous sulfuric acid mixed with an equal volume of benzene, and the calcium sulfate that separated was removed by filtration. The calcium sulfate precipitate was added to another portion of 75% to 85% sulfuric acid mixed with an equal volume of benzene to remove any decoxy-succinic acid adhering thereto. The solutions were then combined and the benzene and sulfuric acid layers were separated. The sulfuric acid layer was further extracted with benzene and the benzene extracts were combined and filtered. The filtered benzene extracts were then evaporated and the acid solidified on cooling.

The neutralization number of the decoxy-succinic acid obtained in this manner was 151. The molecular weight of decoxy-succinic acid is 274, hence the theoretical neutralization number is 137. The acid can be converted to the sodium salt by adding sodium carbonate or sodium hydroxide thereto.

Standard soil launderometer tests

Standard soil launderometer tests were made with the sodium salts of triisobutylene-succinic acid and the lauroxy-succinic acid prepared in Example 1, in comparison under identical conditions with the commercial detergent "Santomerse," a sodium salt of an alkylated aromatic sulfonic acid. The standard soil washing test is conducted as follows: To a cotton fabric is applied under controlled conditions a standard soil solution. This solution is composed of a suspension of carbon black, vegetable oils and mineral

oils in water. The fabric is then aged for a predetermined period. The aging of the fabric is important because the soil is more difficult to remove as it becomes older. The soiled fabric is then washed in a launderometer and each sample is tested in triplicate at various wash intervals (10, 20, 30 and 40 minutes). The washed sample is then dried and the lightening of the fabric is determined, using a Pulfrich photometer. The relative detergency is then established.

The table illustrates the improvement in whiteness expressed as "per cent baryta white units" obtained with the detergents when used in soft water.

	"Santomeres"	Sodium salt of triisobutylene-succinic acid	Sodium salt of lauroxy-succinic acid
Soft water (50 ppm.):			
1st wash (10 min.)	8	5	9
2nd wash (20 min.)	15	7	11
3rd wash (30 min.)	18	9	13
4th wash (40 min.)	21	11	14

The compounds of the invention are of value in the preparation of detergents, polishes, wax and hydrocarbon-oil emulsions, insecticidal emulsions, cold-water paints and as thickening agents for rubber latex, as flotation reagents, as pigment-treating agents to improve dispersibility and grinding properties, as rubber-compounding ingredients and the like. They are of especial value for the preparation of detergents, for which purpose they are equal to or superior to sulfonated detergents such as alkyl aromatic sulfonic acids. The calcium salts of the compounds are soluble in water, and the compounds are well-adapted for use in alkaline washing operations.

By the term "wetting agent" as used in the specification and claims is to be understood an agent suitable for use as a detergent, emulsifying agent, textile assistant, dispersing agent, etc., or, in general, agents whose properties of reducing surface tension of liquids make them eminently desirable for many applications dependent upon their surface activity.

To the acids and salts of the invention various adjuvants or builders may be added, for example, such materials as sodium carbonate, sodium sulfate, magnesium sulfate, etc., particularly when the products are to be used as detergents. When sodium carbonate is used in this manner the free acid instead of its sodium salt may be incorporated into the composition, since the sodium carbonate converts the acid to the salt in aqueous solution and thus obviates the step of converting the free acid to the salt.

The sodium salt of lauroxy-monoethyl succinate, which is lauroxy-succinic acid in which one hydrogen of the carboxyl group has been replaced by sodium and the hydrogen of the other carboxyl group has been replaced by ethyl, was greatly inferior to the disodium salt of lauroxy-succinic acid. The diesters of lauroxy-succinic acid are relatively insoluble in water and are therefore not suitable wetting agents or detergents.

Inasmuch as the above specification comprises preferred embodiments of the invention it is to be understood that the invention is not limited thereto and that changes and modifications may be made therein without departing substantially from the invention, which is defined in the appended claims.

I claim:

1. Lauroxy-succinic acid, said compound being a waxy solid whose sodium salt is soluble in water and has wetting properties.

2. Sodium lauroxy-succcinate.

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