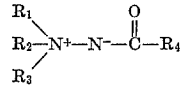
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3,410,880
N-TRIALKYLAMMONIUM IMIDES OF HIGHER FATTY ACIDS

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4 Claims. (Cl. 260—404.5)

This invention relates to a novel class of organic compounds which possess a semi-polar $N^+—N^-$ bond. More especially, this invention relates to N-(trialkylammonium) imide compounds having the following general formula



wherein R_1, R_2 and R_3 are selected from the group consisting of methyl, ethyl, and hydroxyethyl and R_4 is an aliphatic hydrocarbon radical containing from about 9 to about 15 carbon atoms.

It has been discovered that the members of this novel class of compounds possess unique and unusual detergency properties as described and illustrated in detail hereinafter.

At the present time, synthetic detergents used for laundering clothes and other textile fabrics in domestic washing machines are generally used in water at temperatures from 110° F. to 150° F., the normal washing temperature being about 130° F. It is well known, however, that some fabrics, such as wool fabrics and some of the newer drip-dry fabrics such as synthetic-resin treated cotton, Dacron, Orlon, etc., tend to shrink or to wrinkle or draw up when washed at temperatures in the range 110° F. to 150° F. This shrinkage not only reduces the size of the article but also changes the characteristic feel of the fabric making it less soft and less pleasant to the touch. To offset these disadvantages, such delicate fabrics are, therefore, usually washed in lukewarm or cool water, i.e., temperatures below 100° F., so that shrinkage is kept to a minimum. At these reduced temperatures, the conventional synthetic detergents such as dodecyl benzene sulphonates and alkyl sulphates have a considerably reduced detergent effect and in some instances also reduced lathering effect. Whiteness maintenance of the fabrics is also not as good as at higher water temperatures.

A detergent which has effective cleaning action below 100° F. is also of advantage in areas of the world where domestic laundry operations are frequently carried out by crude methods employing cool water, for example, by sloshing in ponds and streams.

An effective low temperature detergent also has an advantage in saving fuel for heating the washing water.

The members of the new group of compounds have valuable surface active properties which render them useful as ingredients of detergent compositions. In particular they serve as the active ingredient, particularly for washing in cool water e.g. at temperatures below 100° F.

The compounds of this invention have valuable surface active properties which render them useful as cool water detergents. In addition, the members of this new group of compounds are also effective lime soap dispersing agents.

It is a principal object of this invention to provide new organic compositions of matter. A further object is to provide a new class of organic detergent compounds which possess a semi-polar $N^+—N^-$ bond and which are

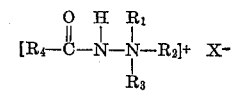
especially useful as cleaning agents in conjunction with cool water.

Yet another object is to provide detergent compositions containing one or more members of the new class of compounds. Another object is to provide so-called built detergent compositions wherein the compounds of this invention are the active cleaning agents whose cleaning properties are improved by builder compounds.

The following listed compounds are examples of the new class of compounds prepared according to this invention:

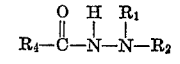
N-(trimethylammonium)caprimide
N-(dimethylethylammonium)caprimide
N-(diethylmethylammonium)caprimide
N-(triethylammonium)caprimide
N-(dimethylhydroxyethyl)caprimide
N-[di(hydroxyethyl)methyl]caprimide
N-[tri(hydroxyethyl)]caprimide
N-(diethylhydroxyethyl)caprimide
N-[ethyldi(hydroxyethyl)]caprimide
N-(methylethylhydroxyethyl)caprimide
N-(trimethylammonium)laurimide
N-(dimethylethylammonium)laurimide
N-(diethylmethylammonium)laurimide
N-(triethylammonium)laurimide
N-(dimethylhydroxyethyl)laurimide
N-[di(hydroxyethyl)methyl]laurimide
N-[tri(hydroxyethyl)]laurimide
N-(diethylhydroxyethyl)laurimide
N-[ethyldi(hydroxyethyl)]laurimide
N-(methylethylhydroxyethyl)laurimide
N-(trimethylammonium)myristimide
N-(dimethylethylammonium)myristimide
N-(diethylmethylammonium)myristimide
N-(triethylammonium)myristimide
N-(dimethylhydroxyethyl)myristimide
N-[di(hydroxyethyl)methyl]myristimide
N-[tri(hydroxyethyl)]myristimide
N-(diethylhydroxyethyl)myristimide
N-[ethyldi(hydroxyethyl)]myristimide
N-(methylethylhydroxyethyl)myristimide
N-(trimethylammonium)palmitimide
N-(dimethylethylammonium)palmitimide
N-(diethylmethylammonium)palmitimide
N-(triethylammonium)palmitimide
N-(dimethylhydroxyethyl)palmitimide
N-[di(hydroxyethyl)methyl]palmitimide
N-[tri(hydroxyethyl)]palmitimide
N-(diethylhydroxyethyl)palmitimide
N-[ethyldi(hydroxyethyl)]palmitimide
N-(methylethylhydroxyethyl)palmitimide

Each of the compounds of this invention are obtainable by treating, with an alkali metal hydroxide, quaternary hydrozonium compounds of the general formula



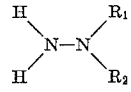
wherein R_1, R_2, R_3 and R_4 have the same meaning as above specified and X is a halogen atom such as chlorine, bromine, and iodine. The alkali metal hydroxide can be either sodium or potassium hydroxide.

The quaternary hydrazonium compounds are obtainable by quaternizing N-acyl-N',N'-dialkyl hydrazines of the general formula

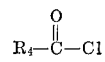


with an alkyl halide, R_3X.

The N-acyl-N',N'-dialkyl hydrazines are themselves obtainable by acylating unsymmetrical dialkyl hydrazines of the general formula



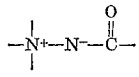
for example, in known manner using fatty acyl chlorides of the general formula



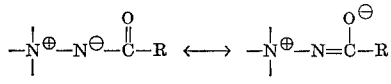
The acyl group (R_4CO—) may be derived from individual fatty acids containing from about 10 to 16 carbon atoms such as capric, lauric, myristic, or palmitic acid, or from a mixture of such acids obtained from natural sources such as coconut oil.

It should be pointed out that the nature of these new compounds is very complex. Thus, while the nature of the ntirogen-nitrogen bonding of this class of compounds has been described above as being "semi-polar," another postulated theory is that they may be more "polar" than semi-polar.

The stability of this class of compounds prepared according to this invention which are characterized by the



structural unit is thought to be attributable to the presence, adjacent to the —N⊖— atom, of two strong electron withdrawing functions. The quaternary nitrogen group, for instance, exerts a strong electron withdrawing inductive effect. The carbonyl group stabilizes the negative charge on an adjacent atom through resonance interactions of the type



The following examples are specific illustrations of how the compounds of this invention can be prepared.

Example I

A mixture of 30 g. of methyl iodide and 46.5 g. of N-lauroyl-N',N'-dimethyl hydrazine in 100 ml. ether was heated at reflux for two hours. The mixture was cooled and a white solid which precipitated from solution was collected by filtration. Recrystallization from water afforded 39 g. (63%) of N-lauroyl-N',N',N'-trimethyl hydrazonium iodide as colorless needles, M.P. 148° C.–148.5° C.

A 30 g. portion of these white solid crystals was triturated at room temperature with 60 ml. of 3 N sodium hydroxide solution and the resulting syrup extracted four times with 75 ml. portions of chloroform. The extracts were combined and the solvent removed by distillation under reduced pressure to yield 16 g. (80%) of N-(trimethylammonium) laurimide, as a white solid. Recrystallization from petroleum ether (B.P. 40° C.–60° C.) gave N-(trimethylammonium)laurimide white needles having a melting point of 35° C.

Analysis.—Calculated for $C_{15}H_{32}ON_2$: C, 70.3%; H, 12.5%; N, 10.9%. Found: C, 69.8%; H, 12.9%; N, 11.1%.

Other compounds of the invention are obtained according to the above method by using suitable starting materials. For instance, by substituting an equivalent amount of N-myristoyl-N',N'-dimethyl hydrazine for the N-

lauroyl-N',N'-dimethyl hydrazine, trimethylamine myristimide is obtained. Similarly, N-(trimethylammonium) caprimide and N-(trimethylammonium palmitimide are obtained by appropriate substitution in very good yields.

	Melting Point, ° C.	Analysis					
		Calculated			Found		
		C	H	N	C	H	N
N-(trimethylammonium) caprimide	20	68.5	12.3	-----	67.3	12.8	-----
N-(trimethylammonium myristimide	45-46	71.9	12.7	9.9	70.2	12.6	9.4
N-(trimethylammonium) palmitimide	68-70	73.1	12.8	9.0	72.9	12.8	8.9

In analogous manner, the corresponding N-(trimethylammonium)imides and N-[tri(hydroxyethyl)ammonium] imides can be obtained. Imides in which the amine nitrogen atom is linked to different groups selected from methyl, ethyl and hydroxyethyl can also be obtained.

The N-(trialkylammonium)imide compounds of this invention are useful, per se, as detergent and surface active agents or they can be used conjointly with other materials to form detergent compositions, as for example, liquid, tablet or granular compositions. Such detergent compositions contain the N-(trialkylammonium)imide compounds of the present invention, water-soluble inorganic alkaline builder salts, water-soluble organic alkaline sequestrant builder salts, or mixtures thereof, in a ratio of the active detergent to builder salt of about 4:1 to about 1:20. A preferred ratio is 2:1 to 1:10. Builders are hereinafter more fully described.

Water-soluble inorganic alkaline builder salts which can be used alone or in admixture are alkali metal carbonates, borates, phosphates, polyphosphates, bicarbonates and silicates. (Ammonium or substituted ammonium salts can also be used.) Specific examples of such salts are sodium tripolyphosphate, sodium carbonate, sodium tetraborate, sodium pyrophosphate, sodium bicarbonate, potassium tripolyphosphate, sodium hexametaphosphate, sodium sesquicarbonate, sodium mono- and di-orthophosphate and potassium bicarbonate.

Examples of organic alkaline sequestrant builder salts which can be used alone or in admixture are alkali metal, ammonium or substituted ammonium, aminopolycarboxylates, e.g., sodium and potassium ethylenediaminetetraacetate, sodium and potasium N-(2-hydroxyethyl) ethylenediaminetriacetates, sodium and potassium nitrilotriacetates and sodium, potassium and triethanolammonium N-(2-hydroxyethyl)nitrilodiacetates. Mixed salts of these polycarboxylates are also suitable. The alkali metal salts of phytic acid, e.g., sodium phytate are also suitable as organic alkaline sequestrant builder salts (see U.S. Patent 2,739,942).

Granular detergent compositions offering each of the foregoing described properties preferably contain about 5% to about 50% of the novel detergent compound or mixtures thereof, and liquid formulations preferably contain about 2% to about 30% of such new compounds, Granular detergent compositions preferably contain at least an equal amount of an alkaline builder salt. Liquid formulations preferably contain from 5% to about 40% of a water-soluble alkaline builder salt, the balance of the composition being a solvent such as water, and/or other liquid vehicles.

In addition to being mixed with the builder materials, the compounds of this invention can be used together with other well known active detergent compounds including anionic and nonionic detergent compounds.

Anionic organic detergents which can be used in the compositions of this invention if desired include both the soap and non-soap detergents. Examples of suitable soaps are the sodium, potassium, ammonium and alkylolammo-

nium salts of higher fatty acids (C_{10}–C_{20}). Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap. Examples of anionic organic non-soap detergents are: alkyl glyceryl ether sulfonates; alkyl sulfates; alkyl monoglyceride sulfates or sulfonates; alkyl polyethenoxy ether sulfates; acyl sarcosinates; acyl esters of isethionates; acyl N-methyl taurides; alkylbenzenesulfonates; alkyl phenol polyethenoxy sulfonates. In these compounds the alkyl and acyl groups, respective, contain 10 to 20 carbon atoms. The compounds are used in the form of water-soluble salts, the sodium, potassium, ammonium, and alkylolammonium salts, for example. Specific examples are: sodium lauryl sulfate; potassium N-methyl lauryl tauride; dodecylbenzene sulfonate.

The examples of nonionic organic detergents which can be used in the compositions of this invention if desired are: polyethylene oxide condensates of alkyl phenols wherein the alkyl group contains from 6 to 12 carbon atoms (e.g., t-octylphenol) and the ethylene oxide is present in a molar ratio of ethylene oxide to alkyl phenol in the range of 10:1 to 25:1, condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine wherein the molecular weight of the condensation products range from 5,000 to 11,000; the condensation products of from about 5 to 30 moles of ethylene oxide with one mole of a straight or branched chain aliphatic alcohol containing from 8 to 18 carbon atoms (e.g., lauryl alcohol); C_{10}–C_{18} alkyl di-(C_1–C_2 alkyl) amine oxides (e.g., dodecyl dimethyl amine oxide).

The detergent composition of this invention can contain any of the usual adjuvants, diluents and additives, for example, ampholytic, cationic or zwitterionic detergents, perfumes, antitarnishing agents, antiredeposition agents, bacteriostatic agents, dyes, fluoresceres, suds builders, suds depressors and the like without detracting from the advantageous properties of the composition.

Cleansing and detergent compositions prepared according to this invention can contain from about 2% to 50% by weight of the N-(trialkylammonium)imide compounds, 25% to 80% by weight of sodium tripolyphosphate, 12% to 45% by weight of sodium sulfate, 0% to 15% by weight of sodium silicate and 0% to about 40% by weight of water.

The effectiveness of the new compounds as cool water detergents is illustrated by the following example.

Example II

A built detergent paste was prepared containing 22% by weight N-(trimethylammonium)laurimide, 36% by weight sodium tripolyphosphate and 42% by weight water, and the detergency properties of this composition were evaluated by using a standardized testing procedure. Soiled white cotton collars were mechanically agitated for a specified length of time in an aqueous washing solution containing .25% by weight of the paste. Tests were conducted in water having a temperature of 80° F. and. 130° F.

Comparative tests were carried out with a similar paste containing 22% sodium dodecyl benzene sulphonate (the dodecyl radical being derived from tetrapropylene) instead of N-trimethylammonium)laurimide and washing at 130° F.

The results clearly showed that N-trimethylammonium) laurimide is equal in detergent power at 80° F. to sodium dodecyl benzene sulphonate at 130° F. both in water having a hardness of 2.4 grains per gallon and water having a hardness of 22 grains per gallon. Moreover, the N-trimethylammonium)laurimide is very much superior as a cleaning agent to sodium dodecyl benzene sulphonate at 80° F. This experiment demonstrates as a surprising advantage that the N-(trialkylammonium) imides of this invention are insensitive to a wide range of water hardness.

If any of the other members of the new class of compounds described herein such as N-(trimethylammonium) myristimide, N-(triethylammonium)palmitimide, and N-[tri(hydroxyethyl)] caprimide are used instead of N-(trimethylammonium)laurimide, comparable cleaning results are obtained.

The compounds of this invention have also been found to be effective lime soap dispersing agents. Thus, if a sodium soap derived from a flat mixture of 80% tallow and 20% coconut oil and containing 20% (by weight of the water-soluble soap content) of N-(trimethylammonium)palmitimide is used in water having a hardness of 22 grains per gallon and the wash water is then run away, no detectable scum is left on the sides of the bowl. The use of 10% of the lime soap dispersion agent produces a very marked reduction in the amount of lime scum which is formed.

Although the compounds of the invention do not prevent insoluble soaps being formed when the soap containing the compound is used in hard water, it has been unexpectedly discovered that these novel compounds do have the property of ensuring that the insoluble soaps which are produced have the form of finely dispersed and well wetted particles which do not tend to cling to the sides of the wash bowl as does the normal lime scum which is formed in the absence of lime soap dispersing agents.

When used as lime soap dispersing agents the new compounds are preferably used in an amount of from 10 %to 20% by weight of the soap. The soap compositions may be in any convenient form such as bar, powder, flake or liquid form, but the new compounds find their most useful application in bar soap compositions for toilet use.

The N-(trialkylammonium)imide compounds, according to this invention, can be used in detergent compositions especially useful in cool water having the following formulations. Percentages are all by weight.

Granular detergent

	Percent
N-(trimethylammonium)myristimide	17.5
Sodium sulfate	23.0
Sodium tripolyphosphate	50.0
Sodium silicate	6.0
Water	3.5

Granular detergent

N-(triethylammonium)laurimide	10
Sodium dodecyl benzene sulfonate (dodecyl group being derived from tetrapropylene)	10
Sodium tripolyphosphate	50
Sodium sulfate	30

Milled toilet bar

N-(trimethylammonium)palmitimide	10
Sodium coconut oil soap	15
Sodium tallow soap	60
Moisture	15

While this invention has been described with respect to certain embodiments, it is not so limited, and it is to be understood that variations and modifications thereof obvious to those skilled in the art may be made without departing from the spirit or scope of this invention.

The embodiments of the invention in which an exclusive property is claimed are defined as follows:

1. N-(trimethylammonium)caprimide.
2. N-(trimethylammonium)laurimide.
3. N-(trimethylammonium)myristimide.
4. N-(trimethylammonium)palmitimide.

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