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N-ACYLAMINOCARBOXYLIC ACID-ETHYLENE OXIDE ADDITION PRODUCTS

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9 Claims. (Cl. 260—404)

This invention relates to N-acylaminocarboxylic acid-ethylene oxide addition products.

N-acylated aminocarboxylic acids may be prepared by reacting an aminocarboxylic acid with a carbonyl chloride, in the presence of an acid binding material. If the carbonyl chlorides are derived from higher molecular carboxylic acids, particularly those which contain a hydrocarbon radical, having an aliphatic component with 8 to 26, and preferably 10 to 20 carbon atoms, the end acylated aminocarboxylic acids have surface active properties and are useful as detergents or detergent components. These N-acylaminocarboxylic acids have the formula:

$$R—CO—NH—(CH_2)_n—COOH$$

in which R is a hydrocarbon radical containing an aliphatic component, with about 8 to 26 carbon atoms and n is a whole number from 3 to 7. These acylaminocarboxylic acids may be used in the form of their water-soluble salts.

In our co-pending application, Serial No. 677,236, filed August 9, 1957, a process is described for the production of N-acylaminocarboxylic acids of the above type, having more than one of the aminocarboxylic acid radicals. These N-acylaminocarboxylic acids have the general formula:

$$R—CO—[NH—(CH_2)_n—CO]_x—OH$$

in which R is a hydrocarbon radical containing an aliphatic component with 8 to 26, and preferably 10 to 20 carbon atoms, n is a whole number from 3 to 7, and x is a whole number from 2 to 10, and preferably not more than 5, and more preferably not more than 3. These N-acylaminocarboxylic acids having more than 1 aminocarboxylic acid radical, may be produced in accordance with the said application, by reacting a lactam, which contains 3 to 9 atoms in its heterocyclic ring with a free carboxylic acid which contains at least 8 carbon atoms in its molecule. These N-acylaminocarboxylic acids may be produced in admixture with a major portion of acylaminocarboxylic acids containing but a single amino carboxylic acid radical and all of the materials may be used as detergents or detergent components, in the form of their water-soluble salts. These materials exhibit excellent washing properties in soft water but these washing properties are detrimentally effected in hard water.

One object of this invention is a surface active derivative of an N-acylaminocarboxylic acid of the above-mentioned type which is not detrimentally effected by hard water.

This, and still further objects will become apparent from the following description:

In accordance with the invention, there has been found that addition products of salts of the abovementioned acylaminocarboxylic acids with ethylene oxide, exhibit excellent washing properties and a high resistance to water hardness.

The addition products, in accordance with the invention, are addition products with 1 to 20 mols of ethylene oxide of salts of N-acylaminocarboxylic acids, having the general formula:

$$R—CO—[NH—(CH_2)_n—CO]_x—OMe$$

in which R is a hydrocarbon radical containing an aliphatic component with about 8 to 26 and preferably 10 to 20 carbon atoms, n is a whole number from 3 to 7, x is a whole number from 1 to 10, preferably not more than 5, and more preferably not more than 3, and Me represents the ion of a monovalent base.

The starting acylaminocarboxylic acids may be any of the known acylaminocarboxylic acids, including those described in co-pending application 677,236, falling under the general formula and in the form of their salts.

The aliphatic component of the hydrocarbon radical R may be aliphatic or cycloaliphatic in nature and may be connected to the carboxyl group through an aromatic radical. The starting materials, in accordance with the invention, are preferably salts of N-acylaminocarboxylic acids, which are derived from straight chain or branch chain fatty acids of natural or synthetic origin, including saturated and unsaturated fatty acids of this type. Examples of these fatty acids include caprylic acid, pelargonic acid, capric acid, undecanoic acid, lauric acid, palmitic acid, stearic acid, oleic acid, linoleic acid, behenic acid, montan acid and the like, or any desired mixture of these acids. The salts may also be derived from cycloaliphatic carboxylic acid such as the resin or naphthene acids, as for example, abietic acid; alkylcyclohexyl carboxylic acids and partially or completely hydrogenated diphenylcarboxylic acids, triphenylcarboxylic acids, benzyl-benzoic acid, benzylnaphthoic acid and their substitution products, particularly alkyl derivatives of the said carboxylic acids. Additionally, salts derived from alkyl or cycloalkylenbenzoic acid as well as from carboxylic acids obtained from these aromatic carboxylic acids by partial or complete hydrogenation may be used.

The starting salts may also be derived from other carboxylic acids, the radicals of which bound to the carboxylic group, do not constitute pure hydrocarbon, as for example, ether carboxylic acid, such as those derived from glycolic acid. These compounds may be obtained, for example, by reacting the alcohols with halogen carboxylates, and particularly with chloracetates in the presence of acid binding agents.

The salts may be salts with any bases, including organic or inorganic bases, so that Me represents an ion of a monovalent base. As inorganic cations, there are included lithium, sodium and potassium, while the organic bases include trimethylamine, triethylamine, and similar amines, and preferably those which do not contain any reactive hydrogen atoms.

The reaction of the starting salts of the N-acylaminocarboxylic acids with the ethylene oxide is effected by heating the two components in contact to a temperature of at least 100° C., preferably in the absence of water. The reaction may be effected at normal or elevated pressures. At normal pressure, it is advisable to employ somewhat higher temperatures, as for example, temperatures between about 150 and 250° C. When working under pressure, the reaction velocity is sufficient even at temperatures within the range of 100 to 150° C. The ethoxylation is aided by the presence of materials of a basic reaction, as, for example, the free bases corresponding to the cations present in the acylaminocarboxylic or their compounds of basic reactions, such as their carbonates, soaps, alcoholates, etc. The quantity of such catalysts can constitute 0.1 to 10% by weight and preferably 0.1 to 2% by weight of the starting material.

If the reaction is effected in an autoclave, the pressure may be varied between any value, from about 1 atmosphere gauge to the saturation pressure of the ethylene oxide at the reaction temperature used. Advantageously, operation is effected in such a manner that fresh ethylene oxide is forced into the autoclave, either continuously or batchwise, as a function of the decrease in pressure.

It is advisable to flush the autoclave with an inert gas, as for example, carbon dioxide or nitrogen, before starting the reaction and possibly to pass small quantities of the inert gas under pressure into the autoclave, so that a small pressure, as for example, between about 0.5–5 atmospheres gauge is obtained prior to the reaction.

The quantity of the ethylene oxide to be added depends on the desired properties of the reaction product. Upon the addition of even 1 mol of ethylene oxide per mol of the N-acylaminocarboxylate, there is obtained a noticeable improvement in the solubility properties, and particularly the resistance to hard water. Of particular technical interest are compounds containing from 3 to 10 mols of ethylene oxide, though larger amounts, as for example, up to about 20 mols of ethylene oxide may be added.

The addition compounds, in accordance with the invention, exhibit low foaming, high resistance to hard water and excellent washing properties. The compounds are particularly suitable as non-foaming white laundering detergents, especially adapted for washing machine use.

When used as detergents for white goods the addition compounds are preferably employed in the form of their water-soluble salts, with inorganic or organic bases, in an aqueous solution, at a concentration of at least 0.5–15 grams per liter, and preferably 1 to 6 grams per liter. The addition compounds may be combined with all the customary components of washing agents. These include the washing alkalis or neutral salts. As washing alkalis there may be used, in particular, the carbonates or orthophosphates of the alkalis or organic bases, while as neutral salt, sodium sulfate may be mentioned. As further washing-agent components, there enter into question the anhydric phosphates, primarily the pyrophosphates, polyphosphates and metaphosphates. The two latter include, in particular $Na_3P_5O_{10}$ and $(NaPO_3)_6$. The washing-agents or components may additionally contain peroxy compounds, and in particular, perborates in order to obtain a bleaching action. The washing effect may further be increased by the addition of known water-soluble colloid substances, such as ether carboxylic acids or ether sulfonic acids of cellulose or starch, cellulose sulfates, alginates, methyl cellulose, glue, gelatins, etc. The detergents containing a novel addition compound, in accordance with the invention, may, for example, have the following composition:

5–70%, preferably 15–50% surface-active N-oxyethylated acylaminocaproic acids or their water-soluble salts
0–70%, preferably 10–50% washing alkalis
0–50%, preferably 0–20% neutral salts
0–2%, preferably 0.05–1% colloids
0–40%, preferably 5–20% other washing agent additives
0–0.5%, preferably 0.01–0.2% optical brighteners

The following examples are given by way of illustration and not limitation. In all of the examples, the percentages are percentages by weight:

Example 1

In a stainless steel autoclave provided with an agitator 210 grams of the sodium salt of stearoylaminocaproic acid (0.5 mol) are heated to 120° C. under a nitrogen atmosphere of 3 atmospheres and thereupon 176 grams of liquid ethylene oxide (4 mols) are introduced from a storage autoclave by nitrogen pressure in such portions that the pressure increase is not more than 10 atm. The absorption of the ethylene oxide can be noted from the pressure decrease which occurs. The solid reaction product obtained after cooling can be recrystallized from methyl alcohol.

Example 2

In a stainless steel autoclave provided with an agitator 196 grams of the sodium salt of palmitoylaminocaproic acid (0.5 mol) are heated to 120–130° C. under a nitrogen atmosphere of 3 atmospheres and thereupon reacted with 132 grams (3 mols) of ethylene oxide, which is added in portions from a storage autoclave in accordance with the drop in pressure observed. A practically colorless mass is obtained as reaction product.

Example 3

In a four-neck glass flask of 500 cc. capacity provided with agitator, thermometer, gas inlet and gas outlet tubes, 210 grams of the sodium salt of stearolyaminocaproic acid are heated in a stream of nitrogen up to the melting point, i.e., up to 210° C., whereupon ethylene oxide is introduced into the molten mass until the increase in weight is 88 grams (2 mols ethylene oxide). The cooled solid reaction product can be recrystallized from methyl alcohol for its purification.

Example 4

Detergents of the following composition are prepared in a manner known per se:

	Percent by weight
Active substance	15
$Na_5P_3O_{10}$	14
$Na_4P_2O_7$	21
Na_2SO_4	20
Cellulose glycolate	0.2
Balance water	

As active substances, there are employed the compounds prepared in accordance with Examples 1 to 3. All of these detergents when used in concentrations of 2–10 grams per liter active substance have excellent white-laundry washing properties. The washing agents (detergents) can contain in addition to the abovementioned substances also 10% by weight $NaBO_2 \cdot H_2O_2 \cdot 3H_2O$ and 3% by weight $MgSiO_3$.

We claim:

1. The addition product of 1 to 20 mols of ethylene oxide with a salt of an N-acylaminocarboxylic acid, having the general formula:

$$R—CO—[NH—(CH_2)_n—CO]_x—OMe$$

26 carbon atoms, n is a whole number from 3 to 7 and x is a whole number from 1 to 5 and Me is an inorganic cation selected from the group consisting of sodium, potassium, and lithium.

2. Addition compounds, according to claim 1, containing from 3 to 10 mols of ethylene oxide.

3. Addition compound, according to claim 1, in which R is a fatty acid radical containing from 10 to 20 carbon atoms.

4. A detergent containing the addition product of 1 to 20 mols of ethylene oxide with a salt of an N-acylaminocarboxylic acid, having the general formula: $R—CO—[NH—(CH_2)_n—CO]_x—OMe$ in which R is a fatty acid radical containing from 8 to 26 carbon atoms, n is a whole number from 3 to 7 and x is a whole number from 1 to 5 and Me is an inorganic cation selected from the group consisting of sodium, potassium and lithium.

5. Method for the preparation of hard-water resistant surface active derivatives of N-acylaminocarboxylic acid which comprises contacting an N-acylaminocarboxylic acid salt containing a higher fatty acid radical with ethylene oxide at a temperature of at least 100° C., and recovering the addition product formed.

6. Method according to claim 5, in which said N-acylaminocarboxylic acid salt has the general formula:

$$R—CO—[NH—(CH_2)_n—CO]_x—OMe$$

in which R is a fatty acid radical containing from 8 to 26 carbon atoms, n is a whole number between 3 and 7, x is a whole number between 1 and 5 and Me is an inorganic cation selected from the group consisting of sodium, potassium, and lithium.

7. Method according to claim 6, in which said contacting is effected at a temperature between about 100 and 250° C.

8. Process according to claim 7, in which said contacting is effected at an elevated pressure at temperature between about 100 and 150° C.

9. Process according to claim 5, in which said contacting is effected in the presence from about 0.1 to 10% of an alkaline material.

References Cited in the file of this patent

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2,131,142 Orthner et al. ---------- Sept. 27, 1938

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,943,099 June 28, 1960

Manfred Dohr et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 17, for "stearolyaminocaproic" read -- stearoylaminocaproic --; line 49, before "26 carbon atoms," insert -- in which R is a fatty acid radical containing from 8 to --.

Signed and sealed this 29th day of November 1960.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
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