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3,147,295

TERTIARY ARSINE OXIDE DETERGENT COMPOUNDS

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This invention relates to novel tertiary arsine oxide detergents and detergent compositions containing them.

In the constant improvement of organic detergent compounds, certain features have been found to be highly desirable. These features include resistance toward the ingredients imparting hardness to water, a high degree of detergency, and capacity for solubilization of hard water soaps, such as calcium soap. Although there are a number of organic detergents which have these characteristics, detergent compounds having additional desirable characteristics find a wider scope of application.

A degree of bacteriostatic activity is also desirable in organic detergent compounds.

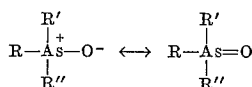
Another advantageous property for an organic detergent is a high degree of water solubility, particularly in electrolyte systems. This property is especially advantageous when formulating liquid detergent compositions containing high amounts of builder salts.

It is a principal object of this invention to provide organic detergents and detergent compositions which have excellent detergency and alkaline earth soap solubilization characteristics as well as high aqueous solubility and a degree of bacteriostatic activity.

It is another object to provide preferred detergent compositions which have these characteristics and also have synergistic mildness properties.

It was found that these and other objects are achieved in a novel class of tertiary arsine oxides having the structure set forth below and in detergent compositions containing such compounds as hereinafter more fully described.

The arsine oxides of this invention are probably resonance hybrids, the major canonical forms of which are:



In the above formulas, R is an alkyl, alkenyl, 2-hydroxyalkyl or 3-hydroxyalkyl radical ranging from 10 to 18 carbon atoms in chain length and R' and R'' are each alkyl, 2-hydroxyalkyl or 3-hydroxyalkyl groups containing from 1 to 3 carbon atoms. The class of compounds described above will hereinafter be referred to more simply as RR'R''As=O.

Examples of the compounds of this invention are dimethyldodecylarsine oxide, dimethyltetradecylarsine oxide, methylethyltetradecylarsine oxide, dimethylhexadecylarsine oxide, dimethyloctadecylarsine oxide, ethylpropylhexadecylarsine oxide, diethyldodecylarsine oxide, diethyltetradecylarsine oxide, dipropyldodecylarsine oxide, bis(2-hydroxyethyl)-dodecylarsine oxide, bis(3-hydroxypropyl)dodecylarsine oxide, methyl-2-hydroxypropyltetradecylarsine oxide, dimethyloleylarsine oxide, and dimethyl-2-hydroxydodecylarsine oxide.

Short chain tertiary arsine oxides as a broad class of compounds are known. It was surprising to find, however, that the particular trialkyl arsine oxides described above have highly desirable properties for use as organic detergents.

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It appears that only certain tertiary arsine oxides have the aforementioned desired characteristics; in these certain arsine oxides, R, R' and R'' must be as described above. If R is longer in chain length than 18 carbon atoms or shorter in chain length than 10 carbon atoms, desired detergency characteristics are not obtained. Likewise, if R' and R'' contain more than 3 carbon atoms, desired detergency characteristics are not obtained.

The most preferred tertiary arsine oxides are the C₁₀-C₁₈ alkylidimethylarsine oxides; particularly desirable are C₁₂-C₁₄ alkylidimethylarsine oxides. The C₁₀-C₁₈ alkylidimethylarsine oxides show bacteriostatic activity against Gram positive and Gram negative organisms. These arsine oxides also exhibit a desirable high degree of water solubility.

Tertiary arsine oxides of this invention can be prepared by oxidizing the corresponding tertiary arsine, for example, with hydrogen peroxide. In tertiary arsine oxides of this invention, R can be derived from naturally occurring fats and oils or from synthetic sources. Mixtures of arsine oxides are very suitable wherein the R groups vary in chain length in the C₁₀ to C₁₈ range, as for example, the alkyl groups from coconut fatty alcohol (or distilled coconut fatty alcohol).

Compounds of this invention are useful per se as detergent and surface active agents. Desirably they are used with other materials to form detergent compositions, as for example, liquid, bar or granular compositions. Such detergent compositions can contain the tertiary arsine oxides of this invention and water-soluble inorganic alkaline builder salts, water-soluble organic alkaline sequestrant builder salts or mixtures thereof in a ratio of arsine oxide to builder salt of about 4:1 to about 1:20.

Granular detergent compositions preferably contain about 5% to about 50% of the arsine oxides of this invention and liquid formulations preferably contain about 2% to about 30% of such arsine oxides. Granular detergent compositions preferably contain at least an equal amount of an alkaline builder salt. Liquid formulations preferably contain from about 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.

Water-soluble inorganic alkaline builder salts 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 triphosphate, sodium carbonate, sodium tetraborate, sodium pyrophosphate, sodium bicarbonate, potassium triphosphate, sodium hexametaphosphate, sodium sesquicarbonate, sodium mono- and diortho phosphate and potassium bicarbonate, such inorganic builder salts enhance the detergency of the subject arsine oxides.

Examples of organic alkaline sequestrant builder salts used alone or in admixture are alkali metal, ammonium or substituted ammonium, aminopolycarboxylates, e.g., sodium and potassium ethylenediaminetetraacetate, sodium and potassium N-(2-hydroxyethyl)-ethylenediaminetriacetates, sodium and potassium nitrilotriacetates and sodium, potassium and triethanolammonium N-(2-hydroxyethyl)-nitrilotriacetates. 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).

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 alkylammonium salts of higher fatty acids (C₁₀-C₂₀). 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, respectively, contain 10 to 20 carbon atoms. They are used in the form of water-soluble salts, the sodium, potassium, ammonium, and alkylammonium salts, for example. Specific examples are: sodium lauryl sulfate; potassium N-methyl lauroyl tauride; triethanolamine dodecyl benzene 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-octyl-phenol) 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 ranges from 5000 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); C₁₀-C₁₈ alkyl di-(C₁-C₂ alkyl) amine oxides (e.g., dodecyl dimethyl amine oxide).

Preferred liquid detergent compositions contain about 2 to about 30% of the tertiary arsine oxides of the invention and about 5% to about 40% potassium pyrophosphate. Desirably the C₁₂-C₁₄ alkyl dimethylarsine oxides are used in such preferred compositions. Particularly desirable is dimethyldodecylarsine oxide which has good sudsing characteristics.

The detergent compositions of this invention can contain any of the usual adjuvants, diluents and additives, for example, ampholytic, cationic or zwitterionic detergents, perfumes, anti-tarnishing agents, anti-redeposition agents, bacteriostatic agents, dyes, fluorescers, suds builder, suds depressors and the like, without detracting from the advantageous properties of the composition.

Certain mixtures of the arsine oxides of this invention and alkylbenzenesulfonates exhibit superior and unexpected mildness characteristics. In certain ranges, and under comparable conditions of exposure, mixtures of these two detergent compounds in aqueous solution are milder to the skin than either one alone. Thickening, dryness and cracking of the skin of test animals under exaggerated exposures to solutions of such mixtures are markedly reduced and in some cases disappear. This mildness effect is very advantageous since combinations of the alkylbenzenesulfonates and arsine oxides in compositions of the present invention are efficient detergents. The cleansing compositions of this invention having superior mildness characteristics comprise mixtures of alkylbenzenesulfonates having alkyl radicals ranging from about 9 to about 15 carbon atoms and the tertiary arsine oxides of this invention, the ratio of the respective ingredients being in the range of about 10:1 to about 1:2.

The alkylbenzenesulfonates in compositions of this invention are the water soluble salts, such as the alkali metal (e.g., sodium, potassium and lithium), ammonium and substituted ammonium (e.g., triethanolamine) salts, of sulfonated alkylbenzene in which the alkyl radicals range from about 9 to about 15 carbon atoms. Alkylbenzenesulfonates usually contain mixtures of alkyl radicals in this range. The preferred alkylbenzenesulfonate

is one in which the alkyl radicals in the mixture average about 12 carbon atoms and are derived from a polypropylene which is predominantly tetrapropylene. This alkylbenzenesulfonate is hereinafter referred to as dodecylbenzenesulfonate and is most commonly used as a sodium salt.

In the testing of detergent compounds and compositions for mildness and for the unexpected mildness effect, skin is contacted by immersion or other means with a solution of the detergent under standardized conditions as more fully described below. A 1 to 10 scale is used to rate the effects of prolonged exposure on the skin. Grade 10 represents ideal or perfect skin (soft, smooth and flexible) and the effect of a theoretically perfectly mild detergent; grade 1 represents severely irritated skin. Other values represent gradations of severity between these extremes. Grade 1 in a guinea pig immersion test indicates severely thickened, dry, cracked and bleeding skin, i.e., extreme irritation. Grade 1 in exaggerated tests on human subjects indicates severe redness and dryness of the skin. Thus, the exaggerated exposure tests on animals are much more extreme than those conducted on human subjects.

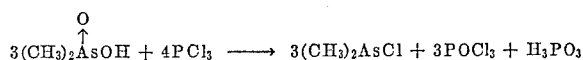
There is a good correlation between the results of exaggerated exposure tests on animals and the results of normal use tests on humans; the former can be relied on to grade the relative mildness of detergents toward the human skin.

As used in the example, the graded guinea pig immersion tests consist of immersing the animal up to the thorax in the test solutions of 37° C. for a 4½ hour period per day for 3 consecutive days. The animals are graded 3 days after the last immersion. The grades given in the examples are the average of the results on not less than three animals. It will be understood by those with experience in biological experiments that there is variation in the reactions of individuals, within a group, to exposure to chemical solutions; this is true whether the individuals are guinea pigs or humans.

The following are examples which illustrate the tertiary arsine oxide compounds and compositions of this invention.

Example I

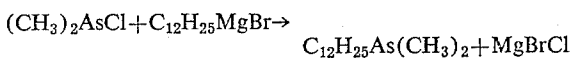
200 grams of PCI₃ were placed in a 500 ml. glass flask with an open neck and paddle stirrer. The flask was cooled in an ice bath. 50 grams of cacodylic acid were added very slowly. The temperature was kept at 25-27° C. and the mixture was stirred. The temperature was allowed to rise to 30° C. and stirring continued. The mixture was cooled to 10° C. in ice.



This mixture was acidified with 200 ml. of concentrated HCl (added slowly). Hydrolysis resulted and the mixture separated into two layers. The mixture was poured into a separatory funnel and the lower layer (dimethylchloroarsine) was drawn off and dried and distilled.

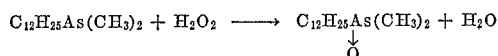
Dodecyl magnesium bromide was formed by slowly reacting 39.2 grams of dodecylbromide and 3.82 grams of magnesium metal in 315 ml. of dry ethyl ether in a 500 ml. flask while stirring. 22.1 grams of the dimethylchloroarsine formed above was added drop-wise to the thus formed dodecyl magnesium bromide at 10° C. over a period of 30 minutes. A white precipitate formed.

The reaction mixture was added to 200 grams of ice in a 1 liter beaker and dissolved with stirring. The solution was transferred to a separatory funnel; Na₂SO₄ was added to the emulsion. The mixture separated and the lower aqueous layer was discarded. The ether layer was dried and filtered. The ether was then distilled off.



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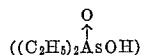
22.85 grams of the dimethyldodecylarsine formed above was added drop-wise to 100 ml. of 15% aqueous H_2O_2 in a 600 ml. beaker at 45° C. The mixture was freeze-dried.



The resulting dimethyldodecylarsine oxide was extracted with acetone. The acetone was then blown off with a nitrogen steam. The arsine oxide had the following elemental analysis:

	Calculated	Found
C-----	58.0	56.5
H-----	10.7	10.6
As-----	25.8	25.2
O (by difference)-----	5.5	7.7

Dimethylhexadecylarsine oxide can be prepared by using a molar equivalent amount of hexadecyl bromide in the above example. Diethyldodecylarsine oxide can be prepared by using a molar equivalent amount of diethylarsinic acid



in the above example.

Water solubility of dimethyldodecylarsine oxide at room temperature was 40%. The solubility of this compound in an electrolyte system was also excellent; 35 grams of the compound dissolved in 100 grams of a 20% aqueous solution of tetrapotassium ethylenediaminetetraacetate.

The bacteriostatic efficacy of dimethyldodecylarsine oxide was determined. In an aqueous matrix, it required a concentration of only 20 p.p.m. of this compound to arrive at the bacteriostatic breakpoint of *M. aureus* (Gram positive) and of *P. aeruginosa* (Gram negative). Bacteriostatic breakpoint is that concentration of material at which the multiplication of an organism is stopped. This degree of bacteriostatic efficacy is significant.

The following aqueous solutions (distilled water) were compared in graded guinea pig immersion tests.

Test solution:	Grade
0.2% sodium dodecylbenzenesulfonate -----	3
0.2% dimethyldodecylarsine oxide ----- (1)	
0.2% sodium dodecylbenzenesulfonate+0.1% dimethyldodecylarsine oxide -----	9

¹ Ungraded but extremely irritating.

A significant unexpected mildness effect is apparent in the solution of a mixture of alkylbenzene sulfonate and arsine oxide in a 2:1 ratio as compared to solutions of the individual detergents alone.

Built laundry detergent compositions containing 50% sodium tripolyphosphate, 30% sodium sulfate and 20% dimethyldodecylarsine oxide, diethyldodecylarsine oxide, dimethyltetradecylarsine oxide or diethyltetradecylarsine oxide, result in lipid soil detergency properties (using natural soiled cloth) superior to like formulations containing sodium dodecylbenzenesulfonate and approaching like formulations containing sodium tallow alkyl sulfate. The same basic formulation, but containing dimethyloctadecylarsine oxide or dimethylhexadecylarsine oxide or diethylhexadecylarsine oxide have satisfactory detergent characteristics but not as desirable as those compositions containing the C_{12} and C_{14} homologues.

The above described arsine oxides are efficient solubilizers of calcium soap.

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The following granular detergent composition was prepared:

	Percent
Dimethyldodecylarsine oxide -----	17.5
5 Sodium sulfate -----	23.0
Sodium tripolyphosphate -----	50.0
Sodium silicate -----	6.0
Water -----	3.5

A 0.436% water solution of this composition was used to wash soiled dishes. The water was at 115° F. and 7 grain hardness. 40 seconds of mechanical agitation provided more than 1" of stable suds.

The arsine oxides of this invention can be used in effective detergent compositions having the following formulations:

Granular detergent:	Percent
Diethyldodecylarsine oxide -----	10
Sodium dodecylbenzenesulfonate (the dodecyl group being derived from tetrapropylene) -----	10
20 Sodium tripolyphosphate -----	50
Sodium sulfate -----	30

Granular detergent:	
Dimethyltetradecylarsine oxide -----	10
Condensation product of one mole of nonyl phenol and nine moles of ethylene oxide -----	10
25 Sodium pyrophosphate -----	50
Sodium carbonate -----	3
Trisodium phosphate -----	3
Sodium sulfate -----	24

30 Liquid detergent:	
Dimethyldodecylarsine oxide -----	6
Sodium dodecylbenzenesulfonate -----	6
Potassium pyrophosphate -----	20
Potassium toluene sulfonate -----	8
35 Sodium silicate -----	3.8
Carboxymethyl hydroxyethyl cellulose -----	0.3
Water -----	Balance

Liquid detergent:	
Diethyltetradecylarsine oxide -----	10
40 Tetrasodium ethylenediaminetetraacetate -----	25
Water -----	65

Scouring cleanser:	
Silica flour -----	85
45 Detergent consisting of 85% trisodium phosphate and 15% bis(2-hydroxyethyl)-2-hydroxydodecylarsine oxide -----	15

What is claimed is:

1. Tertiary arsine oxide detergent compounds having the formula $\text{RR}'\text{R}''\text{As}\rightarrow\text{O}$, wherein R is selected from the group consisting of alkyl, alkenyl, 2-hydroxyalkyl and 3-hydroxyalkyl radicals ranging in chain length from 10 to 18 carbon atoms and R' and R'' are each selected from the group consisting of alkyl, 2-hydroxyalkyl and 3-hydroxyalkyl radicals containing from 1 to 3 carbon atoms.
2. Dimethylalkylarsine oxide wherein the alkyl radical ranges in chain length from 10 to 18 carbon atoms.
3. Dimethylalkylarsine oxide wherein the alkyl radical ranges in chain length from 12 to 14 carbon atoms.
4. Dimethyldodecylarsine oxide.

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