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3,707,511

ANIONIC DETERGENT COMPOSITIONS CONTAINING FOAM BOOSTING SUCCINIC ACID DERIVATIVES

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6 Claims

ABSTRACT OF THE DISCLOSURE

This disclosure relates to water-soluble nitrogen-containing derivatives of succinic acid characterized by an alkyl or 2-alkenyl substituent containing from 10 to 16 carbon atoms therein. These compounds are useful as suds-boosters, suds-stabilizers, and as active detergents. The specification discloses the preparation of these compounds and their use in conjunction with various detergents.

This application is a division of our copending U.S. application Ser. No. 645,636, filed June 13, 1967 now abandoned.

This invention is directed to water-soluble nitrogen-containing compounds and to detergent compositions containing said compounds.

One of the conspicuous properties of surface active agents is an ability to produce suds or a foam. However, all detergents are not good foam producers. Accordingly, it is often necessary to enhance both the amount of foam produced and the stability of the foam since many consumers consider the appearance of foam to be an empirical measure of the activity of the detergent and as a criterion by which to estimate the amount of detergent formulation to be used.

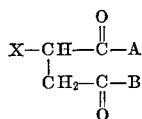
A principal object of this invention is to provide novel compositions of matter.

Another object of the invention is to provide compounds which are suitable for use as detergent-active ingredients, i.e., cleaning agents, in detergent solutions.

A further object of the invention is to provide compounds suitable for use as adjuvants, i.e., foam boosters and stabilizers, in detergent formulations.

A still further object of the invention is to provide improved detergent formulations.

These and other related objects are achieved by providing nitrogen-containing compounds of the general formula:



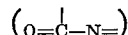
wherein: X is an acyclic hydrocarbyl group, i.e., an alkyl group or an alkenyl group, of from about 10 to about 16 carbon atoms, preferably 11 to 15 carbon atoms; A and B are selected from the following groups: 2-hydroxyethyl-amino $[\text{NHCH}_2\text{CH}_2\text{OH}]$, N-methyl-2-hydroxyethylamino $[\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}]$, 2-hydroxyethylammoniumoxy $[\text{O}-\text{N}^+\text{H}_3\text{CH}_2\text{CH}_2\text{OH}]$; and N-methyl-2-hydroxyethylammoniumoxy $[\text{O}-\text{N}^+\text{H}_2(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}]$; ammoni-

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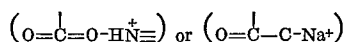
um oxy $[\text{—O}-\text{N}^+\text{H}_4]$ and alkali metal oxy groups $[\text{—O}-\text{M}^+]$ wherein M is an alkali metal, preferably sodium or potassium, with the proviso that at least one of the groups A or B must be a nitrogen-containing group, preferably a nitrogen-containing organic group of the groups mentioned above.

The nitrogen-containing compounds, generically defined above, can be prepared by reacting a suitable aliphatically substituted succinic acid-producing compound with at least about an equivalent amount of a nitrogen-containing compound, or mixture thereof, having within its structure an imino group $(=\text{NH})$, e.g., a primary or secondary amino compound. The term "equivalent amount" means an amount which is sufficient to react with both carboxyl groups of the succinic acid. Suitable nitrogen-containing reactants include lower alkanolamines, i.e., 1-4 carbon atoms, such as ethanolamine and N-methylethanolamine, and mixtures of these compounds.

The above described reaction for the preparation of the herein described compounds involves the reaction of the aliphatically substituted succinic acid-producing compound, e.g., an aliphatically substituted succinic anhydride, with an amino compound to provide direct attachment of the nitrogen atom to an acyl radical, either directly or through an intermediate oxygen atom to form either amide linkages



a salt linkage



or a mixed product, i.e., one having an amide linkage and a salt linkage.

Reaction products of the above described reaction can be illustrated by the following classes of compounds:

N,N'-bis(hydroxyethyl)-alkenylsuccinamide;
N,N'-methyl-N,N'-(hydroxyethyl)-alkenylsuccinamide;
N-(hydroxyethyl)-N'-(hydroxyethyl) ammonium-alkenyl-succinamate; and
(N-methyl-N-hydroxyethyl)-N'-methyl-N'-(hydroxyethyl) ammonium-alkenylsuccinamate,
alkali metal-beta-alkenyl-N-(2-hydroxyethyl) succinamate,
ammonium-beta-alkenyl-N-(2-hydroxyethyl) succinamate,
alkali metal-alpha-alkyl-N-(2-hydroxyethyl) succinamate,

and the like, wherein the hydrocarbyl groups are alkenyl or alkyl groups containing from about 10 to about 16 carbon atoms such as decenyl, undecenyl, dodecenyl, tridecenyl, tetradecenyl, pentadecenyl, decyl, dodecyl, tridecyl, pentadecyl, and the like. Preferred substituent groups on the succinic acid molecule are those containing from about 11 to about 15 carbon atoms.

The alkenyl, and particularly 2-alkenyl, nitrogen-containing derivatives constitute preferred groups of compounds for use as suds boosters, stabilizers, and detergent actives.

It will be appreciated that the position of the hydrocarbyl substituent, as shown above, is merely relative. In the case of a bis-amide derivative, the location of the hydrocarbyl substituent is immaterial since the compound is symmetrical. However, when A or B has an ionic linkage, e.g., in the case of an ammonium salt or an alkali metal salt, the compound is not symmetrical. In such case, the

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hydrocarbyl group can be located on either the alpha or beta carbons with respect to the carboxy group.

Specific compounds having good foam boosting and stabilizing properties include N-hydroxyethyl-N'-hydroxyethyl-ammonium-2-dodecenylsuccinamate; N,N'-bis(hydroxyethyl)-2-dodecenylsuccinamide; N,N'-bis(hydroxyethyl)-2-hexadecenylsuccinamide; and the like.

The herein described succinic acid derivatives have been found to be effective as foam improving adjuvants, e.g., foam boosters and foam stabilizers. They have utility as a component of organic detergent formulations, particularly formulations containing organic detergents, such as alkylaryl sulfonates. The compounds of this invention can be incorporated into known detergent formulations, generally in such amounts that the weight to weight ratio of detergent to succinic acid derivative is from about 5:1 to 1:1 and preferably from about 4:1 to about 3:1.

The term "detergent" as used herein refers to organic compounds which clean by a physico-chemical action involving alternation of surface tension rather than by direct solution or chemical reaction. The term "detergent formulation" refers to mixtures containing, in addition to a detergent, any of the well known materials conventionally admixed with detergents. Such materials include fillers, builders, bleaching agents, optical brighteners, dyes, perfumes, soil-suspending agents, suds-boosters, and the like.

The herein disclosed foam boosters and stabilizers have particularly beneficial effects when used in conjunction with alkylaryl sulfonates of both the biodegradable (LAS) and non-biodegradable types, wherein the alkyl chain contains an average of from about 7 to about 18 carbon atoms. Preferably, the alkyl group contains an average of from about 10 to about 14 carbon atoms, such as may be obtained from olefins or kerosene. These detergents are made in a known manner by alkylating the aromatic hydrocarbon and thereafter sulfonating and neutralizing the product with an alkali metal or ammonium-containing compound, e.g., a hydroxide.

Illustrative detergent formulations are shown in Table 1, below.

TABLE 1

	1	2	3	4	5	6	7	8
Na alkenesulfonate ¹	30					5		
NH ₄ alkylsulfate.3EO condensate ²	12		15				15	
Na dodecyl sulfate.....				15				15
Na alkylbenzenesulfonate ³	12				25	10		5
Na tripolysphosphate.....		20	55	45	30	50		
Na toluenesulfonate.....		5	1	3	2	2	2	
Na xylenesulfonate.....	10							3
Na nitrilotriacetate.....							40	
Na ₂ CO ₃		5						
Tetrapotassium pyrophosphate.....	5							
Suds booster ⁴		6			6			
Do ⁵			12			5		
Do ⁶								7
Do ⁷				15			5	
Do ⁸		9						
Sodium silicate solids (2.4 ratio).....		6	6	6	6	6	6	
Sodium tetraborate.....		5			10			
Sodium sulfate.....		13		8	14	16	22	
Water.....	52	10	11	8	7	6	10	70
Total.....	100	100	100	100	100	100	100	100

¹ Derived from alpha olefins having 12 to 14 carbon atoms.

² Ammonium salt of a sulfated condensate of ethylene oxide and long-chain mixed primary alcohols in the molar ratio of 3 moles of ethylene oxide per mole of alcohol wherein the mixed alcohols have 12 and 14 carbon atoms in a ratio of 1:2.

³ In which the phenyl group is randomly positioned in the secondary positions along a straight hydrocarbon chain of 10 to 14 carbon atoms.

⁴ N-hydroxyethylammonium N'-hydroxyethyl-2-dodecenyl succinamate.

⁵ N,N'-bis(hydroxyethyl)-2-decenylsuccinamide.

⁶ N-methyl-N'-hydroxyethylammonium-N'-methyl-N'-hydroxyethyl-2-hexadecenylsuccinamate.

⁷ N,N'-bis(hydroxyethyl)-2-hexadecenylsuccinamide.

⁸ N,N'-bis(hydroxyethyl)-2-alkenylsuccinamide wherein the alkenyl group contains from 11 to 15 carbon atoms.

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EXAMPLE I

Preparation of bis-monoalkanolamide derivative

Forty-two grams (0.15 mole) of a mixture of 2-alkenylsuccinic anhydride having from 11 to 15 carbon atoms in the alkenyl chain, were added to 50 grams (0.82 mole) of monoethanolamine, with stirring, at a temperature of between 5° C. and 15° C. The mixture was then distilled at a temperature of about 146° C. to 151° C., for about 2.3 hours, during which time about 2 grams of distillate were collected.

The temperature of the remaining reaction product was then reduced to about 80° C. and an additional 30 grams of distillate were removed under a vacuum of 2.5 millimeters of mercury.

The residue was found to be about 57 grams of the crude reaction product (0.148 mole calculated as the bis-amide) having only one infra-red absorption peak in the carbonyl region at about 6.03 microns.

EXAMPLE II

Preparation of amide ammonium salt derivative

A chloroform solution comprising 6.4 grams (0.024 mole) of 2-dodecenylsuccinic anhydride and 30 millimeters of chloroform was mixed with 2.9 grams (0.048 mole) of ethanolamine. A slight warming of the mixture was noted. The solvent was evaporated off at room temperature, the last traces being removed under vacuum at a temperature below 50° C. The residue was the monoethanolamide-monoethanol ammonium salt derivative of 2-dodecenylsuccinic acid.

EXAMPLE III

N,N'-bis(hydroxyethyl) alkylsuccinamide is prepared from a mixture of alkylsuccinic anhydrides having from 11 to 15 carbon atoms in the alkyl chain by the procedure shown in Example I, above. The alkylsuccinic anhydride is prepared by hydrogenating the corresponding alkenylsuccinic anhydride.

EXAMPLE IV

N,N'-bis(hydroxyethyl) dodecyl succinamide is prepared from dodecylsuccinic anhydride following the procedure outlined in Example I.

EXAMPLE V

Example V illustrates the detergent properties of representative compounds within the scope of this invention, as compared with a standard detergent, i.e., an alkyl benzene sulfonate derived from tetra- and penta-propylene. Detergency was evaluated by means of a Tergo-o-Tometer, as described in the May 1950 issue of the Journal of the American Oil Chemists Society, pages 153-159.

In these tests, the apparatus was immersed in a water bath adjusted to maintain the temperature of the wash solution at 120° F.±2°. The paddle of the apparatus was adjusted to oscillate through an arc of 320° F. at 90 cycles per minute.

In conducting each test the detergent was added to the washpot of the machine and then 1,250 milliliters of water having a hardness of 120 parts per million, calculated as CaCO₃, was added. The machine was started and the solution agitated until the detergent was dissolved. Four pieces of cloth 4½ inches x 6 inches, soiled with a standard soil prepared from vacuum cleaner dirt, were placed in the machine and washed for 20 minutes. The cloths were then removed and hand squeezed. The washpot was emptied and refilled with clear rinse water having the same hardness as the wash water at a temperature of 120° F.±2°. The cloths were then agitated in the rinse water for 5 minutes. The cloths were then removed, hand squeezed, and ironed dry.

Detergent efficiency was evaluated by measuring and comparing the reflectance of the soiled cloth before

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washing and the reflectance of the cloth after the washing cycle. Detergency units are the differences between these readings. Reflectance was measured with a Hunter Reflectometer equipped with a green filter.

The following table tabulates the relative detergency data in terms of Detergency Units:

TABLE 2

Compounds	Detergency units unbuilt 0.05% compound
1..... Ethanolammonium salt of N-hydroxyethyl-2-dodecenylsuccinamic acid.	3.4
2..... Ethanolammonium salt of N-hydroxyethyl-2-hexadecenylsuccinamic acid.	2.2
3..... N,N'-bis(hydroxyethyl)-2-dodecenylsuccinamide.	5.0
4..... Sodium alkylbenzene sulfonate (derived from tetra- and pentapropylene).	-0.4

EXAMPLE VI

This example illustrates the ability of representative compounds to clean dishes in a standard test which measures the number of uniformly soiled dinner plates which can be cleaned under standard conditions with the composition being tested. The dishes are soiled with a blend of 9 parts by weight of emulsifier-free vegetable shortening, 8 parts by weight of bread flour, and a green dye. In the test each plate is soiled with 1 teaspoonful of the soiling material which is spread evenly over each plate. The dishes are then washed by a standard technique in six quarts of water of uniform hardness (120 p.p.m. as CaCO_3) at a temperature of 116° F. containing a measured amount of the cleaning agents being tested. The end point of the test is reached when the foam produced by the test composition no longer covers the surface of the washing solution.

Table 3, below, shows the number of dishes cleaned by a linear alkyl benzene sulfonate (LAS) having from 9 to about 15 carbon atoms and sodium lauryl sulfate, each with and without a representative N,N'-bis(hydroxyethyl)-2-alkenylsuccinamide additive, as shown in column 2.

TABLE 3

Detergent (1.8 grams)	Additive (0.54 gram)	Number of dishes
LAS.....	None.....	28
	Alkenyl (C_{11} - C_{15}).....	42, 37
Sodium lauryl sulfate.....	None.....	17
	Alkenyl (C_{11} - C_{15}).....	25
LAS.....	Dodecenyl.....	38

EXAMPLE VII

This example illustrates the ability of the herein disclosed alkenyl succinic acid derivatives to function as foam stabilizers as measured by a standard test in which the weight of soil necessary to destroy the foam produced by 9 grams of the detergent materials in six quarts of 120 p.p.m. hardness (calculated as CaCO_3) was measured.

In this test, a solution containing only detergent and stabilizer was prepared by dissolving these materials in sufficient water to provide a concentration equivalent to 9 grams per six quarts of water of a detergent composition comprising 30% sodium alkylbenzene sulfonate (propylene tetramer type) and 9% of the stabilizer. Therefore, the solution contained 2.7 grams of sulfonate and 0.81 gram of the stabilizer. The control contained only the detergent. Three hundred milliliters of this solution

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were placed in a beaker and heated to 125° F. The solution was then transferred to a Waring Blendor and agitated at low speed for one minute, at which point the temperature was about 116° F. Then, while continuing agitation, soil comprising 9 parts by weight of an emulsifier-free vegetable shortening and 8 parts by weight of bread flour was added dropwise from a weighed beaker of the soil. The soiling agent was warmed to the softening point, but not melted, while being added to the solution. When the foam had substantially disappeared into the vortex of the agitated solution, the addition of soil was stopped and the beaker of soil reweighed. The difference in weight for two identical tests was determined and the average reported as a measure of the stability of the foam obtained from the active materials employed.

TABLE 4

Foam stabilizer:	Soil (grams)
None (control)	2.11
Coconut monoethanolamide	2.90
Monoethanolamide - monoethanolammonium salt of 2-dodecenylsuccinic acid	4.25
Monoethanolamide - monoethanolammonium salt of 2-hexadecenylsuccinic acid	2.41
N,N'-bis - monoethanolamide of 2 - dodecenylsuccinic acid	4.05

What is claimed is:

1. A foamable detergent formulation capable of producing an enhanced amount of foam comprising:

(1) an anionic organic detergent selected from the group consisting of:

- (a) alkene sulfonates,
- (b) alkylbenzene sulfonates,
- (c) alkyl sulfates, and
- (d) ethoxylated alkyl sulfates; and

(2) a foam improving adjuvant compound selected from the group consisting of:

- (a) N-hydroxyethyl-N'-hydroxyethylammonium-2-dodecenylsuccinamate,
- (b) N,N'-bis(hydroxyethyl)-2 - dodecenylsuccinamide,
- (c) N,N'-bis(hydroxyethyl)-2-hexadecenylsuccinamide,
- (d) N,N'-bis(hydroxyethyl)-2-decenylsuccinamide,
- (e) N-methyl-N-hydroxyethyl - ammonium - N'-methyl-N'-hydroxyethyl - 2 - hexadecenylsuccinamate,
- (f) a mixed N,N' - bis(hydroxyethyl) C_{11} - C_{15} 2-alkenylsuccinamide,
- (g) a mixed N,N'-bis(hydroxyethyl) C_{11} - C_{15} alkylsuccinamide,
- (h) N,N'-bis(hydroxyethyl) - dodecylsuccinamide, and
- (i) monoethanolamide - monoethanolammonium salt of 2-hexadecenylsuccinic acid;

the weight ratio of said detergent to said adjuvant compound being from about 5:1 to about 1:1.

2. The foamable detergent formulation defined by claim 1 wherein the weight ratio of detergent to adjuvant compound is from about 4:1 to about 3:1.

3. The foamable detergent formulation defined by claim 2 wherein the foam improving adjuvant compound is a mixed N,N'-bis(hydroxyethyl) C_{11} - C_{15} 2-alkenyl succinamide.

4. The foamable detergent formulation defined by claim 2 wherein the foam improving adjuvant compound is N,N'-bis(hydroxyethyl)-2-dodecenylsuccinamide.

5. The foamable detergent formulation defined by claim 2 wherein the foam improving adjuvant compound is N,N'-bis(hydroxyethyl)-2-hexadecenylsuccinamide.

6. The foamable detergent formulation defined by claim 2 wherein the foam improving adjuvant compound is the

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