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DETERGENT COMPOSITION CONTAINING MONOAMIDE HYDROCARBYL SULFONIC ACID SALTS OF HYDROCARBYL SUCCINIC ACID

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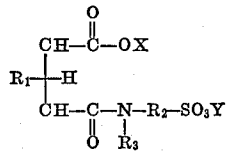
No Drawing. Original application Dec. 17, 1969, Ser. No. 885,977, now Patent No. 3,732,290. Divided and this application Sept. 27, 1971, Ser. No. 184,203

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ABSTRACT OF THE DISCLOSURE

Detergent composition containing as active materials monoamide hydrocarbyl sulfonic acid salts of hydrocarbyl succinic acid of the formula



in which R_1 is a hydrocarbyl group of 8 to 30 carbon atoms; R_2 is a hydrocarbylene group of 1 to 8 carbon atoms; R_3 is H, a hydrocarbyl group of 1 to 8 carbon atoms, or $—R_2—SO_3Y$; X is H or Y; and Y is a water-soluble salt-forming cation; and non-phosphate builders and additives.

CROSS-REFERENCE TO RELATED APPLICATION

This application is a division of U.S. application Ser. No. 885,977, filed Dec. 17, 1969, now Pat. No. 3,732,290.

BACKGROUND OF THE INVENTION

The present invention is concerned with the field of synthetic detergents, and more particularly with monoamide hydrocarbyl sulfonic acid salts of hydrocarbyl succinic acid suitable for use as active detergent components in biodegradable and phosphate-free detergent compositions.

Increased concern over water pollution has resulted in significant changes in household detergents. Initially the major emphasis was placed upon producing biodegradable surface active components for detergent compositions. The resulting shift from surface active materials containing branched hydrocarbyl groups to linear materials such as linear alkyl benzene sulfonates and alpha olefin sulfonates has resulted in a significant decrease in pollution attributed to non-biodegradability. Thus, the undesirable foam which had formerly been carried by sewage effluents into the lakes and streams is no longer increasing because the linear alkyl groups are susceptible to bacterial attack. However, the shift to the linear materials has placed an enormous burden upon the chemical industry in attempting to meet the ever increasing demand for the linear detergent precursors.

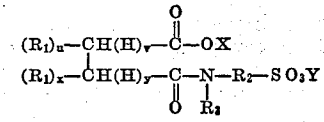
The previously mentioned conventional detergents, the branched and linear alkyl benzene sulfonates and the alpha olefin sulfonates are inadequate in ordinary detergent uses in respect to soil removal in the absence of sequestering type builders such as phosphates. Increasing evidence appears to indicate that phosphates contribute to the growth of algae in the Nation's streams and lakes. This algae growth poses a serious pollution threat to the maintenance of clear good domestic water supply. Thus, it is important that detergent compositions be provided

which neither produce undesirable foam nor contain phosphates which contribute to algae growth.

In contrast to the problems encountered in utilizing the conventional detergent compositions, the present invention provides novel biodegradable detergent compositions which exhibit high detergency and soil removal ability in the absence of phosphate builders.

SUMMARY OF THE INVENTION

Novel compositions of matter useful as phosphate-free detergent compositions comprise monoamide hydrocarbyl sulfonic acid salts of hydrocarbyl succinic acid. These materials may be represented by the following structural formula:



in which u, v, x and y are 0 or 1, the sum of u and v is 1, the sum of x and y is 1, the sum of u and x is 1, the sum of v and y is 1, R_1 is a hydrocarbyl group of 8 to 30 carbon atoms; R_2 is a hydrocarbylene group of 1 to 8 carbon atoms; R_3 is H, a hydrocarbyl group of 1 to 8 carbon atoms, or $—R_2—SO_3Y$; X is H or Y; and Y is a water-soluble, salt-forming cation. In a preferred embodiment, the hydrocarbyl radical, R_1, contains from 12 to 22 carbon atoms. It is also preferred that X and R_3 are H and R_2 is ethylene.

The salt forming cations represented by Y in the above formula are exemplified by alkali metal and alkaline earth metal cations, ammonia, and various organic cations such as tertiary amino materials. Examples of these cations are those of the following structure:

$NH_2^+(CH_2CH_2OH)_2$ or $NH^+(CH_2CH_2OH)_3$

Generally the alkali metal cations are preferred, and most particularly sodium ion is preferred.

In general, when the compounds of the present invention are formulated as detergent compositions, additional compatible ingredients may be incorporated therein to enhance their detergent properties. Such ingredients may include, but are not limited to, anti-corrosion, anti-redeposition, bleaching, and sequestering agents, and certain organic and inorganic alkali, alkaline earth salts other than phosphates, such as inorganic sulfates, carbonates or borates and organic salts of polycarboxylic acids, e.g., trisodium salt of nitrilo triacetic acid, the tetrasodium salt of ethylene diamine tetracetic acid, the polysodium salt of ethylene-maleic acid copolymer, etc.

Surprisingly, the novel compounds of the present invention exhibit high detersive characteristics in the absence of phosphate builders. In particular, formulations containing sodium or potassium sulfates as a major additive ingredient are preferred. As previously noted, this is significant in view of the fact that most household heavy-duty detergent compositions require the presence of sequestering-type builders such as phosphates in order to achieve satisfactory detergency.

In general, compatible ingredients other than water may be employed in amounts ranging from 60 to 900 parts and, preferably, from 70 to 250 parts by weight per 100 parts of the active material. In addition, the detergent compositions may comprise from 0 to 700 parts by weight of water per 100 parts of active material. The lower range of water concentration is used for compounding particulate formulations which may contain up to about 15 parts of water per 100 parts of the active material. The

upper range of water concentration is used to prepare liquid formulations. For this use a range of 100 to 400 parts of water per 100 parts of the amide is preferred.

The compounds of this invention are preferably prepared by the direct reaction of a hydrocarbyl succinic anhydride with the aminohydrocarbyl sulfonic acid salt. The succinic anhydride compounds are well known in the art and are produced by the condensation of maleic anhydride with a mono olefin. This reaction which leaves residual unsaturation in the adjunctive hydrocarbyl group yields materials which may be characterized as alkenyl or substituted alkenyl succinic anhydrides. Mild hydrogenation of these materials may be effected to produce alkyl or substituted alkyl succinic anhydrides which are of equal effectiveness in producing the active compositions of this invention.

Examples of the hydrocarbyl radicals include alkyl or alkenyl or aromatic substituted alkyl or alkenyl materials. Examples of the alkyl groups include tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triacontyl, etc. The alkenyl groups include dodecenyl, tridecenyl, tetradecenyl, pentadecenyl, hexadecenyl, heptadecenyl, octadecenyl, nonadecenyl, eicosenyl, heneicosenyl, docosenyl, tricosenyl, tetracosenyl, pentacosenyl, hexacosenyl, heptacosenyl, octacosenyl, nonacosenyl and tricontenyl, etc. These groups may be either straight or branched chained. The point of attachment may be at any place on the chain. Aromatic substitution may be employed if appropriately placed.

The amidification reaction is accomplished by contacting stoichiometric quantities of the anhydride with the amino sulfonic acid salts at temperatures in the range of 100 to 220° C. These salts, such as the taurine salts, are readily available in commercial quantities. Temperatures higher than about 250° C. should be avoided because significant quantities of succinimides which are not suitable for the purpose of this invention may be produced.

The amino hydrocarbyl sulfonic acids which are employed in the amidification reaction are of the formula:

$$\begin{array}{l} NH-R_2-SO_3Y \\ | \\ R_3 \end{array}$$

in which R_2, R_3, and Y are as previously described. Thus R_2 may be saturated or unsaturated, aliphatic, alicyclic or aromatic and the groups $-SO_3Y$ and $-NH-R_3$ may be attached at any point on the hydrocarbylene radical. Examples of the materials include salts of taurine, N-methyltaurine, N-ethyltaurine, N-hexyltaurine, amino aromatic sulfonates such as ortho, meta and para amino benzene sulfonic acids, 4-amino-2-toluene sulfonic acid, 4-amino-2-xylene sulfonic acid, etc.

The following examples describe the preparation of the detergent compounds of this invention. The examples are intended to be illustrative and non-limiting.

Example 1—Preparation of hexadecenyl succinic anhydride

A mixture of 336 g. (1.5 mols) of an alpha olefin having an average of 16 carbon atoms and an average molecular weight of 224 was stirred slowly with 49 g. (0.5 mols) of maleic anhydride in a 1-liter, 3-neck round bottom flask equipped with an explosion-proof stirrer, a drying tube condenser, and dropping funnel, and continuously flushed with nitrogen. The reaction was continued for about seven hours at a gradually increasing temperature starting at 85° C. and stopping at 238° C. At the end of this time, infrared analysis showed less than 1% of maleic anhydride remaining. The mixture was transferred to a distillation flask. Excess olefins were removed by distillation at approximately 1 mm. pressure until about 5% olefin remained. The stirred bottoms product from this distillation was then heated and filtered through Celite to give 100 g. of crude alkenyl succinic anhydride.

Example 2—Hydrogenation of C_{16} alkenyl succinic anhydrides to produce alkyl succinic anhydride

In a 500 ml. Fisher-Porter bottle, 40.0 g. of 2-n-hexadecenyl succinic anhydride was dissolved in 250 ml. of absolute ethanol. To this was added 4.0 g. of palladium on carbon catalyst. Hydrogen was added to the bottle to give 60 p.s.i.g. of pressure. The contents were heated to 50° C. and agitated with incremental addition of hydrogen until a total of 200 p.s.i. of hydrogen was taken up. The solution was filtered while warm to remove the catalyst, and then the alcohol was removed by evaporation at 50° C. to give 37 g. of hexadecyl succinic anhydride. An infrared spectrum showed the complete absence of double bonds.

Example 3.—Preparation of monoamide of C_{16} alkyl succinic anhydride with taurine

12.5 g. (0.1 mol) of taurine was dissolved in 100 ml. of water in a beaker. Sodium hydroxide was added to a pH of 9–10. The material was then dried by evaporation. 2.94 g. (.02 mol) of the dry salt was combined with 6.44 g. (.02 mol) of alkyl succinic anhydride produced in Example 2. The mixture was placed in a beaker and heated to its melting point and stirred for two hours. The material was allowed to cool, was dissolved in ethanol and recrystallized. Based on a hyamine titration,[1] the recovered product was 97% pure. The product had infrared spectra which showed strong amide adsorptions at 1690–1710 $cm.^{-1}$ and sulfonate absorptions at 1170–1230 and 1050 $cm.^{-1}$, indicating the production of the monoamide sulfonate salt of the anhydride. The presence of hydrogen ion indicates that the carboxylic group remains unneutralized.

Example 4.—Preparation of monoamide of C_{16} alkyl succinic anhydride with p-aminophenyl sulfonic acid

The same procedure was followed as in Example 3, using 9.66 g. C_{16} alkyl succinic anhydride (0.03 mol) and 5.85 g. (.03 mol) of the sodium salt of p-aminophenylsulfonic acid.

Detergency of the compounds of the present invention is measured by their ability to remove natural sebum soil from cotton cloth. By this method, small swatches of cloth, soiled by rubbing over face and neck, are washed with test solutions of detergents in a miniature laboratory washer, and the reflections of the various cloths measured and compared. The results obtained are expressed as relative detergency values.

The relative detergency value is obtained by comparing and correlating the reflectance value results from the test solution with the results from two defined standard solutions.

The two standard solutions are selected to represent a detergent system exhibiting relatively high detersive characteristics and a system exhibiting relatively low detersive characteristics.

By testing each soiled cotton cloth against the standardized solutions, as well as the test solutions, the results can be accurately correlated. The two standard solutions were prepared from the following detergent formulations:

Low detersive standard (Control A)

Ingredient:	Weight percent
Alkylbenzene sulfonate	35
Sodium triphosphate	40
Water	8.5
Sodium sulfate	8
Sodium silicate	7
Carboxymethylcellulose	0.8

[1] By the method of House and Darragh, Analytical Chemistry, 26 1492 (1954).

High detersive standard (Control B)

Ingredient:	Weight percent
Linear alkylbenzene sulfonate (LAS)	7.5
Tallow alcohol sulfate	10
Sodium triphosphate	47.5
Water	10
Sodium sulfate	13
Sodium silicate	5
Carboxymethylcellulose	1

The standard exhibiting high-detersive characteristics was prepared by dissolving a relatively large amount of the above formulation (2.0 g.) in 1 liter of 300 p.p.m. hard water (calculated at ⅔ calcium carbonate and ⅓ magnesium carbonate). The low detersive standard contained a relatively low concentration of the formulation (1.0 g.) dissolved in 1 liter of 300 p.p.m. water (same basis).

formulations could be used to wash different parts of the same swatch. This arrangement ensured that all four formulations were working on identical soil (natural facial soil). Relative detergency (RD) values were calculated from soil removals (SR), according to the equation:

$$RD=2+4\frac{\text{Percent } SR_{Test}-\text{Percent } SR_{Control\ A}}{\text{Percent } SR_{Control\ B}-\text{Percent } SR_{Control\ A}}$$

For comparison, a commercial available 20% active LAS detergent formulation was measured at 0.1 percent by weight concentration in 50 p.p.m. hard water.

Detergency test results obtained on a variety of the subject monoamide phosphate-free formulations are given in the following table. The components of each amide are identified by reference to the structural formula in column 2 of the specification. In each test Y is Na.

TABLE

Test	Active: Amide components Type	R_1 [1]	R_2	R_3	X	Active: Weight percent	Builder: Type	Builder: Weight percent	Detergency index concentrations [2]: 0.1%	0.2%
1	LAS [3]					25	Phosphate	40	6.2	6.6
2	Amide [4]	C_{14}	Ethylene	H	H	15	NTA [5]	20	5.7	6.4
3	do.[4]	C_{14}	do	H	H	25		0	3.9	4.6
4	do.[4]	C_{16}	do	H	H	15	NTA	20	5.4	6.7
5	do.[4]	C_{16}	do	H	H	25		0	4.1	5.0
6	do.[4]	C_{18}	do	H	H	15	NTA	20	3.8	5.5
7	do.[4]	C_{18}	do	H	H	25		0	3.0	4.1
8	do.[4]	C_{20}	do	H	H	15	HTA	20	3.4	5.4
9	do.[4]	C_{16}	do	Methyl	H	15	NTA	20	3.7	6.0
10	do.[4]	C_{16}	do	do	H	25		0	3.3	6.0
11	do.[4]	C_{18}	do	do	H	15	NTA	20	4.9	6.4
12	do.[4]	C_{18}	do	do	H	25		0	3.6	5.3
13	do.[4]	C_{18}	do	do	H	15	EMA [6]	20	4.5	5.6
14	do.[4]	C_{20}[7]	do	do	H	15	NTA	20	4.9	6.3
15	do.[4]	C_{20}[7]	do	do	H	25		0	3.8	5.7
16	do.[4]	C_{14}	p-Phenylene	H	H	15	NTA	20	4.9	6.1
17	do.[4]	C_{14}	do	H	H	25		0	3.6	4.8
18	do.[4]	C_{16}	do	H	H	15	NTA	20	4.0	6.0
19	do.[4]	C_{16}	do	H	H	25		0	4.2	5.2
20	do.[4]	C_{18}	do	H	H	15	NTA	20	3.5	5.4
21	do.[4]	C_{18}	do	H	H	25		0	2.2	3.2
22	do.[4]	C_{16}	Ethylene	H	Na	25		0	4.6	5.5
23	do.[4]	C_{16}	do	H	Na	15	NTA	20	4.5	6.4

[1] Linear alkyl groups derived from 1-olefins, except linear alkenyl groups in tests 8, 14–15. See footnote 7.
[2] Percent concentration by weight of detergent formulation in water of 50 p.p.m. hardness.
[3] Commercial linear alkyl benzene sulfonate composition containing about 20% LAS.
[4] Monoamides of hydrocarbyl succinic acids with amino hydrocarbyl sulfonic acid salts.
[5] Trisodium nitrilotriacetic acid.
[6] Hydrolyzed ethylene-maleic anhydride copolymer (sodium salt).
[7] C_{20} linear alkenyl group derived from 1-eicosene.

The test solutions consisted of monoamides of hydrocarbyl succinic acids prepared in accordance with Example 2 and formulated with trisodium nitrol triacetic acid and other ingredients to give the following phosphate-free formulation:

Ingredient:	Weight percent
Monoamide detergent active	15
Trisodium nitrilo triacetic acid	20
Sodium sulfate	49
Carboxymethylcellulose	1
Sodium silicate	7
Water	8

Two test solutions were prepared from each formulation. The first consisted of 1 g. of formulation dissolved in 1 liter of 50 p.p.m. hard water. The second consisted of 2.0 g. of the formulation dissolved in 1 liter of 50 p.p.m. hard water.

The second test solutions were prepared employing 25% by weight of the monoamide with no sequestering-type builder added. These materials had the following formulation:

Ingredient:	Weight percent
Monoamide detergent active	25
Sodium sulfate	59
Carboxymethylcellulose	1
Sodium silicate	7
Water	8

The miniature laboratory washer used was so constructed that the two standard formulations and two test

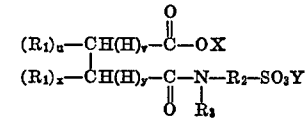
The results set forth in the above table show the effectiveness of the amide detergents of this invention in the absence of any builder and particularly in the presence of nonphosphate builders. Thus the tests illustrate that effective detergent compositions can be provided in the absence of the undesirable phosphate builders. It may be noted from a comparison of the results of tests 22 and 23 with tests 4 and 5 that detergent activity is present when the free carboxyl group is either in the acid or salt form; however, the acid form is preferred.

As will be evident to those skilled in the art, various modifications of the present invention can be made or followed in light of the foregoing disclosure and discussion without departing from the spirit or scope of the following claims.

I claim:

1. A phosphate-free detergent composition consisting essentially of:

(1) as an active ingredient, the compounds of the formula



in which u, v, x and y are 0 or 1, the sum of u and v is 1, the sum of x and y is 1, the sum of u and x is 1, the sum of v and y is 1, R_1 is an alkyl or alkenyl, or aromatic-substituted alkyl or alkenyl group of 8 to 30 carbon atoms; R_2 is an aliphatic, alicyclic or

aromatic hydrocarbon group of 1 to 8 carbon atoms, R_3 is an aliphatic hydrocarbon group of 1 to 8 carbon atoms; X is H or Y; and Y is an alkali metal, alkaline earth metal, or a tertiary lower hydroxy alkyl amino cation; and

(2) water soluble inorganic builder salts and organic polyelectrolytes in an amount of from 60 to 900 parts by weight per 100 parts of active ingredient.

2. A detergent composition as in claim 1 wherein the active ingredient X is H.

3. The detergent composition of claim 1 in which the water soluble inorganic builder salt is an alkali metal or alkaline earth metal sulfate, borate, or carbonate.

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